Processing of fly ash and associated waste materials as cement replacements

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Declaration

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Abstract

Being one of the most versatile, durable and cost-effective building materials in use today, concrete is the most widely used construction material in the world. In the production of concrete, cement manufacture accounts for the highest cost and is the most energy intensive process from all its constituents.

This research has focused on the requirement to reduce the use of cement within concrete by the use of a partial cement replacement material. An established cement replacement, Ground Granulated Blast Furnace Slag, exists but with changes in steel manufacture this material could soon be short in supply. Industry as a whole produces materials which are routinely sent to landfill as waste, through analysis of these materials, and logging of their properties, a select few may be regarded as possible cement replacement materials. Knowing the required properties of any replacement allows this analysis to be complete within hours and a decision made prior to performing the mixing and testing of concretes containing the replacement.

A fly ash has been subjected to an electrostatic precipitation process (STi) and then to an air swept classification process. The fly ash has been examined in its raw, processed and classified conditions and compared through chemical and physical analysis and through its performance when used in concrete. From this some basic requirements of a cement replacement material were documented. The ash was also inter-ground with clinker using a ball mill to produce a blended CEM II cement to test against the post blend material.

It was found that applying the STi process to the fly ash produced results comparable to those of the GGBS controls at 33% which were bettered when the fly ash was subject to a classification process. No further benefits were to be had from the inter-grinding of the fly ash when used in concrete. Further materials have been introduced to the study to test their properties against that of the fly ash and their performance as partial cement replacements.

A scoring matrix was produced which rated a materials properties by comparing them to the ideal properties of a processed fly ash. This is a novel approach which links the properties of a potential partial cement replacement and its compressive strength as concrete. A review of the physical and chemical properties of the materials used within this research is presented which provide guidelines against which future potential replacements may be compared and assessed.

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1.1 Scope

With a plethora of legislation being introduced within the UK and the European Union, restricting the disposal of industrial waste, coupled with the increased costs associated with waste disposal, outlets are now being sought to re-use waste rather than landfill it. With the introduction of the EC Directive on the Landfill of Waste 1999/31/EC [1999/31/EC,1999], stricter controls aimed at improving the standards of landfilling through setting specific requirements for the design, operation and aftercare of landfills, and for the types of waste that can be accepted in landfills have been introduced.

The past ten years have shown an increasing emphasis on sustainable development within industry throughout the UK. By the ratification of the Kyoto protocol, industrialised countries have targets set to lower overall emissions of greenhouse gases. In the UK a climate change levy has been introduced which taxes the use of energy in industry, commerce and the public sector, with offsetting cuts in employers National Insurance Contributions and additional support for energy efficient schemes and renewable sources of energy. The introduction of the EC Directive on the Landfill of Wastes 1999/31/EC requires the appropriate treatment of waste streams prior to landfill to reduce their hazard, volume and facilitate handling

and/or enhance recovery (Davies, 2003). Industry is being encouraged to minimise its waste and is being penalised through landfill taxes for not doing so.

1.2   Ordinary Portland cement

In the production of concrete, cement manufacture accounts for the highest cost and is the most energy intensive process from all its constituents. The production of Ordinary Portland cement (OPC) is environmentally sensitive in two areas, first the mining of the materials and second its manufacture. To make 1 tonne of cement approximately 1.7 tonne of non-fuel raw materials are used. The bulk of this, around 85%, is limestone or similar rocks which when blended with clay or shale and other minor constituents achieve the correct chemical balance to produce cement. The output of an individual quarry may not be substantial, as compared to the output from mining certain other minerals, however, the existence of thousands of cement plants worldwide ensures the cumulative output of material is significant. Current world cement output requires almost 3 Gt/yr of non-fuel raw materials; associated fuel consumption is roughly 200 Mt/yr in straight mass terms (i.e., not on a common fuel basis), or about 0.15 to 0.2t fuel/t clinker. The concrete and mortars (about 13 to 14 Gt/yr) incorporating this cement require a total of about 15 Gt/yr of raw materials, mostly aggregates (Van Oss 2002).

The production of OPC contributes significantly to CO_2 emissions with a range of figures being quoted in the literature of between 0.74 tonnes CO_2 / tonne cement to as high as 1.3 tonne (Harrison 2005). It is however, generally accepted that for every tonne of Portland cement produced, approximately one ton of CO_2 is released into the atmosphere (Bouzoubaa et al., 1997). This equates to 5% of total global emissions originating from cement production (Hendricks et al., 2004).

Cement manufacture creates CO_2 in two ways: by the conversion of calcium carbonate to calcium oxide inside the kilns, and by burning large quantities of fossil fuels to heat the kilns to the 1450°C necessary. Previous estimates for CO_2 emissions from cement production have concentrated only on the former source. The UN's Intergovernmental Panel on Climate Change puts the industry's total contribution to

CO_2 emissions at 2.4 per cent of global emissions; the Carbon Dioxide Information Analysis Centre at the Oak Ridge National Laboratory in Tennessee quotes 2.6 per cent (Pearce 1997).

As part of the Kyoto agreement, European countries have agreed to an 8% reduction in Greenhouse Gas emissions, based on 1990 levels, by the year 2012. The cement manufacturing industry is one where quotas have been imposed by the European Union (EU) to cap hazardous emissions. Failure to meet the obligations of the agreement will result in heavy fines. However, improving on these limits can provide financial benefits through carbon trading (Defra, 2007). Already the industry has demonstrated its ability to improve its climate change performance. Between 2001 and 2004 an improvement in energy consumption of 21.2% had been achieved and is well on its way to the 2010 target of 26.8% reduction (British Cement Association 2005).

1.3 Concrete

From material extraction, processing, component assembly, transport and construction, to maintenance and disposal, construction products have an environmental impact over their entire life cycle. Some of the key sustainable issues within the industry at present are (BRE 2007):

o 10% of the UK CO_2 emissions arise from the production and use of building materials.

o Each year the UK construction industry uses 6 tonnes of building materials per head of population.

o Materials production and construction accounts for an estimated 122 million tonnes of waste, or 30% of the total arising in the UK.

The environmental impact of buildings and infrastructures is significantly large compared with other industries and concrete makes up a major part of this impact (Katz, 2006).

Being one of the most versatile, durable and cost-effective building materials in use today concrete is the most widely used construction material in the world, only fresh water is consumed in larger amounts and this is generally because it is wasted (Aitcen, 2000). Approximately 100 million tonnes of concrete is used annually in the UK with concrete sales amounting to £5 billion. Concrete has the obvious environmental impacts embodied in the quarrying of raw materials for aggregates; the energy used in its production and associated carbon dioxide (CO_2) emissions. As with all products it will eventually reach the end of its useful life and require recycling too. Many are actively involved in activities to reduce the environmental impacts of the production of concrete, including (Concrete centre, 2007):

o Reduction in the amount of polluting and 'greenhouse' gases emitted during the creation of concrete

o More efficient use of resources in concrete production, including re-used materials and byproducts from other industrial processes

o Better re-use of waste and other secondary materials such as water, aggregate, fuel or other cementitious material

o Lower reliance on quarrying material or sending construction and demolition waste to landfill by maximising the use of recycled material where practical

o Development of low-energy, long-lasting yet flexible buildings and structures;

o Exploiting the thermal mass of concrete in a structure to reduce energy demand over the lifetime of a building

o Environmental restoration after industrial activity has ceased.

1.4   Waste in concrete

Traditionally the UK has been heavily reliant on landfill: of a total 23.6 million tonnes of (kerbside collected) municipal waste produced in 2009/10, 47% (about 11 million tonnes) was land filled, 41% was recycled or composted and 11% was incinerated with energy recovery. Compared with 2008-09, where 27.3 million tonnes of municipal waste was collected by local authorities, 50.3% was sent to landfill; 36.9% was recycled or composted and 12.2% was incinerated for energy recovery (Defra 2011), it can be seen that municipal waste is slowly on the decrease (www1.1).

For every tonne of household waste we produce, commercial, industrial and construction businesses produce another six tonnes. Nearly one tonne is produced by services (shops, banks and insurance companies); a further two tonnes by the industries which make the goods we buy; and three tonnes are produced by the construction industry (Environment agency 2007).

Announcing the review of the Governments waste policy at the Future Source conference, Environment Secretary Caroline Spelman said:

"There is an economic and environmental urgency to developing the right waste strategy. We have been slowly moving in the right direction with recycling rates. The direction of travel is right – it's the pace that's the problem. We need to go faster and we need to go further." She continued "Finding ways not just to use less energy, water and natural resources – but by using the waste we do produce as the valuable raw material it actually is" (www1.2).

It would appear that the Government have realised that waste and industrial by-products should be regarded as potential assets and not merely discarded as a waste material. With suitable treatment a waste product may be improved and reclassified as a useable resource or valuable commodity. Now that businesses are being asked to take greater responsibility for the environmental impact of their

products and operations, industry is looking into the options available for the safe disposal of their waste.

Concrete plays an important role in the beneficial use of these materials in construction. Although some of these materials may be beneficially incorporated in concrete, both as part of the cementitious binder phase or as aggregate, it is important to realise that not all waste materials are suitable for such use (Environmental Working Party 2003).

1.5   Aim and objectives

This thesis examines how waste material can be utilised as a cement replacement in the making of concrete. It looks at materials already established and accepted in industry and what elements a new waste material would have to possess, both physical and chemical, in order for it to be a suitable cement replacement. This study aims to be an initial reference point in the selection of, or rejection of, a waste material for use as a cement replacement.

This research is being run in conjunction with an industrial partner, Minimix Concrete, with whom the Author has maintained a good relationship. The partnership has shared results and knowledge gained from the industry and results from this research work. The use of waste materials within concrete was the link between both parties the outcome being to introduce a new material (materials) as a cement replacement into the standard concrete recipes used at the plant. Consideration for concrete quality, strength and durability, was paramount but ultimately providing an economic incentive to use the material was also required. The quality of the concretes produced is discussed within this thesis whilst the financial aspect was examined using the "Cost Analysis Model" which can be seen in Appendix 4. This model was created by the Author to examine the effect a change of material quantity and / or cost would have had on the sales figures at Minimix Concrete during the previous 12 months.

The inter-grinding of the fly ash with clinker and the use of admixtures within the blended cement was carried out in collaboration with Lafarge cement works,

Aberthaw. The Author worked within the technical department at the works carrying out much of the analysis and reporting back with results and recommendations to the Lafarge cement management team.

2. Literature review

2.1   Introduction

As presented in the introduction to this thesis, in today's industry there is considerable pressure to re-use and recycle materials rather than send them to landfill. With an increased public awareness as to the environmental damage being caused by industry, political parties both locally and worldwide now place targets for CO_2 reduction and energy efficiency high on the political agenda.

The U.K. government is consulting on targets to reduce carbon emissions by 80 per cent, following reactions by campaigners who warned that the 60 per cent target set out in the climate change bill was not ambitious enough to stem climate change (www2.1). The fact that the government is prepared to rethink its objectives in line with views brought about by campaigners indicates the importance of this policy. In view of these pressures on the concrete industry a review of waste and emissions is presented before consideration of issues related to concrete.

Waste in the UK

Waste is an ever growing problem and has been causing increasing problems since the industrial revolution and population explosion in the nineteenth century. This is due to the link between waste generation and economic growth, which is further exacerbated by population growth which further increases waste generation (Owen 2007).

Landfilling is the most common form of waste disposal across Europe. However, differences in technical standards and operating practices between member states have led to numerous incidents of gross land and water pollution. In response, the European Commission has introduced a number of measures to regulate landfill disposal and to establish a common framework that promotes waste prevention, minimisation, re-use, recycling and recovery as alternatives to landfill disposal. The EC Landfill Directive introduces progressive measures to further prevent or reduce as far as possible the negative effects of landfilling waste on the environment and on human health (www2.1.1).

In 2004 the UK produced about 335 million tonnes of waste. Figure 2.1 below, shows the estimated proportion produced by each sector annually. This includes nearly 100 million tonnes of minerals waste from mining and quarrying, which is not subject to control under the EU Waste Framework Directive, and 220 million tonnes of controlled wastes from households, commerce and industry (including construction and demolition wastes) (www2.2).

Household waste includes household bin waste and also waste from civic amenity sites, other household collections and recycling sites. Although the classification of wastes contained within each sector is not specific it can be said that all wastes arising from sources other than households should be deemed as industrial or commercial waste as a charge is levied for their disposal. It can be seen from Figure 2.1 that household waste represents about 9 per cent of the total waste produced and therefore focus should be placed on industry in a bid to significantly reduce waste.

Legend:
- Agriculture (inc.Fishing)
- Mining and Quarrying
- Sewage sludge
- Dredged materials
- Household
- Commercial
- Industrial
- Construction and Demolition

Pie chart values: <1%, 29%, 32%, <1%, 5%, 9%, 12%, 13%

Total = 335 million tonnes
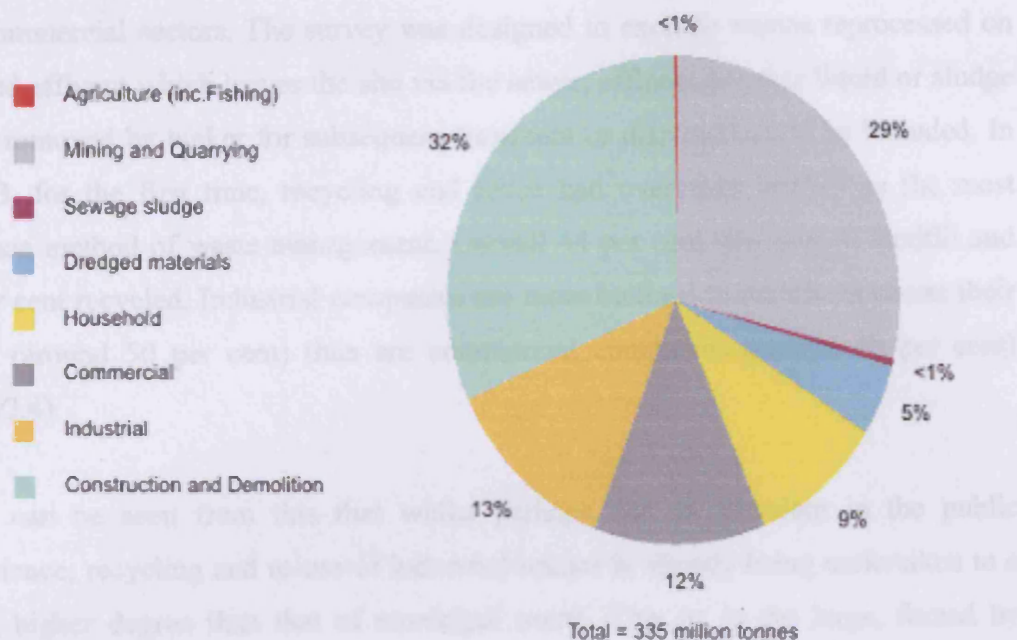
Figure 2.1 UK waste annual arisings by sector 2004
(Source DEFRA www2.2)

The Environment Agency carried out a survey of some 4,500 industrial and commercial businesses in 2002/3. The information collected for each business included the type of waste, quantity of waste, the waste form, waste disposal or recovery method. Data collection was limited to controlled waste and relates to England only. The estimate of industrial waste includes power station ash, blast furnace and steel slag.

In 2002/3, Industrial and Commercial waste in England totalled 68 million tonnes. Of this about 38 million tonnes was attributable to industry and 30 million to commerce. The individual sector that produced the most waste was the retail sector, which generated nearly 13 million tonnes of waste. This was followed by food, drink and tobacco manufacturing, and the professional services and other businesses, both producing more than 7 million tonnes, and the coke, oil, gas, electricity and water industries at just over 6 million tonnes (www2.3).

Table 2.1 shows the waste management routes employed by the various industrial and commercial sectors. The survey was designed to exclude wastes reprocessed on site and effluent which leaves the site via the sewer; effluent or other liquid or sludge waste removed by tanker for subsequent treatment or disposal would be included. In 2002/3, for the first time, recycling and reuse had overtaken landfill as the most common method of waste management. Overall 44 per cent was sent to landfill and 45 per cent recycled. Industrial companies are more inclined to recycle or re-use their waste (around 50 per cent) than are commercial companies (around 40 per cent) (www2.4).

It can be seen from this that whilst perhaps not so prevalent in the public conscience, recycling and re-use of industrial wastes is already being undertaken to a much higher degree than that of municipal waste. This is, in the large, forced by government policy through the introduction of a landfill tax which penalises companies financially for landfilling waste materials. Landfill Tax is a tax on the disposal of waste. It aims to encourage waste producers to produce less waste, recover more value from waste, for example through recycling or composting and to use more environmentally friendly methods of waste disposal. At present landfill tax stands at £48.00 per tonne; however, in a push to achieve future environmental targets this figure is set to increase by £8.00 each year rising to £80 per tonne in 2014 / 15 (www2.5).

Table 2.1
Waste management routes
Source DEFRA (www2.4)

	Sector Description	Land disposal	Land recovery	Re-used	Recycled	Thermal	Transfer	Treatment	Unrecorded	Unsampled	Total
1	Industrial Food, drink and tobacco	1,696	730	1,520	1,620	484	134	539	419	90	7,230
2	Manufacture of textiles, wearing apparel, leather, luggage, handbags and footwear	496	66	69	339	24	23	159	35	24	1,234
3	Wood and wood products	343	3	221	795	31	28	7	43	1	1,471
4	Manufacture of pulp, paper and paper products	458	103	69	700	27	23	48	103	290	1,822
5	Publishing, printing and recording	569	10	44	1,307	44	52	25	61	62	2,174
6	Production of coke, oil, gas, electricity, water	2,897	39	43	3,011	38	14	71	41	28	6,182
7	Manufacture of chemicals and chemical products; cleaning products, man-made fibres etc; rubber and plastic products	2,102	333	508	822	488	92	685	208	19	5,257
8	Other non-metallic mineral products	1,281	9	175	574	13	34	23	119	44	2,272
9	Manufacture of basic metals	1,652	9	1,477	1,480	45	14	87	29	23	4,815
10	Manufacture of fabricated metal products	381	10	54	868	47	31	68	61	5	1,525
11	Manufacture of machinery and equipment	370	3	59	391	19	20	20	47	11	939
12	Manufacture of office machinery, computers, electrical, radio, television and communication equipment; medical and optical instruments and clocks	218	3	18	186	23	17	26	25	1	515
13	Manufacture of motor vehicles and other transport equipment	405	4	59	846	24	32	38	55	11	1,475
14	Furniture and other manufacturing	327	2	41	240	16	20	5	23	0	675
	Total ind. (000s) tonnes	13,194	1,324	4,358	13,178	1,321	534	1,801	1,267	610	37,587

Given the substantial costs involved with the transportation, and landfilling, of waste materials it would seem to make sense that alternatives should be sought. There are, however, a number of significant barriers to the sustained uptake of materials recovered for recycling (www2.6):

o **Market demand.** A lack of demand for products with increased recycled content means that companies have little incentive to manufacture such products.

o **Feedstock substitution.** Manufacturers are often reluctant to modify their production processes to use recovered materials in place of virgin materials, or to move from the tried and tested to the unknown.

o **Price differentials.** Recovered materials are not always price competitive with virgin raw materials, particularly when systems for collecting such materials are sub-optimal and the costs of collection are high.

o **Standards and specifications.** The use of recovered materials is often constrained by the absence of recognised industry standards for such materials, affecting both the adoption of recovered materials as a feedstock and the marketing of products with recycled content.

For these reasons, efforts to develop markets are vital if recycling is to be substantially expanded. Market development is first and foremost a regional economic development issue, aimed at the creation of new jobs and business opportunities at a regional/local level, using recovered materials as a raw material in the development of new products and processes.

The UK cement and concrete industry is continuing to contribute to UK Waste Strategy by consuming waste produced by other industries and recycling its own waste. Through a combination of market forces, government intervention and the industry's own initiatives, the cement and concrete industries have steadily improved their environmental performance (The Concrete Centre 2007). There is considerable potential for use of specific wastes and by-products in each concrete component, including admixtures and mixing water. However, the major use, by volume, has been in cementitious binders or aggregates after the 'beneficiation', improving properties and reducing variability, of various inorganic waste streams (Environmental working party 2003).

2.2   Concrete and its constituents

What is concrete?

Concrete is a composite mixture formed from Portland cement, water and aggregate. The aggregates form the bulk of the volume, typically 70 – 80%. Other materials, such as admixtures and partial cement replacement materials may also be added to the basic constituents (Illston 1994). Portland cement is a hydraulic binder with the term 'hydraulic' referring to the cement's ability to set (stiffen and hold shape) and harden (develop full strength) in the presence of sufficient water. This makes concrete an extremely useful material in that it can be made to form or fill any shape that may be required. In terms of final product, concrete is arguably the most important construction material of the past century (Hendrick 2002).

Concrete is a two state process with each state having its own properties and requirements towards application needs and governing standards.

Fresh state

The first state is its 'Fresh state'. Although fresh concrete is only of transient interest, as its properties are in continuous change, it should be understood that the strength of concrete of given mix proportions is very seriously affected by the degree of its compaction. It is vital therefore, that the consistence of the mix be such that the concrete can be transported, placed, compacted and finished sufficiently easily and without segregation (Neville 1995).

Consistency is the term used in BS EN 206-1 (BS EN 206, 2005) and BS 8500 (BS 8500, 2002) for what was known in BS 5328 as 'workability'. Consistence is the measure which indicates the concrete's ability to overcome internal friction and become self compacting. The consistence of concrete is the measure of three main qualities of plastic concrete:

o	Compactability	the ease with which the concrete can be compacted and that air voids within the concrete are removed
o	Mobility	the ease with which concrete flows and can be remoulded
o	Cohesiveness	the ability that the concrete has to maintain a homogenous mass and not become segregated

While there are many ways of measuring consistence, BS EN 12350 'Testing fresh concrete' has four standardised tests in its series. The Slump test (BS EN 12350-2), the Flow table test (BS EN 12350-5) the Vebe test (BS EN 12350-3) and the Compactability test (BS EN 12350-4).

These tests give a single measurement and are therefore commonly known as 'single-point' tests. The most famous and oldest test is the Slump test. Because of its simplicity, this method is used extensively in site work all over the world. The apparatus was developed in the USA around 1910 and it is believed that it was first used by Chapman although in many countries the test apparatus is associated with Abrams (Bartos 2002).

Although work continues to find a more comprehensive measurement for the rheology of concrete (Li 2007), the simplicity of the measurement and low cost are among the reasons why the slump test remains the most common method for quality control evaluations of fresh concrete in the field (Saak 2004).

a) True slump   b) Shear slump
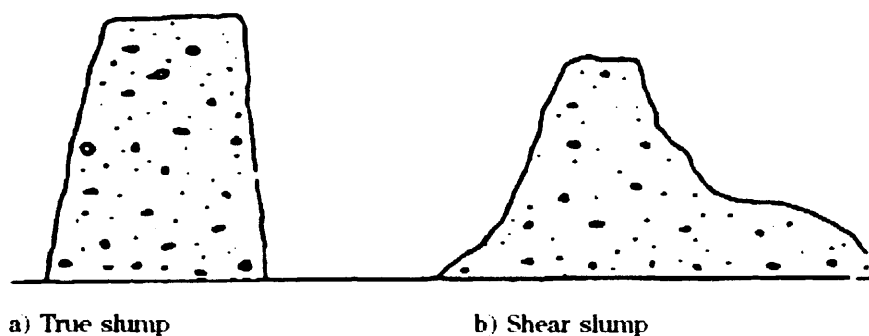
Figure 2.2 Forms of slump as recognised by the European standards

(Source BS EN 12350 - 2)

Despite these benefits the Slump test is not without its drawbacks. The European standard only recognizes a true slump form as in Figure 2.2, the recording of values from shear or collapsed slump is not allowed. Also, the standard recognises that the test is sensitive to changes in consistency corresponding to slumps between 10 and 200mm, and the test is not considered suitable beyond these extremes. As well as these drawbacks there are also differences in practice. The test is heavily operator dependent with differing styles affecting test results. Also, the European standards differ from the American standard as to the point from which the measurement is to be taken (Domone 2003).

Although slump provides a qualitative measure of workability, the relationship between slump and more quantitative rheological parameters is not fully understood. However, despite their inherent limitations, single-point workability tests continue to be used for the specification and quality control of concrete (Saak 2004).

Hardened state

By far the most common test carried out on hardened concrete is the compressive strength test. The main reason for this is the fact that this kind of test is easy and relatively inexpensive to carry out. The European Standards covering the testing requirements use different geometries of specimens to determine the compressive concrete strength, fc (notation for the concrete cube strength). The geometries most used are cylinders with a slenderness (height / diameter ratio) equal to two and cubes (del Viso 2007).

Cylinders (Ø150mm×300 mm) are used in the United States, South Korea, France, Canada, Australia, whereas 150mm and 100mm cubes are the standard specimens used in the United Kingdom, Germany, and many other European countries. There are several countries (e.g. Norway), where tests are made on both cylinders and cubes (Yi 2006).

Under favourable conditions the strength development of concrete increases for many months. This strength development is dependent on the temperature and humidity conditions during curing. Higher temperatures increase the rate of chemical reaction and thus the rate of strength development, and in order to achieve higher strengths at later ages loss of water from the concrete must be prevented. For test purposes the concrete test specimens are stored in water at a constant temperature until the date of testing as in BS EN 12390 – 2 (BS EN12390 2000). The compressive strength of concrete is determined on specimens tested at 28 days (BS EN 206 2000). During production there are inevitable variations in the characteristics of the materials used. The overall variation in the measured strength of concrete obtained during a project can be considered to be made up of three component sources which are (BRE 1997):

- o Variation in the quality of the material used.
- o Variation in the mix proportions due to the batching process.
- o Variation due to sampling and testing.

From purely a mix design perspective Lydon 1982 suggests that the compressive strength of concrete is empirically a function of the following:

Water / cement ratio (w/c) - The influence of the water-cement ratio and cement content on the compressive strength is well documented. The compressive strength decreases with a higher water-cement ratio but is not influenced much by the cement content (Schulze 1999); therefore, the w/c ratio has a greater bearing on the compressive strength as with less water in the mix, the stronger and less porous the concrete. However, the rheology of low W/C ratio concretes is no longer dictated by the amount of water used to make them or by the shape of coarse aggregates, but rather by what is now called the compatibility between the cement and the admixtures used (Aitcin 2000). Erdogdu (2000) in his research into this compatibility concluded that the cement content providing the highest strength gain in concrete changes with the kind of cement used. This indicates that the effect of a superplasticising admixture depends on the composition of cement rather than the amount used.

Compaction - In his study to determine the effect of compaction on concrete, Gonen (2007) found that the compaction pores seem to have a very important effect on carbonation and sorptivity. The maximum carbonation and sorptivity coefficient were observed on non-compacted specimens. The minimum carbonation and sorptivity coefficient were obtained on specimens compacted by vibration.

Cement type - It has been very well established that concretes prepared from fly ash and slag have significantly lower permeability which results in a highly durable concrete but the compressive strength development is slower than concrete prepared from normal Portland cement (Balendran et al. 1995). This is due to latent reaction between the silica within the fly ash and the calcium hydroxide, or lime, a by-product of the hydration of Portland cement, pozzolanic reaction. Little pozzolanic reaction occurs within the first 24 hours thus for a given cementitious content, with increasing fly ash content, lower early strengths are achieved (Lewis 2003).

Aggregate type – Concrete may be considered as a kind of three-phase composite material with the three phases being hardened cement paste, aggregate and the interfacial zone between the hardened cement paste and aggregate. The strength is mainly determined by the properties of the weakest phase of a composite. In low- or middle-strength concrete, normal weight aggregate is the strongest phase. Failures always happen within the hardened cement paste and/or along the interfacial zone. Therefore, there is no need to pay attention to aggregate's strength (or elastic modulus) in the common mix design procedures regarding the strength of concrete (Wu et al. 2001). Dhir et al.1999, showed that the compressive strength of a particular concrete with 100% of the coarse aggregate and 50% fine aggregate as recycled aggregate was between 20% and 30% lower than that of the corresponding natural aggregate concrete.

Aggregate / cement ratio (a/c) – Lydon (1982) states that for a given w/c ratio the higher the aggregate / cement ratio the higher the compressive strength tends to be for mixes of the same aggregate type.

Curing - The objective of curing is to provide an appropriate environmental condition within a concrete structure (temperature and humidity) to ensure the

progress of hydration reactions causing the filling and separation of capillary voids by hydrated compounds (Bonavetti et al. 2000). Malhotra and Ramezanianpour (1995) stated that "if the potential of concrete with regards to strength and durability is to be fully realized, it is most essential that it be cured adequately. The curing becomes even more important if the concrete contains supplementary cementing materials such as fly ash, or ground, granulated blast-furnace slag or silica fume, and is subjected to hot and dry environments immediately after casting".

Durability

The new European standard EN 206 addresses the design and specification of concrete to meet specific durability requirements. Agreement has not yet been reached between all member countries on a single set of durability provisions that would apply. Each country has thus decided on its own prescriptive requirements for mix limitations (e.g. maximum water cement ratio, minimum cement content) for concretes to satisfy each exposure condition within a common classification (Marsh 2000). Whilst considering the provision of a durable concrete to cope with the most aggressive environments, the most important property is permeability. Most serious reactions, such as sulfate attack, alkali-aggregate reaction, corrosion of reinforcement and freeze thaw problems, initially involve the ingress or movement of water containing aggressive solutions (Hooton 1993).

Grube and Lawrence (1984) conducted a number of studies showing that both the change in the concrete mix and the degree of curing affect the permeability of concrete to both air and moisture. Research generally demonstrates that the effects of permeability on concrete falls into two broad areas, one related to external changes (e.g. curing and environmental conditions) and the other related to internal changes (e.g. mix proportions and type of materials). Both affect the capillary voids in the concrete and micro-structure (Tombs 2003). For this research the curing, environmental conditions and the mix proportions are all constants with the main focus being applied to the type of materials used within the mix design.

2.3 Aggregates

Aggregates not only make concrete economical by occupying more volume, but also give volume stability and an increase in the durability of the concrete. Their size, shape, grading and surface texture have a significant influence on the properties of concrete both in the fresh and hardened states (Jamkar 2004).

The UK has large resources of material suitable for use as aggregate. Historically, therefore, the UK has been self sufficient in the supply of primary or natural aggregates (crushed rock, sand and gravel). However, the distribution of these resources is uneven. In particular, there is an almost total absence of hard rock suitable for crushed rock aggregate in southern and eastern England, where demand is high (Highley 2005).

The usefulness of mixing together stones, sand and some form of binder or cement to form 'concrete' has been recognised since Stone Age times. The Romans developed a rather advanced appreciation of concrete technology; the stones and sand, or 'aggregates', were only included as bulking materials, but the writings of Vitruvius in *De Architectura* demonstrate that the Romans recognised the influence of rock types and particle size distribution on the selection of aggregates for good quality concrete and mortars (Hewlett 2003).

The European standard EN 12620 'Aggregates for concrete' (BS EN 12620 2002) differentiate between coarse and fine aggregates dependent on whether they are retained on a 4mm screen. Those aggregates retained are deemed 'coarse' whilst those which pass through are 'fine'. Product sizes are now based on the respective lower (d) and upper (D) sieve sizes expressed as "d/D" Hence aggregates for concrete compared against the replaced standard BS 882 are shown as follows:

- o   20mm single size becomes 10/20
- o   10mm single size becomes 4/10
- o   20 to 5mm graded becomes 4/20
- o   M (medium) sand becomes 0/4 or 0/2 (MP)

In his study on pumice as a lightweight aggregate, Sari (2005) found that the gradation of aggregate has a positive effect on the concrete strength. He reported that the concrete strength increases with increasing fine-to coarse ratio, up to a maximum value. When this maximum is achieved an increase in fine material begins to have an adverse effect on the concrete strength.

Neville (1995) shows how the results of a sieve analysis can be better understood if represented graphically. Through the use of a chart it is possible to see whether the aggregate grading is coarse or fine. He states that the strength of fully compacted concrete, with a given water / cement ratio, is independent of the aggregate grading, with the grading being of importance in so far as it affects workability (To achieve the maximum compressive strength for a given water / cement ratio requires full compaction and this can only be obtained with a sufficiently workable mix). Neville also recognises that the ideal grading curve must be a compromise between the physical requirements and economic aspects of the concrete mix.

However, as the concrete fluidity increases, its stability decreases. This is due to the reduction in viscosity of the fresh concrete. To enhance its stability so that the paste can maintain the coarse aggregates in uniform suspension, higher powder content is required. The main target is to enhance the grain size distribution and particle packing, thus ensuring greater cohesiveness and resistance to segregation (Safawi, et al. 2004).

Good segregation resistance means that the distributions of aggregate particles in the concrete are relatively equivalent at all locations and at all levels. It also means that concrete should not segregate in vertical and horizontal directions (Buia et al.., 2002).

The European product standards give two options for the selection of sieves for grading and product description purposes. The UK has elected to use "basic set plus set 2" with the recommended sequence for coarse and fine aggregates as shown in Tables 2.2 (a) and (b).

Table 2.2

Sieve sizes for the determination of aggregate grading to BS EN 12620

(a)
Coarse aggregate
80mm
63mm
40mm
31.5mm
20mm
16mm
14mm
10mm
8mm
6.3mm
4mm

(b)
Fine aggregate
2.8mm
2mm
1mm
0.500mm
0.250mm
0.125mm
0.063mm

Natural rock, sands and gravel are by far the commonest source of aggregates worldwide. Artificial and recycled materials account for only a tiny fraction of the total aggregate produced. Sands and gravels are the products of erosion of pre-existing rocks and are typically deposited in relatively thin layers at the foot of mountains, in river valleys or along shorelines. Crushed rock is obtained from rock quarries which imply that appropriate rock must occur at the Earth's surface where a quarry can be developed (Poole, 2003).

In South Wales the Blue Lias limestone of Aberthaw was a source of hydraulic lime from early times, and was made famous when it was selected by John Smeaton for the construction of the Eddystone Lighthouse. Blue Lias is a sequence of layers of limestones and shales, laid down in Jurassic times, between 195 and 200 million years ago. In geology, it corresponds with the Hettangian stage of the Jurassic. It is the lowest of the three divisions of the Lower Jurassic period and, as such, is also given the name *Lower Lias*. It is a prevalent rock around Dorset, Somerset and South Wales (www2.7).
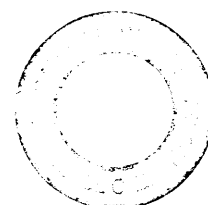
Limestones belong to the group of sedimentary rocks known as chemical sediments. They are formed in a marine environment from the precipitation of calcium carbonate, the calcium having been brought into the sea via the hydrological cycle. Fossil shells are often found in limestones, and show that biological activity is very important too. Carboniferous Limestone is a well-cemented rock of low porosity which occurs in thick beds. It is a very tough rock, and is commonly used as roadstone, but can also be used for cement making because it is often quite pure, and as a source of calcium carbonate for the chemical industry (www2.8).

The aggregates employed in the UK reflect a rich geological record and cover a vast range of different geological types of material. Typical problems encountered may include (Grantham 2003):

- o The presence of impurities such as organic matter, sulfates, chlorides or sodium or potassium salts.
- o Some aggregates may have poor physical properties such as aggregate crushing value or flakiness. Further more, they may be shrinkable, expandable, porous or frost susceptible.
- o The presence of constituents which are susceptible to alkali reaction.
- o Poorly graded material.

The Aggregates Levy was introduced in April 2002 as a result of independent research, which verified the environmental costs associated with quarrying that are not already covered by regulation. These include noise, dust, visual intrusion, and loss of amenity and damage to biodiversity and geo-diversity.

The aggregates levy

The Aggregates Levy Sustainability Fund (ALSF) was introduced initially as a two-year pilot scheme, to provide funds to tackle a wide range of problems in areas affected by the extraction of aggregates. Following a three-year second round of the Fund, a further one year extension to the scheme was announced by the Chancellor of the Exchequer in the pre-Budget Statement on 6th December 2006 (www2.9).

The Levy is set at £1.60 per tonne of aggregates extracted and sold, and is broadly revenue neutral (the Levy rose to £1.95 per tonne from April 2008). Most of the revenue generated has been used to fund a cut in employers National Insurance Contributions, but £35 million has been set aside annually to be used as a UK Sustainability Fund. In Wales, the Aggregates Levy Sustainability Fund has been devolved to the Welsh Assembly Government and under the Barnett Formula, has been allocated an annual budget of £1.7 million (www2.10).

It is due to this levy that in recent years the recycling of concrete, to produce aggregates suitable for non-structural concrete applications, has emerged as a commercially viable and technically feasible operation. This situation has risen over two decades of intensive research, predominantly centred on laboratory crushed concrete. Recent advances in aggregate – production technologies in the area of rubble screening and aggregate washing, and tighter regulation of the recycling industry have contributed to significant improvements in aggregate quality (Sagoe-Crentsil, 2001).

Concrete demolition waste has been proved to be an excellent source of aggregates for new concrete production. There are many studies that prove that concrete made with this type of coarse aggregates can have mechanical properties similar to those of conventional concretes and even high-strength concrete is nowadays a possible goal for this environmentally sound practice (Evangelista, 2007).

2.4 Admixtures

Of the many innovations in concrete technology during the last century, the use of chemical admixtures, and in particular, that of water-reducing agents and air-entraining agents, would probably rank as the most relevant, appropriate and critical to the enhancement of the quality of concrete. The combined use of chemical admixtures and mineral admixtures, such as supplementary cementitious materials, should then be able to bring out the unique properties of each of these concrete components, and show that the synergic interaction between them can produce a

much more durable and stronger concrete than when either of these materials is used alone with Portland cement (Swamy 1999).

The European standard controlling admixtures is BS EN 934-2 and defines admixtures as:

'Materials added during the mixing process of concrete in a quantity not more than 5% by mass of the cement to modify the properties of the mix in the fresh and / or hardened state'

Additive is a term often used synonymously with admixture; however, strictly speaking, additive refers to a substance which is added at the cement manufacturing stage, while admixture implies addition at the mixing stage (Neville 1987)

Admixtures are now widely accepted as materials that contribute to the production of durable and cost-effective concrete structures. The contributions include improving the handling properties of fresh concrete, making placing and compaction easier, reducing the permeability of hardened concrete and providing freeze/thaw resistance (BCA, 2000a).

The need for durable concrete with low water/cement ratios has made superplasticisers irreplaceable as it would not have been possible to achieve an acceptable fluidity (consistence) of the concrete. Today concrete is no more a three component system, but a multi component system with different chemical admixtures (i.e. superplasticisers, air entraining agent) and concrete mineral additions (i.e. fly ash, silica fume) (Griesser, 2005). High performance concrete with high strength, superior fluidity, and self compactability can only be realised because of chemical admixtures (Hanehara 1999).

The quantity of admixture added is usually based on the cement content and for most admixtures is in the range 0.2 to 2.0% by weight. In terms of active chemical this equates to less than 0.15% on a typical concrete mix. Even at this low content

they have a powerful effect, modifying the water requirement, setting time or other properties. Admixture use optimises a concrete mix, improving properties including strength and durability as well helping to reduce its environmental impact (www2.11).

Types of admixtures available

Almost all types of admixtures are covered by a European or National Standard that requires them to meet basic performance requirements, provide information on properties that can be used to check uniformity of supply and to have a factory production control system that gives assured quality. The two main admixture Standards are BS EN 934 and BS 8443. Those conforming to BS EN 934 can be CE marked (Dransfield 2006).

BS EN 934 consists of six parts with Part 2 being the most important to concrete. Some of the most widely used admixture types covered by EN 934 are:

- o   Normal plasticizing/water reducing (WRA)   EN 934-2

Often Lignosulphonate based, they are used to increase workability at constant water content and / or reduce water by up to 10%. This is used by most ready mix companies to optimise concrete performance for normal concrete.

- o   Super plasticizing/high range water reducing   EN 934-2

Based on Sulphonated Naphthalene or Melamine Formaldehyde Condensates, Vinyl Polymers or Polycarboxylate Ethers. These admixtures give a much higher performance than the normal plasticizers. They are used to give very high levels of workability or water reductions from 12 to over 30%. They are used extensively on larger projects where congested reinforcing steel requires high workability concrete to penetrate between the reinforcement. They are also used in pre-cast and on site where the large water reduction provides very high early strength and improved durability.

  o Retarding and retarding plasticizing   EN 934-2

These admixtures slow the rate of cement hydration, preventing the cement from setting before it can be placed and compacted. This type of admixture is mainly used in hot conditions and climates or on very large pours.

  o Accelerating set and hardening types   EN 934-2

These are used to speed up the rate of early hydration of the cement. They can accelerate the setting or the early strength development of concrete. These are used mainly in cold conditions or where very early use of a concrete pavement is required to provide access.

  o Air entraining   EN 934-2

Based on special surfactants, these admixtures cause tiny air bubbles < 0.3mm in diameter to stabilise within the cement paste. This air helps to prevent the concrete from cracking and scaling as a result of frost action. In low workability mixes, air helps lubricate the aggregate aiding compaction under vibration closing voids and reducing bleed water and segregation of the aggregate before the concrete can set.

  o Water resisting (water proofing)   EN 934-2

These water repellent admixtures act on the capillary structure to block the pores and impede the flow of water through the natural capillaries in hardened concrete. These are generally used in structures below the water table or in water retaining structures.

  o Retarded ready-to-use mortar admixtures   EN 934-3

They increase the cohesion and retard the setting of mortar for masonry, allowing it to be delivered to a building site by ready mix in large volumes that can be used over an extended period, usually of 1 to 2 days. Setting is initiated when water/admixture is sucked out by the in-situ masonry unit

o Sprayed concrete EN 934-5

These admixtures provide a very rapid set to concrete that is sprayed onto vertical and overhead applications, preventing it from falling off before it has time to set. This type is mainly used in tunnelling applications for early roof support. Dosage may exceed 5% (www2.12).

This research

This study has employed the use of a number of Plasticising/water reducing admixtures, some being designed specifically for this type of application (i.e. with fly ash) and some general "off the shelf" admixtures.

These dispersing admixtures are usually based on refined lignosulphonate, a by-product of the paper pulping industry. They are effective at dosages of around 0.3 to 0.5% on cement weight but their water reducing effect is limited to about 12%. At higher dosage, secondary effects such as air entrainment and retardation may limit their use. Blending with superplasticisers may extend their dosage and performance to give a mid-range product.

The low dose and relatively low cost make these admixtures particularly suitable for a wide range of general applications. Used to reduce both water and cement content, they can optimise the mix design for both cost and environmental impact. Most will also slightly increase cohesion, reducing bleed and making placing and finishing easier (www2.13).

2.5 Cement

The manufacture and use of hydraulic cements is ancient and is generally accredited to the Greeks and Romans; however, the use of lime as a binder dates back to the 6th millennium B.C. whereby a terrazzo floor excavated in Canjenü in Eastern Turkey laid with a lime mortar has been dated between 12 000 and 5000 BC (Elsen J 2006).

In the mid eighteenth century whilst looking for a material with which to build the new Eddystone Lighthouse, John Smeaton made two important discoveries. First, the use of a new kind of interlocking stone construction, and second, the development of a water-resistant (hydraulic) mortar to bind the blocks together by mixing blue lime and pozzolanic material from Civita Vecchia, near Rome. Indeed, Smeaton's seminal observation that the best hydraulic cements were those made from limestone containing certain proportions of clayey material is regarded as the starting point of the modern engineering use of cement and concrete (www2.14).

The term "Portland cement" was first applied by Joseph Aspdin in his British patent No. 5022 (1824), which describes a process for making artificial stone by mixing lime with clay in the form of a slurry and calcining (heating to drive off carbon dioxide and water) the dried lumps of material in a shaft kiln. The calcined material (clinker) was ground to produce cement. The term "Portland" was used because of the similarity of the hardened product to that of Portland stone from Dorset and also because this stone had an excellent reputation for performance (Moir 2003).

There are three broad categories of cement products: Portland cement, Portland cement with the addition of pulverised fuel ash or blast furnace slag and special cements. All but certain special cements are manufactured using substantially the same process route. Portland cement, which is manufactured to British Standard BS12:1991, is defined as an active hydraulic binder based on ground clinker formed from a predetermined homogeneous mixture of materials comprising lime (CaO), silica (SiO_2) and a small proportion of alumina (Al_2O_3) and generally iron oxide (Fe_2O_3).

The vast majority of cement used in construction work is described as being a Portland cement and it is this general type that this research is concentrated on. Portland cement is essentially a calcium silicate cement, which is produced by firing to partial fusion, at a temperature of approximately 1500^0C, a well homogenised and finely ground mixture of limestone or chalk (calcium carbonate) and an appropriate quantity of clay or shale (Moir 2003).

Cement process overview

The second half of the twentieth century saw significant advances made in cement manufacture, culminating in the development of the pre-calciner dry process kiln (Moir 2003). Figure 2.3 is an illustration of the full cement manufacture process.

The raw materials are ground to a fineness which enables a satisfactory combination to be achieved under normal operating temperatures. The homogenised raw meal is introduced into the top of a pre-heater tower working its way down until it arrives at the Pre-calciner vessel. Here the meal is flash heated to approximately 900^0C using the hot exhaust gases from the kiln itself and , although the material is suspended for a few seconds only, approximately 90% of the limestone in the meal is de-carbonated before entering the kiln. This is the point whereby cement manufacture contributes greenhouse gases both directly through the production of carbon dioxide, when calcium carbonate is heated, producing lime and carbon dioxide (Hewlett 1998), and also indirectly through the use of energy, particularly if the energy is sourced from fossil fuels. As reported in Chapter 1, the cement industry produces 5% of global man-made CO_2 emissions, of which 50% is from the chemical process, and 40% from burning fuel (www2.14.1) with 10% from ancillary operations.

In the rotary kiln the feed is heated to approximately 1500^0C and as a result of the tumbling action and the partial melting it is converted into the granular material known as clinker. A rotary kiln typically comprises a long cylinder of 50 to 150 metres, inclined slightly from the horizontal (3% to 4% gradient) which is rotated at about 1 to 4 revolutions per minute. The solid material passes down the kiln as a

result of rolling and slipping as the kiln rotates. The material flow is counter current to the combustion gases and fuel is fired at the lower (front) end of the kiln. Kilns are lined throughout with refractory bricks providing varying degrees of insulation to the steel shell. Brick compositions vary from around 25% to 30% alumina at the cooler back end, to 45% alumina in the calcining zone and rising to 70% alumina as the burning zone is approached. Dense magnesite or dolomite bricks are used in the burning zone. Heat transfer within the kiln system results from a complex interchange between the gas, inner kiln walls and feed surface (www2.15).

The material remains in the rotary kiln for approximately thirty minutes and exits as clinker at around 1200^0C. The clinker immediately enters the cooler and the temperature is reduced to approximately 60^0C before going to storage. A small portion, typically around 5%, of calcium sulfate in the form of gypsum is added to the clinker and the milling of the materials, using a ball mill, proceeds until the required fineness has been achieved.
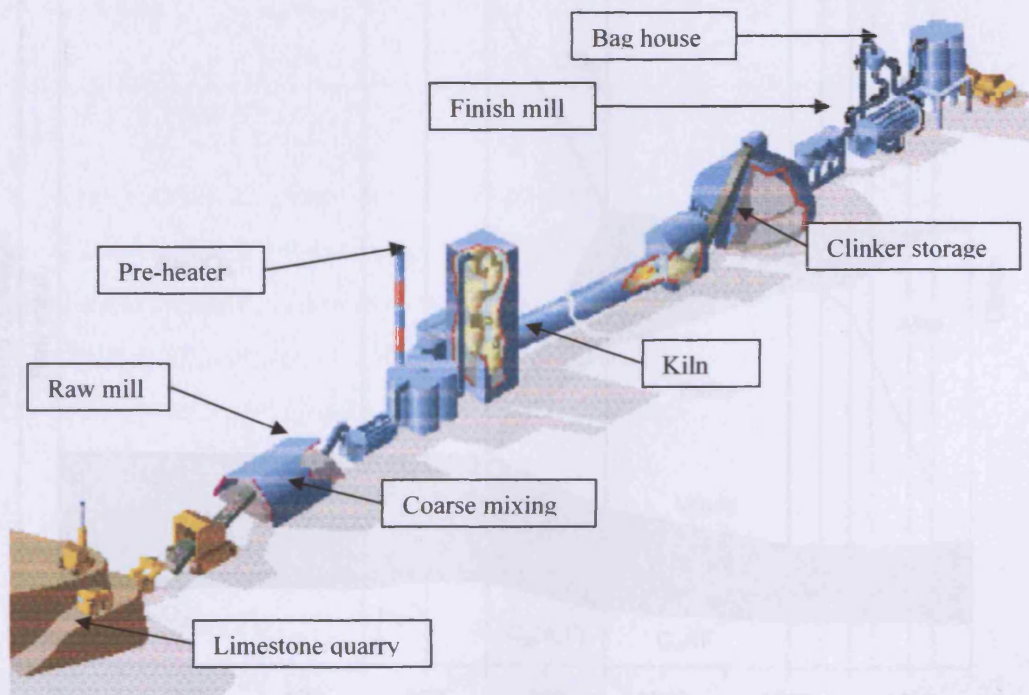
Figure 2.3 The cement manufacturing process
(Source World Business Council for Sustainable Development)

A typical pre-heater kiln processing diagram is illustrated in Figure 2.4 showing the broad variation in chemical composition and temperature with time and position within the kiln system (Environment Agency 1996). The heating of the raw materials follows certain stages, as follows:

o drying, with the removal of any moisture present;

o calcination at approximately 800-900°C, with the conversion of the limestone to free lime with the release of carbon dioxide;

o Sintering at approximately 1450°C in a liquid state, where the free lime reacts with the other components to form calcium silicates, aluminates and aluminoferrite (the principal ingredients of Portland cement). This sintered product is known as cement clinker and this process stage is also referred to as 'burning' or 'clinkering'; and

o Cooling where the temperature of the liquid is reduced from 1450 to 1100°C to form stable crystals within the kiln followed by cooling to about 250°C in a clinker cooler.
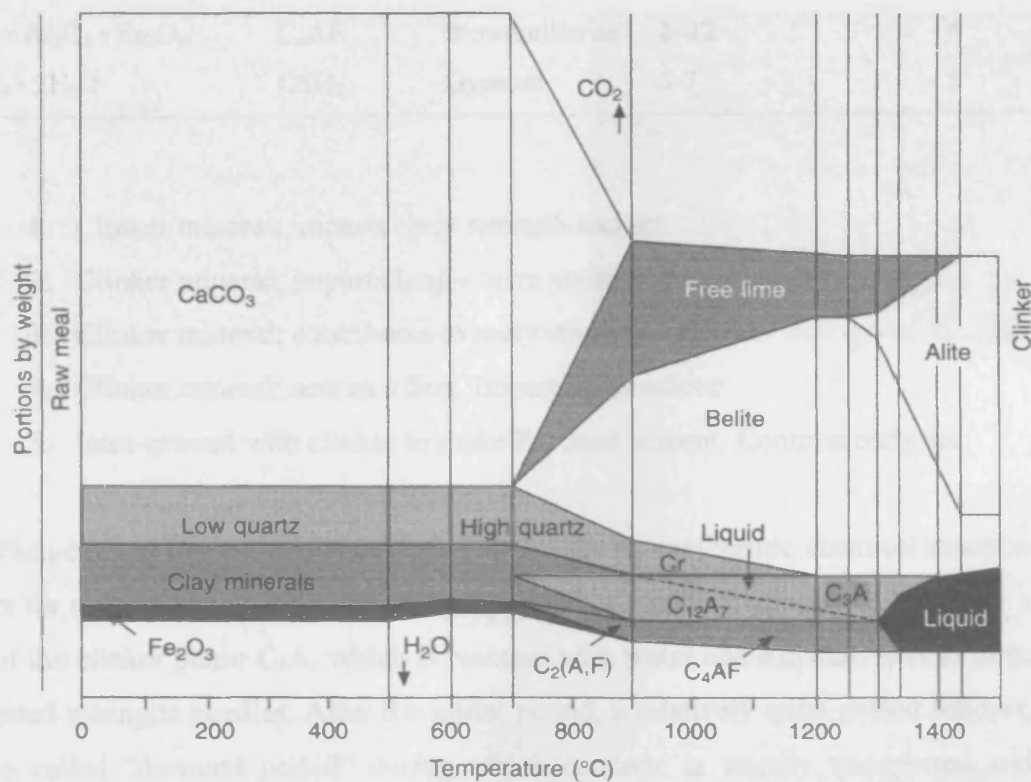
Figure 2.4 Typical pre-heater kiln processing system
(Source Moir 2003)

2.6   Chemistry of Cement

The principal chemical constituents formed during cement manufacture are tricalcium silicate, dicalcium silicate, tricalcium aluminate and tetracalcium aluminoferrite, often abbreviated to C_3S, C_2S, C_3A and C_4AF respectively. Of these, the first two are particularly important because they provide the cementing action – the higher the proportion of C_3S relative to the C_2S, the more quickly strength is gained after mixing (Moir 2003, Corish 1985). Table 2.3 shows the range of the principal materials that make up modern Portland cement.

Table 2.3

Ranges of principal minerals in European clinkers

(Source Moir 2005)

Oxide Composition	Cement Notation	Common Name	Concentration (wt%)	Comment
$3CaO \cdot SiO_2$	C_3S	alite	55–65	1
$2CaO \cdot SiO_2$	C_2S	belite	15–25	2
$3CaO \cdot Al_2O_3$	C_3A	aluminate	8–14	3
$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF	brownmillerite	8–12	4
$CaSO_4 \cdot 2H_2O$	CSH_2	Gypsum	3-7	5

1. Clinker mineral; imparts early strength and set
2. Clinker mineral; imparts long – term strength
3. Clinker mineral; contributes to early strength and set
4. Clinker mineral; acts as a flux. Imparts grey colour
5. Inter-ground with clinker to make Portland cement. Controls early set

When cement comes in contact with water a strong exothermic chemical reaction occurs for some minutes called the "initial period" of cement hydration. It is mainly a part of the clinker phase C_3A, which is reacting with water and sulphate ions to form elongated ettringite needles. After the initial period, a relatively quiet period follows, the so called "dormant period" during which concrete is usually transported and placed (Griesser, 2005).

The mineral C_3S (alite) hydrates quickly and so imparts early strength and set to the cement, whereas C_2S (belite) hydrates slowly and is the main contributor of long-term strength. Both minerals hydrate to form tricalcium silicate hydrate gel (sometimes called tobermorite) plus lime; the exact reaction stoichiometries vary considerably in the number of waters of hydration incorporated, but a typical hydration reaction, shown for C_3S, would be:

$2C_3S + 6H$ (water)

$$\rightarrow C_3\,S_2\,H_3 \text{ (tobermorite gel)} + 3CH \text{ (lime)}. \tag{1}$$
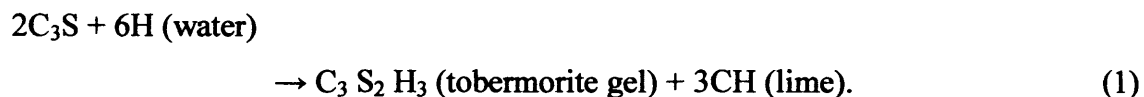
The tobermorite (the formula shown is only representative of a family of similar calcium silicate hydrates CSH) gel is the actual binder in the hydrated cement. The lime released in the hydration reaction is in small part taken up by hydration of C_3A and C_4AF (reactions not shown), but most remain unreacted and thus available to activate any pozzolans added in the finished cement (molecular formula of Lime mixed with water is $Ca(OH)_2$). Hydration of C_3A is almost instantaneous and highly exothermic. The mineral thus speeds the development of early strength and set, sometimes to the point of causing flash set (which is undesirable); as noted earlier, gypsum is used to control this. The main function of the aluminoferrite mineral (C_4AF) is as a flux, that is, it acts to lower the temperature at which the clinker minerals form (i.e., clinkering temperature). This mineral also imparts the grey colour to Portland cement and for this reason its formation is avoided, through the use of only iron-free raw materials and higher clinkering temperatures, in the production of white (Portland) cement, which is a much higher priced product than grey ("ordinary") Portland cement (Van Oss 2002).

Pozzolans

Pozzolanic materials can be natural in origin or artificial and are available widely. They have been used throughout the world to make good quality concrete. The natural pozzolanic materials most commonly met with are: volcanic ash which is the original pozzolan, pumicite, opaline shales and cherts, calcined diatomaceous earth, and burnt

clays (Davraz et al.. 2005). Artificial pozzolanic materials are generally siliceous by-products, such as fly ashes, condensed silica fume and metallurgical slags (blast furnace slag, steel slag and nonferrous slags) (Papadakis et al.. 2002).

According to ASTM C 595, a pozzolan is defined as:

"a siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide to form compounds possessing cementitious properties (pozzolanic activity)."

The CaO content of a pozzolanic material is generally insufficient to react with all the pozzolanic compounds it contains; however, it exhibits some pozzolanic activity (pozzolanic and cementitious materials). Thus, a pozzolanic material requires $Ca(OH)_2$ (calcium hydroxide) in order to form strength products, whereas a cementitious material itself contains quantities of CaO and can exhibit a self-cementitious (hydraulic) activity. Therefore, pozzolanic materials are often used in combination with Portland cement, which contain essential compounds for their activation, $Ca(OH)_2$ from cement hydration (Papadakis et al.. 2002). Lewis enhances this statement adding that the silica in pozzolana has to be amorphous or glassy to be reactive and must be finely divided in order to expose a large surface area to the alkali solutions for the reaction to proceed (Lewis et al.. 2003).

It has been shown that Portland cement is both resource and energy intensive. Every tonne (t) of cement requires about 1.5t of raw material and about 4000 to 7500 Megajoul (MJ) of energy for production. The energy to produce a tonne of cement is estimated to account for 40-45 percent of the plant production cost. Much more importantly, every tonne of cement releases 1.0 to 1.2t of CO_2 into the environment by the time the material is put in place. In the world we live in, the use of resources and energy, and the degree of atmospheric pollution that it inflicts are most important (Swamy 2003).

Large volumes of by-product materials generated from industrial and post-consumer sources are landfilled. The amount of waste generation is increasing, while

landfill space is decreasing. Additionally, due to stricter environment regulations, it is difficult to obtain approval for developing new disposal facilities. The cost of disposal is escalating. Recycling not only saves on huge disposal costs, but also conserves natural resources, and in some cases it provides technical and economic benefits. Various uses of by-products generated from industrial and post-consumer sources exist (Naik et al.. 1999). It may be that some of this industrial waste can be used as a pozzolanic cement replacement in concrete. Identification of the important elements and physical properties of these wastes could be extremely cost effective for industry and beneficial to the environment if their use in concrete was established.

2.7   Additives

The construction industry accounts for over 90% of mineral consumption in the UK and, of this; one-third is used in road construction. Other uses include buildings, railways and manufacturing of cement, lime, plaster and a variety of other products such as glass and ceramics. (www2.16).

Quarry products including stone, crushed rock, aggregate and sand make up between 51% and 62% of the resource flow of the construction industry, Figure 2.5. This amounts to some 240Mt of material. According to the Quarry Products Association, 18% of the UK's aggregate demand is met from recycled sources. The Minerals Planning Guidance (MPG 6) set a target of 55Mt for use of recycled and secondary material by 2006 (www2.16). This equates to ~23% or an additional 12Mt compared with current practice. In the House Building Quick Wins guide, WRAP estimate that an additional 20Mt of recycled and secondary material could be used in place of virgin material if best practice is adopted (Lazarus 2005).

DTI - Resource flow

☐	Crushed rock
■	Sand & gravel
☐	Cement
☐	Clinker
■	Slate
■	Ready made concrete
■	Concrete building blocks
☐	Concrete roofing tiles
■	Fibre cement products
■	Bricks
☐	Glass
■	Steel
■	Other metals
■	Timber
■	Plastics
■	Paints
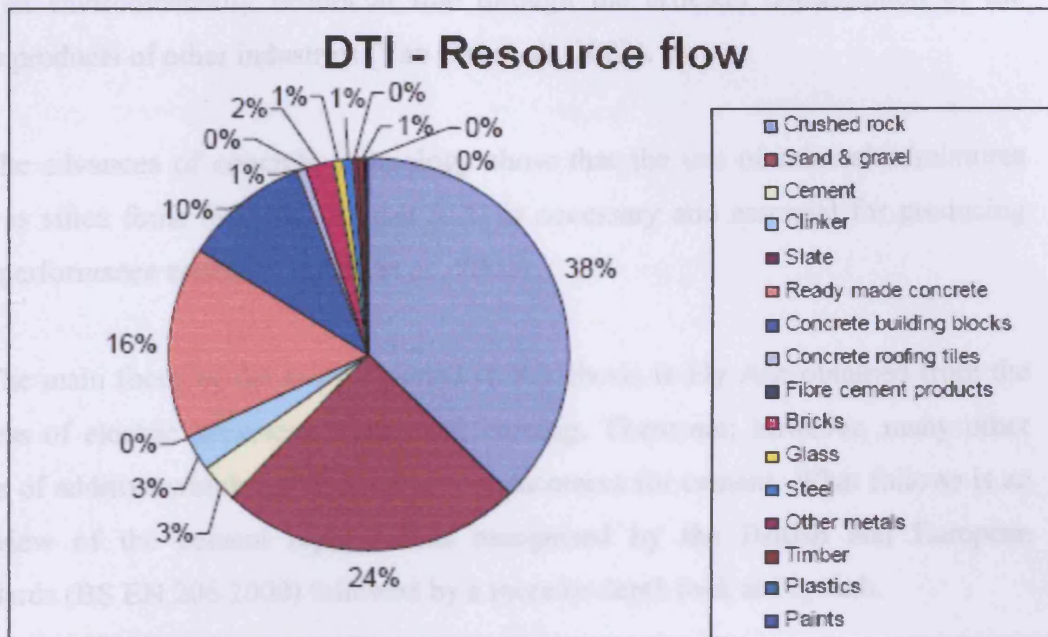
Figure 2.5 Resource use within the construction industry
(Source DTI)

The need to reduce the environmental impact of cementitious materials is, and will continue to be, a major driver for innovation. The use of supplementary materials is now so well established that the average clinker content of cements in Europe is less than 80%. The most commonly used Supplementary Cementitious Materials (SCMs), blast furnace slag, fly ash, limestone, and silica fume, are industrial by-products that, by and large, can be obtained in large and regular amounts, with a consistent composition. Many other materials containing reactive silica, reactive alumina or both can be used to similar effect. But these products are more variable or available in relatively small quantities (Scrivener et al. 2008).

Wastes and secondary materials are being increasingly used in the production of cements. They may be added as raw meal substitutes, fuels or as mineral additives (Johnson 2006). Although in many respects more benign than most mining and mineral processing activities, cement manufacture is nevertheless associated with important environmental issues, most notably the problem of greenhouse gas generation. With its huge appetite and yet flexible requirements for fuel and non-fuel raw materials however, cement manufacture also offers significant opportunities to

play an environmentally beneficial role through the efficient consumption of the waste products of other industries (Van Oss et al.. 2002).

The advances of concrete technology show that the use of mineral admixtures such as silica fume (SF) and fly ash (FA) is necessary and essential for producing high performance concrete (Poona et al.. 2001).

The main focus of the work reported in this thesis is Fly Ash obtained from the process of electric generation from coal burning. There are; however, many other forms of additive which can be used as a replacement for cement. What follows is an overview of the cement replacements recognised by the British and European standards (BS EN 206 2000) followed by a more in-depth look at Fly Ash.

Ground Granulated Blast furnace Slag (GGBS)

Blast furnace slag has been widely used as a successful replacement material for Portland cement, improving some properties and bringing environmental and economic benefits. The production of pig iron has increased progressively in recent years. Considering that approximately 300kg of slag are generated per ton of iron (Escalantea et al.. 2001), it is estimated that about Some 2.2 million tonnes of GGBS are produced each year in the UK at five locations (ww2.16.1).

- o Teesport, Cleveland
- o Scunthorpe, North Lincolnshire
- o Purfleet, Essex
- o Llanwern, nr. Newport, South Wales
- o Port Talbot, South Wales

Chemical reactions

As the chemical composition of steel slag is highly variable, the mineral composition of steel slag also varies. Olivine, Merwinite, C_3S, C_2S, C_4AF, C_2F, RO phase (CaOFeO–MnO– MgO solid solution) and free-CaO are common minerals in steel slag. Its chemical composition consists of CaO 45–60%, SiO_2 10–15%, Al_2O_3 1–5%, Fe_2O_3 3–9%, FeO 7–20%, MgO 3–13%, and P_2O_5 1–4% (Shi et al.. 2000). The presence of C_3S, C_2S, C_4AF and C_2F endorses steel slag hydraulic properties. However, the C_3S content in steel slag is much lower than that in Portland cement. Thus, steel slag can be regarded as a low strength hydraulic material (Kourounis et al.. 2007).

In the presence of water GGBS will react very slowly, making slag on its own of little practical use. Essentially the hydraulicity of the slag is locked within its glassy structure (i.e. it possesses latent hydraulicity) and in order to release this reactivity some form of 'activation' is required. The activators, which are commonly sulphates and/or alkalis, react chemically with the GGBS, increasing the pH of the system. This increase 'disturbs' the glassy structure resulting in activation of the GGBS with the water producing its own cementitious gels. In practice, activation is achieved by the blending of GGBS with Portland cement as the latter contains both alkalis and sulphates (Lewis et al.. 2003).

As good as GGBS has proved to be since its incorporation into the concrete industry, environmental factors which welcome its use will also bring its demise. Although the efficiency of blast furnaces is constantly evolving, the chemical process inside the blast furnace remains the same. According to the American Iron and Steel Institute; "Blast furnaces will survive into the next millennium because the larger, efficient furnaces can produce hot metal at costs competitive with other iron making technologies" (www2.17). However, one of the biggest drawbacks of blast furnaces is the inevitable carbon dioxide production as iron is reduced from iron oxides by carbon and there is no economical substitute - steelmaking is one of the unavoidable industrial contributors of the CO_2 emissions in the world (www2.18).

The Electric Arc Furnace (EAF) is now recognised as the primary method of steel manufacture from scrap metal materials. The environmental benefits attached to the EAF such as the use of scrap steel as feedstock instead of raw iron, low carbon emissions and flexibility with production, adjusting output according to local demand, is aiding in the reduced use of the blast furnace .The precise control of chemistry and temperature encourage the use of electric arc furnaces producing many grades of steel, from concrete reinforcing bars and common merchant-quality standard channels, bars, and flats to special bar quality grades used for the automotive and oil industry.

The main drawback with the EAF is that the process does not produce slag as a result of steel manufacture; therefore, GGBS reserves will begin to decline as blast furnace output reduces (Burridge 2008).

Silica Fume

Silica fume, or Micro-silica as it is also known, is a by-product of the manufacture of silicon and ferrosilicon alloys from high purity quartz and coal in a submerged-arc electric furnace (Neville 1995). Its fineness and high SiO_2 content make this a very efficient pozzolan and, like other pozzolanic materials, it is generally more efficient in concretes having a high water-cement ratio. The expected reduction in compressive strength associated with a high water / cement ratio can be counteracted through the use of super plasticizers which maintain the required slump and show an increased compressive strength at three days and after (Malhotra et al. 1982).

A number of problems are associated with the use of silica fume. First, due to its fineness and high silica content, fears are expressed over its use in the powdered form. Although studies have shown there to be no risk to health, silica fume is supplied 'pelletised' for inter-grinding with cement or as'slurry' mixed with its own weight of water and applied directly into the concrete mix (Lewis 1996). Second, silica fume is a very expensive product (Neville 1995).

Suppliers have recognised the value of silica fume and consequently the price has escalated significantly. In the early 1980's silica fume was regarded as a waste product but as its use has increased so has the price varying from half to twice the cost of normal Portland cement. Further increases in the price may limit the use of fume to specialised applications (Malhotra et al. 1982).

The addition of silica fume to concrete is effective for increasing the compressive strength, decreasing the drying shrinkage, increasing the abrasion resistance, increasing the bond strength with the reinforcing steel, and decreasing the permeability. As a result, silica fume concrete is increasingly used in civil structures (Li et al. 1998). Future design demands with an increasing need for durability and performance of structures will ensure its use escalates into the future (Lewis 2000).

Limestone

The reduced cost of limestone cement is mainly due to energy saving by substitution of a portion of the calcined clinker by a small amount of limestone. In many cases, this has also been facilitated by the presence of limestone deposits near cement kilns. Hence, the limestone additions do not have to be transported over long distances to cement factories (Kenai et al. 2004).

The limestone filler was considered by many as an inert filler, but it has been gradually accepted as contributing to the hydration process by the formation of calcium mono-carboaluminates (C_3A . $CaCO_3$. $11H_2O$) (Lewis 2003).

Although most European countries produce blended cements, limestone cement is mainly produced in France where, in 1990, out of 69 brands of composite cements, 61 brands contained limestone filler alone or with other secondary constituents. Twenty-nine of these had filler contents between 15% and 25% by mass of cement (Bertrandy et al. 1999).

Now the new European Standard BS EN 197-1 identifies two types of Portland limestone cement containing 6-20% limestone (type II/A-L) and 21-35% limestone (type II/B-L). The limestone is inter-ground with the Portland cement clinker which normally produces 32.5N grade cement (Lewis 2003). This recognises that the addition of limestone to Ordinary Portland cement has many benefits. Livesey (1991) reported that cement with 15% limestone gives a similar strength to OPC concrete if the cement content is increased by 10%.

Kenai et al. (2004), showed that water permeability of concrete specimens was lower in concrete with limestone cement and that these findings were consistent with the findings of other research that found concrete with limestone cement has a lower oxygen permeability and higher resistance to sulfate attack than OPC concrete. Tsivilis et al. (1999) conclude that it's the clinker quality which significantly affects the gas permeability and sorptivity of the limestone cement concrete; however, the effect of the limestone quality on the concrete permeability is not well established. They state that limestone additions can improve the permeability properties of the concrete, especially in cements having high C_3A content.

The addition of 20% limestone filler was also found to have no detrimental influence on the resistance to chloride penetration of pastes and mortars (Hornain et al.. 1995). Kenai also reports that limestone cement behaviour in an outdoor, hot climate is good, provided initial curing is sufficient (Kenai et al. 2004).

However, Bonavetti et al. (2003) saw some drawbacks to the use of limestone as a cement replacement. They state that "For low w/c ratio concrete, a large proportion (more than 35%) of Portland cement remains un-hydrated and acts as an expensive and energy-consuming filler". They also report that a reduction in compressive strength, at 28 days, was measured; for concrete containing up to 18.1% of limestone filler a compressive strength reduction in the range of 8– 12% was achieved.

A further drawback is the fact that limestone is a natural resource. Although abundant throughout Europe, preservation of our natural resources must take precedence and the use of this material limited. With so many other waste materials available to replace Portland cement the use of limestone may have a limited lifespan.

Metakaolin

There is no national standard covering the use of metakaolin as a cementitious addition for concrete. The product Metastar Metakaolin is covered by Agrément Certificate Number 98/3540 which relates to a specific product used at levels up to 20% replacement of Portland cement (Lewis 2003).

Metakaolin (MK) is a thermally activated alumino-silicate material obtained by calcining kaolin clay within the temperature range of 700–850^{0}C. It contains typically 50–55% SiO_2 and 40–45% Al_2O_3 and is highly reactive.

In Portland cement concrete, MK reacts at normal temperatures with calcium hydroxide (lime) in the cement paste to form mainly calcium silicate hydrates (C-S-H), C_2ASH_8 (gehlenite hydrate), and C_4AH_{13} (tetracalcium aluminate hydrate) (Rojas et al. 2002)

It has been reported that the replacement of cement by 5–15% MK results in significant increases in compressive strength for high-performance concretes and mortars at ages of up to 28 days, particularly at early ages (Poona et al. 2001).

Replacement of cement in concrete by mineral admixtures produces an immediate dilution effect such that if the replacement material was totally physically and chemically inert, concrete strength would be reduced in approximate proportion to the degree of replacement. However, finely divided mineral admixtures, even if chemically inert, do have a physical effect in that they behave as fillers. This is particularly significant in the interfacial zone regions (The region of the cement paste around the aggregate particles, which is perturbed by the presence of the aggregate. Its origin lies in the packing of the cement grains against the much larger aggregate, which leads to a local increase in porosity and predominance of smaller cement particles in this region) where they produce more efficient packing at the cement paste-aggregate particle interface, reduce the amount of bleeding and produce a denser, more homogeneous, initial transition zone microstructure and also a narrower transition zone. Thus, relative to no cement replacement, partial replacement by ultra-

fine solids results in a reduction in the strength of pastes (due to the dilution effect) but an increase in the strength of concrete (due to an improved transition zone) (Wild et al. 1996).

Wild et al.. (1996) reported that the filler effect is immediate, with OPC having a major impact in the first 24 hours and maximum effect of the pozzolanic reaction occurring at between 7 and 14 days. However, Zhang et al. (1995) recognised that the MK concrete had higher strength properties at all ages up to 180 days compared to a control concrete and reiterated the fact that MK concrete showed a faster strength development at early ages.

Wild et al. (1996) also suggested that an optimum replacement level of 20% should be used to maximise the concretes' long term strength enhancement. However, the increased heat of hydration from the rapid early strength development can be as much as 15% more than that of a 100% OPC mortar, it has been shown that this can be controlled through the use of a replacement level of up to 10% (Frías et al. 2000).

Lagier et al. (2007) confirmed that strong exothermic reactions occurred in all cements blended with MK particularly in the first 24 hours. They reported that the reaction of metakaolin appears to be quite sensitive to variations in total alkali content in the cement in particular when the alkali content increases. They proposed that an increasing rate of metakaolin dissolution with increasing cement alkali content may accelerate or intensify the reaction of the C_3A phase and that the results demonstrated that the reaction of MK during early hydration does vary with cement type.

Municipal Solid Waste Ash (MSWA)

It is difficult to get hold of reliable up to date estimates on the amount of municipal waste landfilled annually. It could be assumed that trends established in the early part of this decade will continue; however, with recycling schemes becoming evermore prevalent some authorities are already reporting annual reductions in their 2004 figures over previous years (www 2.18.1).

The UK produces 420 million tonnes of waste each year, of which 30 million tonnes is municipal waste. In England the total amount of municipal waste has continued to rise to an estimated 28.8 million tonnes in 2001/02 compared to 28.1 million tonnes in 2000/01, an increase of 2.4 per cent. The proportion of municipal waste being recycled or composted increased from 12.3 per cent in 2000/01 to 13.5 per cent in 2001/02. The proportion of waste incinerated with energy recovery has remained roughly constant at just under 9 per cent in 2000/01 and 2001/02. The proportion of municipal waste being disposed in landfill has decreased from 78 per cent in 2000/01 to 77 per cent in 2001/02. However, the actual tonnage of municipal waste disposed of in landfill has still increased slightly from 22.1 million tonnes in 2000/01 to 22.3 million tonnes in 2001/02. Past studies showed that the average Biodegradable Municipal Waste (BMW) content of household waste in England is 63%. In 2009/10, English local authorities sent 8.4 million tonnes of BMW to landfill. This is 1 million tonnes less than the previous year and nearly 3 million tonnes less than local authorities could have landfilled if all 11.2 million tonnes Landfill Allowance Trading Scheme (LATS) allowances had been used (www2.19).

Pan et al. (2007), in their research into the use of MSWA as a cement replacement, recognised the fact that the ash is rich in heavy metals and salts and without proper treatment may cause serious environmental problems.

Studies by Sakai and Hiraoka (2000) indicate that there are much more volatile heavy metals (e.g., Hg, Pb, Cd) and toxic organic substances in fly ash than in bottom ash. The leaching characteristic of these hazardous materials leads to secondary pollution of groundwater after landfilling. Therefore, MSWA fly ash was classified as hazardous waste requiring additional processing in most countries worldwide.

The results from the melting treatment of fly ash collected from MSW incinerators are described in work carried out by Abe et al. (1996). The fly ash used had an average particle size of 22 μm and a melting fluidity point of 1280-1330°C and was melted using a Kubota melting furnace without any additives. They found that 88% of the fly ash was turned to slag and 12% to dust, which contained a lot of heavy metals such as Pb and Zn. The leaching levels of heavy metals from slag was significantly lower than those of bottom and fly ashes from municipal solid waste incinerators;

however, the leaching rates were dependent on pH levels such that leachate increased at lower pH levels.

Lin et al. (2003), discuss the use of this MSW fly ash slag produced via heat treatment. They conclude that MSWA fly ash slag is non-hazardous and can thus be classified as general industrial waste. Thus, the recycling of MSWI fly ash slag would not result in further environmental pollution. They observed the crystalline structure revealing that all mortars with partial MSWI fly ash slag substitutions had a similar crystalline composition, containing $3CaO/SiO_2$, $2CaO/SiO_2$, $Ca(OH)_2$, CSH (Tobermolite), and C_3AH_6 (Calcium Aluminate Hydrate).

It has been shown that MSWA is a stable and effective cement replacement if subjected to a process of heat treatment. This has the effect of reducing use of a natural resource (limestone) in the making of cement, and for the disposal of a waste material; however, much energy and natural resource will be used in providing the temperatures needed to process the ash.

2.8   Fly Ash

The burning of coal supplies around 40% of the UK electricity, as shown in Figure 2.6. With the well publicised issues of security of electricity supply relating to natural gas, the gradual decline of the existing nuclear power stations, the issues and timescales involved with building new nuclear power stations and slow development of renewable forms of electricity generation and their dependence on the forces of nature, it would appear that pulverised coal fired power generation will be necessary for some years to come. Even in future years, the development of clean coal power stations with carbon capture will still lead to the production of ash. As there are estimated to be in excess of 200 years of coal in reserves around the world, such an energy resource cannot simply be ignored (UKQAA 2007).

Mathews (2007) in his paper "Seven steps to curb global warming" states that 'Coal will continue to be the largest source of the world's electricity generation, in the

absence of policy change, accounting for 40% of electric power output overall. As a result, it is projected that coal would account for 35% of the 43.7 billion metric tonnes of carbon dioxide emissions by 2030, in the absence of policy interventions'. His views are that coal-fired power stations are 'the greatest source of Green House Gas emissions' and recommends that a moratorium on the use of coal-fired power stations be implemented with fines on governments persisting with the use of coal-fired power stations being used in the development of sustainable alternatives. However, it is the view of the Author that investment in coal fired generators will continue for many years to come in countries like China, who have extensive stocks of coal and the manufacturing capability to run and maintain the coal industry, yet are struggling to keep up with energy demand.
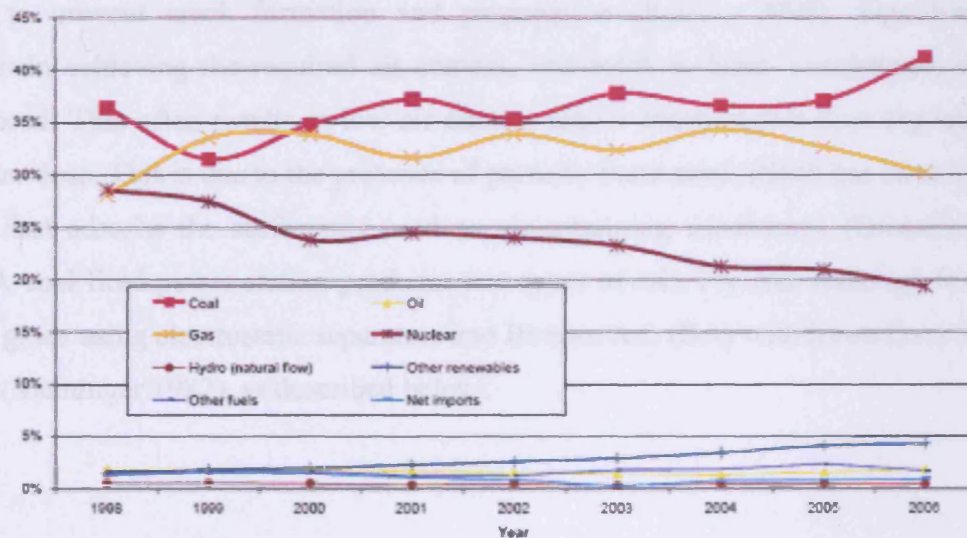
Figure 2.6 Fuel sources for electricity generation

(Source UKQAA 2007)

This fact is reflected by the proposed investments of €3.5 billion (£2.6 billion) and $2.0 billion (£1.0 billion) in new coal fired power stations proposed by Electrabel in Europe and British Petroleum (BP) / Rio Tinto in Western Austrailia (Anon 2007). However, with the new technology available it is possible for new power stations to

be fully integrated with carbon capture and storage to reduce its emissions of greenhouse gases.

The main by-product of coal combustion is Fly Ash (FA). In the European Community electric power stations generate 55 million metric tons (ECOBA, 2003) of coal combustion by-products, 44 million tons of which corresponds to FA. About 50% of this annual production is used in the cement industry, given that FA contains large amounts of silicon dioxide (SiO_2) and aluminium oxide (Al_2O_3) and because of its pozzolanic property after reacting with lime and water. However, nitrogen oxide (NOx) emissions reduction, through the installation of low NOx burners, often results in higher unburned carbon contents, and therefore in a decreased marketability of some ashes. According to BS EN 450, a loss-on-ignition (LOI) greater than 7% renders FA unusable for cement or concrete manufacture. It is generally accepted that the unburned carbon tends to adsorb the air entrainment reagents that are added to the cement to prevent crack formation and propagation (Rubioa 2008). Significant problems in achieving the required air content, and batch to batch consistence, are experienced. This often results in low air content and/or much higher than expected admixture dose. This is due to the presence of partially burnt coal, which has an active surface that adsorbs the surfactants used as air-entraining admixtures (Dransfield. 2005). A coal fired power station produces two types of ash, Fly Ash removed from the flue gases using electrostatic separators and Bottom Ash (BA) withdrawn from the furnace (Meininger 1982), as described below:

Furnace bottom ash

Furnace bottom ash (FBA) is a waste material from coal-fired thermal power plants. Unlike its companion, pulverised fuel ash, it usually has no pozzolanic property which makes it unsuitable to be used as a cement replacement material in concrete. However, its particle distribution is similar to that of sand which makes it attractive to be used as a sand replacement material (Bai, 2005).

The coarse, fused, glassy texture of FBA would normally make an ideal substitute for natural aggregates (Ramme et al.., 1998). An important use of bottom ash is as a base layer material in road construction (Churcill and Amirkhanian, 1999). Also, there has been research concerning whether FBA could partially or entirely replace natural gravel in the production of a concrete presenting a 28-day compressive strength of 25 MPa (Pera et al. 1997).

The primary use for FBA has been for many years in block making. Many still refer to 'breeze blocks', with breeze being the fore-runner to FBA. Because FBA is flushed from the furnace by high pressure water jets, it is a far superior product to 'breeze', which ceased to be available anyway as the older furnaces were replaced. Subsequently FBA became the preferred product by the block manufacturers as a lightweight aggregate. Currently 99% of UK FBA production is used in lightweight aggregate block manufacture (Sear, 2004).

In recent years, due to the contraction in the number of coal burning power stations and changes in burner technologies to reduce emissions, there is reduced production and a shortage of FBA. Block manufacturers are having to source similar materials, ranging from recovered bottom ash, incinerator bottom ash and pumice from a variety of sources, including imports. Unfortunately, many of these options involve greater transport distances, processing or depletion of virgin aggregates adding to the environmental impact (Sear, 2007).

Fly ash

Pulverised Fuel Ash (PFA) has been used in concrete for over 50 years. It has been the subject of research for over 70 years with in excess of 10,000 papers being published (Sear 2005). In the UK, research was carried out which led to the construction of the Lednock, Clatworthy and Lubreoch Dams during the 1950's with fly ash as a partial cementitious material (Lewis et al. 2003).

During the 1970's ready mix concrete suppliers were producing ever more technically demanding concretes of higher strengths and lower water cement ratios. It

was perceived that the variability in quality and the supply problems of PFA when taken directly from the power station were unacceptable (Sear 2001a). In line with Europe, PFA is now referred to as Fly Ash (FA) and its requirements for use in concrete and mortar are covered in the European Standard BS EN 450 (BS EN 450 2005).

As far as the effect of FA variability on the performance of FA concrete is concerned, the most important aspect of physical property is the fineness of the FA, and the most important aspect of chemical property is the carbon content (Balendran et al. 1995).

Carbon content

Residual carbon content and the fineness of FA depend mainly on the condition of the furnace and FA collection system. Atis (2005), whilst looking at high volume fly ash in concrete, reported that high carbon content is believed to reduce the workability and increase the water demand when used in concrete. Comparing two sources of fly ash it was found that the ash with the increased loss on ignition required higher water content and, hence, produced a lower compressive strength. Neville (1995) recognised that carbon content was partially dependent on fineness as carbon particles tend to be the coarser fly ash particles. Jones et al. (2006a) in their study into the effects of fly ash fineness on mortar found that the greatest change noted in bulk chemistry was the reduction in LOI with cycloning the material to remove the coarser fraction (34% difference between the parent FA and the resultant finer FA).

Carbon has other detrimental effects on concrete. Ha et al. (2005) studied the effect of carbon content on reinforcing steel (rebar) and concluded that rebar embedded in Ordinary Portland cement suffered severe corrosion when the carbon level in fly ash was increased, especially beyond 8%.

Residual carbon in fly ash may also interfere with air entraining admixtures (AEAs) added to enhance air entrainment in concrete in order to increase its consistence and resistance toward freezing and thawing conditions. Pedersen et al. (2008) showed that not only the amount, but also the properties of carbon, such as particle size and surface chemistry, have an impact on the adsorption capacity of

AEAs. Owens (1979) concluded that control of the material retained on the 45μm sieve is the key to a less variable material. Dhir et al. (1981), however, believe this not to be the most suitable test but that specific surface may be a somewhat better measure of ash fineness in view of its stronger correlation with strength. However, it would appear that they are both in agreement that fineness is an important characteristic of Fly Ash.

Fineness

Fly ash changes the flow behaviour of the cement paste. With the same consistence, concrete with fly ash is easier to compact than concrete without fly ash, due to the lubricating effect of the spherical fly ash particles in the mix. Also due to the improved cohesiveness of the mix, arising from the contribution of the fine fly ash particles as aggregate supplement and in blocking the bleed water channel, there is less bleeding and segregation (Balendran 1995). It is generally agreed that the use of fine FA improves the properties of concrete. Dhir et al. (1985) regard fineness as the most suitable single parameter with which to classify ashes physically, since it relates to other important ash characteristics.

Erdogdu and Turker (1998) studied the use of various particle gradings of FA and found that a sieved fine FA gives an improved strength relative to that of the original coarser FA. Lee et al. (1999) obtained same source FA with three different fineness values. They concluded that the reactive calcium hydroxide $Ca(OH)_2$ within the fine FA paste was greater than that of the coarser FA cement paste. They also noted that the finer the material the greater the density, lower the carbon content and higher glass content; however, they concluded that it is the fineness of the material rather than the glass content that made the material more reactive.

Chindaprasirt et al. (2004) also studied the effect of FA fineness on mortar and concluded that the different fineness portions of FA appeared to have a slight variation in both physical and chemical properties. Their test results showed that fineness had a marked effect on the compressive strength as well as drying shrinkage and sulfate resistance with the finer FA being more reactive, a better void filler and used less water for the same consistence.

As mentioned earlier, a pozzolanic material works when a large surface area is exposed to the alkaline environment; therefore, fineness of the material is an important property not only for the chemical interactions required but for the reduction in carbon content. The second most important area must be that the fly ash contains the correct chemistry to interact with the cement.

Chemistry

Fly ashes are complex in their range of chemical and phase compositions. They consist of heterogeneous combinations of glassy and crystalline phases (ACI Committee 226 1987).

Fly ash consists principally of the oxides of silicon and iron with varying amounts of constituents containing aluminium and some unburned carbon. Other trace elements such as potassium, phosphorous, cobalt, molybdenum, boron, or manganese may be present (Lane et al. 1982).

Two general classes of fly ash can be defined: low-calcium fly ash (FL) produced by burning anthracite or bituminous coal, and high-calcium fly ash (FH) produced by burning lignite or sub-bituminous coal. FL is categorized as a normal pozzolan, a material consisting of silicate glass, modified with aluminum and iron. The CaO content is less than 10%. FL requires $Ca(OH)_2$ to form strength-developing products (pozzolanic activity), and, therefore, is used in combination with Portland cement, which produces $Ca(OH)_2$ during its hydration (Papadakis 1999).

BS EN 450 deals with siliceous fly ash only, classified by the requirement that the sum of the contents of silicon dioxide (SiO_2), aluminium oxide (Al_2O_3) and iron oxide (Fe_2O_3) shall not be less than 70% by mass; this is a pozzolanic material. Where the reactive calcium oxide exceeds 10% by mass the classification becomes a calcareous fly ash (BS EN 450, BS EN 197).

As was mentioned previously (Section 2.6), the setting and hardening of Portland cement occur as a result of the reaction between the compounds of cement and water.

The form of the two calcium silicates are similar and differ only in the amount of calcium hydroxide formed as shown below (Malhotra 1994):

$$2C_3S \quad + 6H \rightarrow C_3S_2H_3 + \quad 3CH$$
$$\text{tricalcium silicate} + \text{water} \rightarrow C\text{-}S\text{-}H + \text{calcium hydroxide} \qquad (1)$$

$$2C_2S \quad + 4H \rightarrow C_3S_2H_3 + \quad CH$$
$$\text{dicalcium silicate} + \text{water} \rightarrow C\text{-}S\text{-}H + \text{calcium hydroxide} \qquad (2)$$
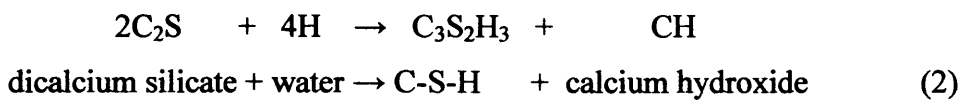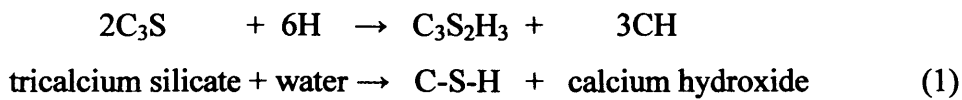
Pozzolanic reactions refer to chemical reactions between active silicon dioxide (SiO_2) within the fly ash and the calcium hydroxide (CH) produced as a by-product from the cement hydration. The chemical reaction is simplified as follows:

$$CH + S + H = C - S - H$$
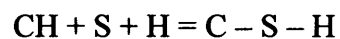
C–S–H gels account for the main strength of concrete, with CH contributing little to concrete build up; for pozzolanic reactions, fly ash combines and consumes CH and forms new C–S–H gels, which contribute more to the strength build up of concrete (Wang 2008). It is the time spent producing the calcium hydroxide that causes this delayed secondary reaction.

Sulphite and sulphate in fly ash

Sulphur generally exists in two forms within concrete, as a sulphite (SO_3) and as a Sulphate (SO_4). When calculating the compound composition of cements the normal convention, within cement manufacture, is to assume that all the SO_3 present is combined with Calcium Oxide (CaO) and is therefore present as calcium sulphate $CaSO_4$ (gypsum) (Moir 2003). Approximately 5% of the dehydrated form of gypsum ($CaSO_4$) is added to the clinker prior to the grinding process. Dehydrated gypsum within cement dissolves rapidly when water is added to the concrete and is beneficial in ensuring that sufficient Ca^{2+} and SO^{2-}_4 ions are available in solution to control the initial reactivity of the tricalcium aluminate (C_3A) through the formation of a protective layer of ettringite $C_3A\bullet3CaSO_4$.

Ettringite is one of the most important substances in conventional portland cement-based concrete. When water is intermixed with portland cement ettringite quickly forms, a reaction which allows normal-setting concrete to be produced. Without the ettringite concrete would set al.most instantaneously in a reaction known as flash set (Hime, W. Erlin, B. 2004).The reaction can be summarised as follows:

$$C_3A + \text{dissolved calcium } (CA^{2+}) + \text{dissolved sulfate } (SO^{2-}_4) + \text{water} = \text{ettringite}$$

If, however, the supply of dehydrated gypsum is too high, then crystals of gypsum crystallise from solution and cause 'false set'. As implied by its name, false set gives the impression that the concrete has hardened but if mixing is continued, or resumed, the initial level of workability is restored (Moir 2003).

Fly ash has SO_4 present at its surface which is released into the mix, delaying the initial setting only, further setting reactions are unaffected (Neville 1995).Typically fresh fly ash contains between 0.35 and 2.5% sulphate as SO_3. The sulphate in fly ash exists as gypsum, which has limited solubility in water. Therefore, when used as a fill material it has the potential to cause sulphate attack, but in practice there is no known case of such attack in concrete adjacent to fly ash (www2.20).

Sulphate attack has long been recognised as responsible for concrete deterioration in a wide variety of structures. Sulphate attack in concrete has been known to occur when sulphate solutions, derived either from a constituent in the concrete such as aggregate or from external sources such as groundwater, react with the calcium aluminate hydrates present in the hardened cement to form ettringite. Formation of ettringite has a deteriorative effect on the mortar strength and, in addition, causes expansion which may result in micro-cracking of the cement paste (Ghafoori, N. Kassel, S. 1999). This expansive reaction can inflict serious damage on concrete, leading to weakening and perhaps ultimately failure of the affected structure.

Besides the conventional sulphate reaction in mortars and concretes involving the formation and the expansive properties of ettringite, another kind of sulphate attack attributed to the formation of thaumasite ($CaSiO_3 . CaCO_3 . CaSO_4 . 15H_2O$) has been

widely discussed during recent years (Skaropoulou, A. et al. 2009). Research has shown that Portland limestone cement pastes are susceptible to the thaumasite formation after only a few months exposure to sulphate solutions. This is a serious problem as limestone has increasingly been used as a filler or as a main cement constituent for many years (Tsivilis, S. et al. 2002). Thaumasite attacks the surfaces of concrete which come into contact with ground containing sulphates which is usually sea water.

Thaumasite formation requires a source of calcium silicate, sulfate and carbonate ions, excess humidity and preferably low temperature within the hardened cement paste to form the mineral. The structural similarity to ettringite allows thaumasite to use this as a template for its initial nucleation. However this mineral is a more complex salt than ettringite, forms at low temperatures (below 15^0C) and is associated with the presence of finely divided limestone sometimes used as filler, though limestone aggregate may also promote the reaction. Thaumasite formation renders the cement paste soft with concomitant loss of strength and disintegration of the concrete (www2.21, Lewis et al. 2003).

Particle shape and pozzolanic activity

The shape, particle size distribution, density and composition of fly ash particles influence the properties of freshly mixed, unhardened concrete and the strength development of hardened concrete (ACI Committee 226 1987). Fly ash particles of less than 50 μm are generally spherical with the larger sizes being more irregular (Lewis 2003). It has been found that the consistence of concrete increases as the replacement of cement with fly ash increases. Siddique (2006) concluded this and reasoned that the "ball bearing" action of the spherical particles of fly ash were responsible for this. However, Jones et al. (2006a) reported that whilst ultra fine fly ash increased the flow of mortars at both 15% and 30%, its coarser parent ash had an adverse effect on mortar consistence, as flow decreased with increasing FA contents. The strength of fly ash concrete will, therefore, depend on whether a water reduction is achieved, plus the pozzolanic performance of the cement/fly ash combination (Lewis 2003).

Therefore, it would seem that fineness affects many aspects of concrete. It affects the particle shape, the water demand of the concrete which in turn affects the strength and the pozzolanic behaviour of the material.

Other requirements affected through the use of fly ash include setting time and curing which are discussed below.

It has been reported that Fly Ash retards the initial hydration of cement and increases the setting time of the concrete. Concrete Society Technical Report No. 40 (Concrete Society 1991), suggests that a 30 per cent FA replacement would lengthen the setting time by up to 4 hours when the mix temperature is 5°C, but such lengthening is reduced to one hour when the mix temperature is 25°C. However, Balendran et al. (1995) recognised that the setting time is influenced by many other factors, including the cementitious content, type, fineness, composition, water content, the presence of admixture, and the adsorption of the admixture by the FA particles. Hence, if setting time is a critical factor, trials using the materials under consideration should be carried out. Longer setting time may increase the chances of plastic shrinkage cracking or surface crusting under conditions of high evaporation rates.

Since the strength of concrete depends considerably upon the hydration of the cement, it is essential that moisture is present to enable hydration to continue (Lydon 1982). If concrete is allowed to dry out, hydration will cease prematurely (Soroka 1998).

Escalante-Garcia et al. (2001) state that the high temperatures achieved in concrete, from hot weather or accumulated heat of hydration, have an adverse effect on the concrete microstructure effecting porosity and that the ultimate degree of hydration of the anhydrous cement phases is reduced. This has a negative effect on the concrete leading to inferior mechanical properties and a concrete prone to chemical attack.

Kim et al. (2002) studied the effect that curing temperature and ageing had on the compressive strength of concrete. They concluded that compressive strength of concrete subject to high temperature at early ages attains higher early-age compressive and splitting tensile strengths, but lower later-age compressive and splitting tensile strength. Elastic modulus has the same tendency; the crossover effect of curing temperature on elastic modulus being not as obvious as the compressive strength. Thus, early temperature rise is detrimental to OPC concrete strength but not to fly ash concrete. A 60°C temperature rise can reduce strength in OPC concrete by up to 30% but can boost fly ash concrete strength by over 10 % (Dhir 1986).

Thermal cracks that usually occur in mass concrete are closely related to the thermal behavior of cement matrix, such as heat liberation, temperature rise and thermal shrinkage. Through the addition of mineral admixtures a reduction in the total heat liberation occurs and lowers the peak temperature of cement pastes, which is favorable for thermal crack prevention. (Lane et al. 1982, Liwu et al. 2006).This makes fly ash application particularly advantageous in pre-cast structural concrete construction and mass concrete or cement-rich concrete sections.

2.9   Conclusion

The latter part of this review has identified a small section of the research that has been, and is currently being, undertaken in an attempt to understand the fundamental use of fly ash. The properties important to its use in concrete have been considered here and this background has been applied to the construction of a methodology for the research work presented in this thesis.

Various prospective cement replacement materials have been identified, some already incorporated within a British and European standard, whilst others are yet to have their full potential realised. Whilst a number of cement replacement materials have been discussed in this review much more work is being carried out on other materials which are not directly relevant to this research.

However, in carrying out this review, no literature was found comparing potential cement replacement materials with materials already accepted within the industry as being a good cement additive. This then leads to the question that if the important elements of a cement replacement can be documented, will it then be possible to measure the potential of a new material seeking to be a cement replacement?

The research will concentrate on the material's physical and chemical composition and the performance within concrete and mortar. This information will then be used to establish what makes it a good cement replacement.

The important factors to be investigated are:

- o Fineness
- o Grading
- o Particle shape
- o Carbon content
- o Elemental make up

On completion it should be possible to analyse a material from an unknown source and within 24 hours have an answer to the question of whether or not this material has the potential to make a good cement replacement. On establishing this, longer term concrete and mortar trials can then be initiated.

3. Experimental methods

3.1 Testing regime and mix details

3.2 Materials

3.3 Traditional strength tests

3.4 Permeability test

3.5 Physical analysis

3.6 Chemical analysis

3.7 Inter-grinding

3.1 Testing regime and mix details

3.1.1 Mix designs

This research programme uses an Ordinary Portland Cement (referred to as CEM I in BS EN 197-1:2000) a Ground Granulated Blast Furnace Slag (GGBS), both conforming to BS EN 197-1:2000, and cement replacement materials obtained from various sources. The cement is a Blue Circle 52.5 Newton CEM I supplied by Lafarge cement at Aberthaw South Wales. The GGBS was supplied by Civil and Marine from their depot at Llanwern, South Wales.

The measure of performance for the new replacement materials was judged against control mixes of 100% CEM I and a blend, 50 / 50 by mass, CEM I / GGBS. The replacement materials were blended in the ranges 20%, 25%, 27%, 30%, 33% and 35% by mass replacement with CEM I. Concrete mix designs containing a range of cement contents, between 140kg/m^3 and 450kg/m^3, were produced using each of these replacement percentages and concrete mixed. The only variable used in the mixing process was the water content which was adjusted to maintain consistence. The S2 consistence class to BS EN 206:1-2000 has been used to achieve a target

slump of 70mm. A Water Reducing Agent (WRA) Sika Plastiment 160 at a quantity of 0.4% of the cement content was used within the concrete.

3.1.2 Mix designs

The mix designs used for this research are the actual recipes taken from the batching plants of Lafarge Aggregates Ltd, South Wales, and can be seen in Appendix 1. This research has had in place a comprehensive mixing and testing regime from the outset and mix volumes were calculated from the samples required. The initial mixes completed the full range of tests and required that 40 litres of concrete be produced whilst subsequent mixes required only 25 litres. A control mix was repeated at 25 litres to ensure that no differences could be attributed to the reduced batch volume.

3.1.3 Mix procedure

When producing trial mixes, the most realistic procedure is to use wet rather than dry aggregates. In the laboratory it is usual to have air dried aggregates and these should be batched and soaked for about thirty minutes with sufficient water to bring them to a saturated condition (Lydon 1982). Ensuring that the aggregates were used in their saturated condition removed the requirement of carrying out moisture content checks before each mix as the moisture content became constant. Also, the aggregates were collected over a period of some years and the quality and quantity of fine particles coating the aggregate may have changed, so this would have affected both the amount of water added to the mix and the strength of the hardened concrete. This issue was overcome by the soaking process removing these fine particles from the material leaving a clean aggregate.

After soaking for thirty minutes the coarse aggregates were sieved, to drain the excess water, and then reweighed to adjust for the increased weight due to water absorption. Mixing of the concrete was carried out using a 160kg capacity Liner horizontal rotary drum mixer. The coarse and fine aggregates were mixed first followed by the CEM I and replacement material. Admixture was weighed and added to a measuring cylinder containing 1 litre of clean water, this was poured into the mix ensuring even distribution throughout. Further water was added until the consistence

of the mix achieved the required 70mm slump. The consistence was checked using the method described in BS EN 12350-2:2000, slump test.

Cube specimens were moulded using 100mm steel cube moulds and compacted in two uniform layers by means of a vibrating table. After casting, specimens were covered with polythene to prevent moisture loss and were stored in the laboratory at an ambient room temperature of $20^0C \pm 5^0C$. After 24 hours, specimens were de-moulded and cured in a water tank, at a controlled temperature of $20^0C \pm 2^0C$, until the day of testing. Specimens were made and cured to BS EN 12390 – 2:2000, (Making and curing specimens for strength tests).

3.2   Materials

3.2.1   Ordinary Portland Cement

The CEM I used throughout this research was a 52.5N CEM I cement corresponding to the requirements of BS EN 197-1. The CEM I was produced at the Lafarge cement works, Aberthaw, South Wales and given the product name OPCRM to distinguish it from other products supplied from that plant. The tests carried out on the cement were completed to the BS EN 196 range as required in BS EN 197-1:2000 Cement - Part 1: Composition, specifications and conformity criteria for common cements. The technical data for this cement was tested for and recorded at the works and are shown in Tables 3.1and 3.2 below.

Table 3.1
Test report results for CEM I strength class 52.5N as recorded at the LaFarge laboratory Aberthaw cement works

	Loss on ignition (%)	Soundness (mm)	Initial setting time (mins)	Compressive strength N/mm^2				Na$_2$O (%)
				1 day	2 day	7 day	28 day	
CEM I	2.55	1.0	155	19.7	29.7	44.3	59.2	0.62
BS EN 197	≤ 5.0	≤ 10	≥ 45	-	≥ 20	-	≥ 52.5	Declared

Table 3.2
Additional Test report results for CEM I as recorded at the LaFarge laboratory Aberthaw cement works

	Free Lime (%)	Fineness (m^2/kg)	SO$_3$ (%)	Alkalis (%)	Chloride (%)
CEM I	0.67	372	3.26	0.61	0.04
Typical Range	0.5 - 3.0	360 - 370		0.3 - 1.0	
BS EN 197			≤ 4.0		≤ 0.1

Chemically, clinker is composed mostly of calcium oxide (CaO) and silica (SiO$_2$), with lesser amounts of aluminum oxide (Al$_2$O$_3$) and iron oxide (Fe$_2$O$_3$) In clinker, these oxides are within a semi-fused intimate mix of (primarily) four hydraulic minerals, denoted in cement industry chemical shorthand as C$_3$S (tricalcium silicate), C$_2$S (dicalcium silicate), C$_3$A (tricalcium aluminate), and C$_4$AF (tetra-calcium aluminoferrite) (Van Oss and Padovani, 2002).

Table 3.3 presents the compounds within the CEM I used throughout this research as compared to the typical composition of a grey Portland cement. These are the four principal chemical compounds contained in cement clinker (Moir 2003).

Table 3.3
Compounds in the CEM I used in this research

Cement Notation	C$_3$S (%)	C$_2$S (%)	C$_3$A (%)	C$_4$AF (%)
Common Name	Alite	Belite	Aluminate	Ferrite
CEM I	51.77	18.26	8.93	6.51
Typical composition	57	16	9	9

The relative proportions of these minerals are adjusted to achieve the desired functional properties of the Portland cement. The mineral C$_3$S (alite) hydrates quickly and so imparts early strength and set to the cement, whereas C$_2$S (belite) hydrates slowly and is the main contributor of long-term strength. Both minerals hydrate to form tricalcium silicate hydrate gel (sometimes called tobermorite) plus lime. The tobermorite gel is the actual binder in the hydrated cement. The lime released in the hydration reaction is in small part taken up by hydration of C$_3$A and C$_4$AF, but most remains unreacted and thus available to activate any pozzolans added in the finished cement. Hydration of C$_3$A is almost instantaneous and highly exothermic. The

mineral thus speeds the development of early strength and set, sometimes to the point of causing flash set, therefore gypsum is added to control this. The main function of the aluminoferrite mineral (C_4AF) is as a flux, that is, it acts to lower the temperature at which the clinker minerals form (i.e. clinkering temperature). This mineral also imparts the grey colour to Portland cement and for this reason its formation avoided, through the use of only iron-free raw materials and higher clinkering temperatures, in the production of white Portland cement, which is a much higher priced product than grey ("ordinary") Portland cement (Van Oss and Padovani, 2002).

3.2.2 Replacement materials

Ground Granulated Blast furnace Slag (GGBS)

The GGBS used throughout this research was supplied by 'Civil and Marine' from their Llanwern works, South Wales and conformed to BS EN 197 – 1: 2000.

Fly ash

The main focus of this study is the fly ash supplied by RWE npower, operators of the power station located at Aberthaw, South Wales. The power station is being upgraded and a new separation process is being installed to convert fly ash collected at the plant from a waste material to a usable one. A similar system is already in operation at Longannet power station, Scotland. The ash produced at Aberthaw power station was transported to Longannet in order to replicate the separation process being installed at Aberthaw. The ash was returned from Longannet in three forms:

- Classified
- Processed
- High Carbon waste product

with the raw ash used coming directly from Aberthaw power station. By processing the ash it is expected that both the processed and the classified ash will conform to BS

EN 450 – 1: 2005, whilst the raw fly ash and High Carbon waste ash will fall outside the limitations of this standard.

A second fly ash examined during this research was supplied from Didcot A power station, Oxforshire; also run by RWE npower. Ash from Didcot A is used to manufacture building blocks at a factory on the adjacent Milton Park and transported to Thatcham (near Newbury, Berkshire) for the manufacture of Thermalite aerated breeze blocks using both decarbonized fly and raw ash, however; most is mixed with water and pumped via a pipeline to former quarries in Radley (www3.1). This ash had been subjected to a decarbonisation processing technique and conformed to BS EN 450 – 1: 2005.

Sewage sludge ash

The Sewage sludge ash used throughout this research was supplied by Yorkshire Water, Bradford, UK. The ash was produced through the incineration of the sludge cake following a drying process which included the use of centrifuges and belt presses and sludge drying beds. The ash particles were removed from the fluidised-bed incinerator flue gases by an electrostatic precipitator.

Municipal solid waste ash

The municipal solid waste ash used throughout this research was supplied by Veolia from their Tyseley waste disposal unit, Birmingham. The waste is delivered to the works directly from the collection vehicles. From there the waste is manoeuvred onto conveyors which transport the waste to the incinerator. The particulate matter (fly ash) is removed from the gas stream by a bag filter before the cleaned gas is released to air. The fly ash was collected from the separator whilst any unburnable wastes and larger ash particles fell to the bottom of the incineration plant and were removed using hydraulic rams.

Industrial materials

The industrial materials used in this research were generated during a previous research project at Cardiff University (Davies 2003), studying cement replacements. Various industries supplied waste material for that project and blends were produced in an attempt to establish a useable cement replacement in mortar alone. Although none of the suppliers of this waste have been identified for this research, the blend used was the one that had demonstrated the potential for achieving positive results when used within concrete. All the materials used were wastes from industry and were collected and supplied by the other study group. The preparation of the materials consisted of sieving and grinding the materials to achieve a required fineness. The required fineness for each material is shown in Table 3.4. These materials were then blended together with CEM I in amounts specified from results collected during the previous research. Table 3.5 shows the amounts of the four industrial waste materials mixed with the CEM I to produce the five cement materials used for subsequent testing. The total per cent of the industrial products varied from 10% to 50% by mass.

The grinding of the materials was carried out by others using a Labtec ESSA, Vibratory Puckmill LM1-P to an exact grinding time as shown in Table 3.4. Sieving was carried out using a Fritsch Vibratory sieve shaker, with various intermittent mesh sizes to avoid clogging the finer mesh. The fineness was measured by the last sieve through which the material was required to pass, the coarser material was returned to storage for possible future use. The materials were stored in a sealed container until required. This was completed by the previous research group.

Table 3.4
Grinding time and required fineness of the various Industrial Materials used

	Materials			
	Mat 1	Mat 2	Mat 3	Mat 4
Grind Time (mins)	5	2	2	2
Fineness (μm)	< 53	< 100	< 100	< 100

Table 3.5
Quantities of CEM I and the four industrial materials required to produce the required blend, for each replacement percentage, as a percentage of the total cementitious content by mass

Percentage	Material (%)				
(%)	CEM I	1	2	3	4
10	90	0	0	5	5
20	77	7	3	4	9
25	70	14	2	3	10
30	64	16	3	5	12
50	42	29	2	8	19

3.2.3   Aggregates

The fine aggregate used in this research was a locally sea dredged sand conforming to BS EN 12620:2002. The coarse aggregates and dust used were a crushed limestone quarried from a single source at Ewenny quarry, South Wales. Selected aggregate properties can be found in Table 3.6 while a more comprehensive study is located in Appendix 2. Four nominal sized coarse aggregates were used to achieve a well graded aggregate mix, these being 6, 10, 14 and 20mm which were graded in accordance with BS EN 12620:2002 Aggregates for Concrete. A limestone dust was also used with a grading of 1 - 5mm. The aggregates were soaked prior to mixing to standardise the moisture content; the dust was mixed using its surface dry condition (i.e. no visible signs of moisture on the surface), with the moisture content measured prior to each mix. Both the sand and the dust were dried using an 850 Watt microwave on full power at two minute maximum cycles. The material was considered dry when the weight remained unchanged over two further drying cycles.

Table 3.6
Selected aggregate properties

Aggregate	Relative density (oven dry) g/m^3	Shape	Water absorption (%)	Surface texture
Sand	2.58	Rounded / irregular	0.5	Smooth
Crushed limestone	2.69	Angular	0.6	Rough

3.2.4   Admixtures

Organic admixtures are added to Portland cement concrete to enhance its properties. Superplasticisers, for instance, produce concrete with high rheological requirements, that is deformation and flow of the concrete, while maintaining a low water/cement (w/c) ratio to guarantee excellent mechanical properties and long durability. There is a wide variety of superplasticiser admixtures, such as lignosulphonates, naphthalene and melamine-based, vinyl copolymers and the so-called "latest generation" of superplasticisers, polycarboxylate derivatives. These admixtures are adsorbed on the cement particles, causing electrostatic or steric (in the case of polycarboxylate admixtures) repulsion that hinders coagulation (Palacios and Puertas 2005).

Sika Plastiment 160

Plastiment 160 is a water reducing agent (WRA) designed for use in concrete. It is a purpose designed WRA and plasticizer, made with a chemical combination of modified lignosulphonates. This allows the manufacture of economic high quality concrete without undesirable side effects. It comes as a ready to use liquid for producing a more uniformly cohesive, quality concrete. Plastiment 160 complies with BS EN 934 - 2 Table 3.1/3.2 - High Range Water Reducing / Superplasticising Admixtures. As the Plastiment 160 is a concrete admixture, it was added to the concrete at the mixing stage.

3.2.5   Mix water

All water used in this research was drinking quality tap water as supplied by Welsh Water.

3.3 Traditional strength tests

3.3.1 Cubes

The cubes used in both the compressive strength tests and the permeability tests were produced using 100mm steel cube moulds to BS EN 12390-1:2000. Compaction of the concrete within the moulds was carried out to the method described in BS EN 12390-2:2000.

3.3.2 Curing

After twenty four hours the cubes were stripped from the moulds, and placed fully submerged in the curing tank. The water in the tank was thermostatically controlled heated to, and maintained at $20^0C \pm 2^0C$ as specified in BS EN 12390-2:2000. The curing period prior to testing varied based on the standard normal testing period for concrete this being 1 day, 2 day, 7 day, 28 day and 56 day.

3.3.3 Slump test

One of the basic attributes of any cementitious material, concrete or mortar, is its consistence or workability, defined as, the ease at which the material can be moved around, pushed or pulled, and a smooth level surface be achieved. This property is generally reliant on the water content of the mix with the wetter concrete being the easier to move and hence having the higher slump value.

For this research the slump test was carried out to the procedures set out in BS EN 12350 - 2

3.3.4 Determination of compressive strength

Compressive strength of concrete is an excellent indicator of concrete quality and it invariably forms the most important basis of specifications and quality control, as many other properties are directly or indirectly related to it (Shibli 2007).

The compressive strength test was performed on 100mm cubes, to BS EN 12390-3:2002, using a Contest GD10A compression testing machine at a pacer rate of 180kN / minute. Although the compressive strengths of the samples were established at various time periods the 28 day strength is the most relevant to industry (BS EN 206-1:2000). The tests for permeability were carried out on cubes removed from the curing tank at 28 days.

3.4 Permeability test

The testing for the relative permeability of the concrete samples was carried out using the method developed by Lydon (1993). This involved the casting of 100mm concrete cubes and subjecting them to 10 bar nitrogen gas pressure, in pairs, and measuring the time taken to reduce the gas pressure to 5 bar. The work was undertaken at Cardiff University by the concrete laboratory technician Mr Andrew Sweeney and the Author. The process used was as follows:

At 28 days the samples were removed from the curing tank and a 6mm diameter hole was drilled through the centre of the cube at right angles to the direction of casting (i.e. not through the top, exposed, face whilst in the cube mould). The drilling process was carried out through the centre of one face to a depth of half the cube, then from the opposite face until the holes met at the centre. This method was employed to prevent the concrete spalling when the drill forces itself out through the bottom of the cube. The sample cubes were then surface dried and placed in an oven at 105^0C. Continuous monitoring of the cube weight was maintained until the weight loss was less than 1% the weight of the cube over a 24 hour period. At this point the cubes were removed from the oven and placed in a dessicator to cool.

Aluminium tape was adhered to the bottom of the cube to cover the hole. A thin layer of petroleum jelly was applied to the top and bottom surfaces of the sample, the drilled faces, and to this rubberised cork pads were placed, held by suction. Petroleum jelly was employed to create the gas tight seal required for this test as it is easily applied and does not require any time to set. It can also be readily removed and reapplied if a retest is required.

The top cork pad contained a hole in its centre which is designed to line up with the hole in the sample and the hole in the lid of the pressure cell, this being the escape route of the gas. The sample cube was placed in the pressure cell bottom face down and centred in line with the hole in the lid. A further seal of petroleum jelly was applied to the lid which was then bolted into place using twelve bolts, as shown in Figure 3.1, which were systematically tightened so as not to deflect the lid or shear any of the bolts. Bolting the lid exerts a pressure onto the cork pads and onto a rubber sealing ring. This pressure is sufficient to stop the gas pressure causing any movement of the pads and the sealing ring prevents gas escape from between the lid and cell body.

Figure 3.1 Pressure cell 105mm deep x 145mm Diameter into which a concrete sample is placed for permeability testing.

Pressure transducer   Pressure transducer

Regulator valve A

Pressure gauge   Pressure gauge

Regulator valve A

Gas reservoir   Gas reservoir

Nitrogen gas bottle

Stop valve B   Stop valve B

Gas flow   Gas flow

Nitrogen gas bottle

Gas out   Gas out

Computer

Pressure cells
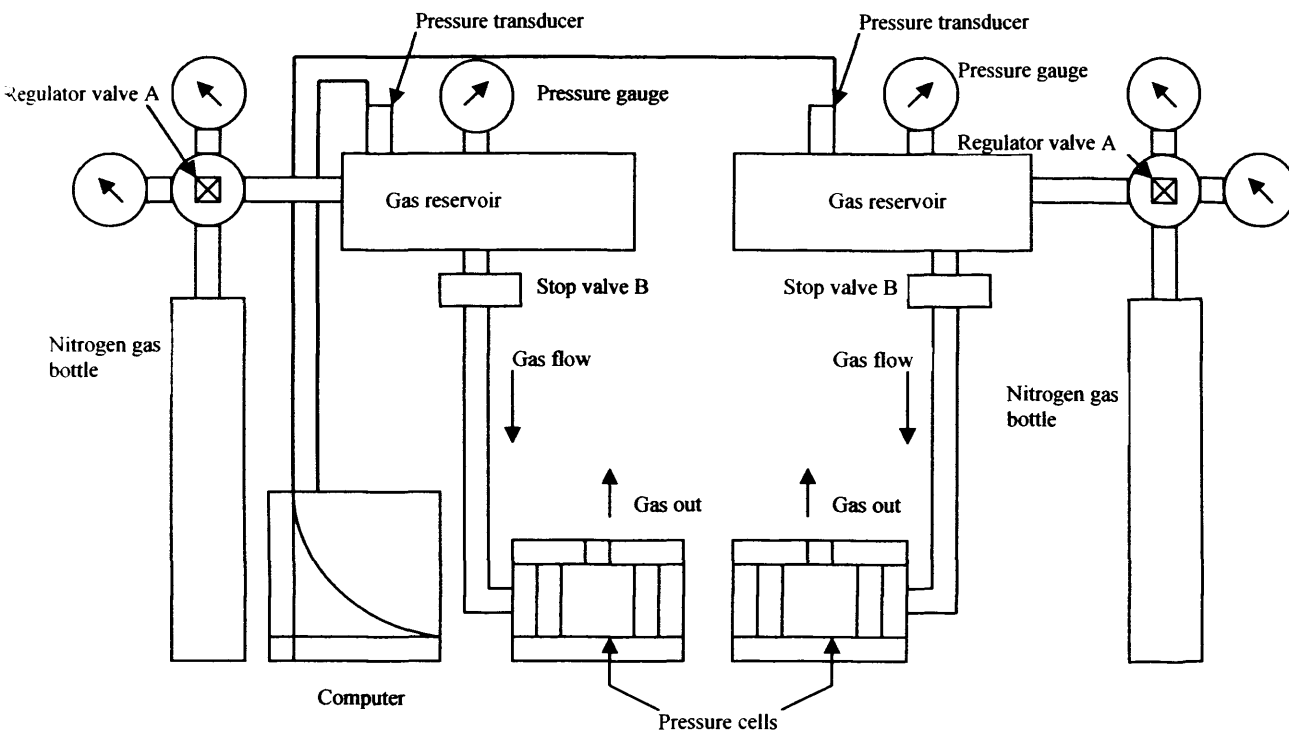
Figure 3.2 Schematic of apparatus for testing permeability of concrete using nitrogen gas

The set up of the apparatus employed highlighting the main components can be seen in Figure 3.2 and in Figure 3.3. Nitrogen gas was allowed to enter the reservoir by the opening of valve 'A'. On reaching a pressure of 10 bar, valve 'A' was closed. Valve 'B' controlled the gas flow between the reservoir and the pressure cell and, on opening, allowed the pressurised gas to fill the pressure cell. The pressure in the reservoir dropped in order to fill the cell, so valve 'B' was closed and the reservoir pressurised again. This process continued until there was no significant drop in pressure in the reservoir when valve 'B' was opened.

Before commencing the test, the computer was recalibrated to zero and valve 'A' was closed, when valve 'B' was opened the test started. The computer was set to monitor the pressure drop at set intervals for the two tests which run concurrently being started simultaneously and recorded together on a single plot. This was arranged mainly to highlight any errors that may occur in the test, for example gas leakage or blockage, thus giving the opportunity to retest any samples that record irregular results.

3-13
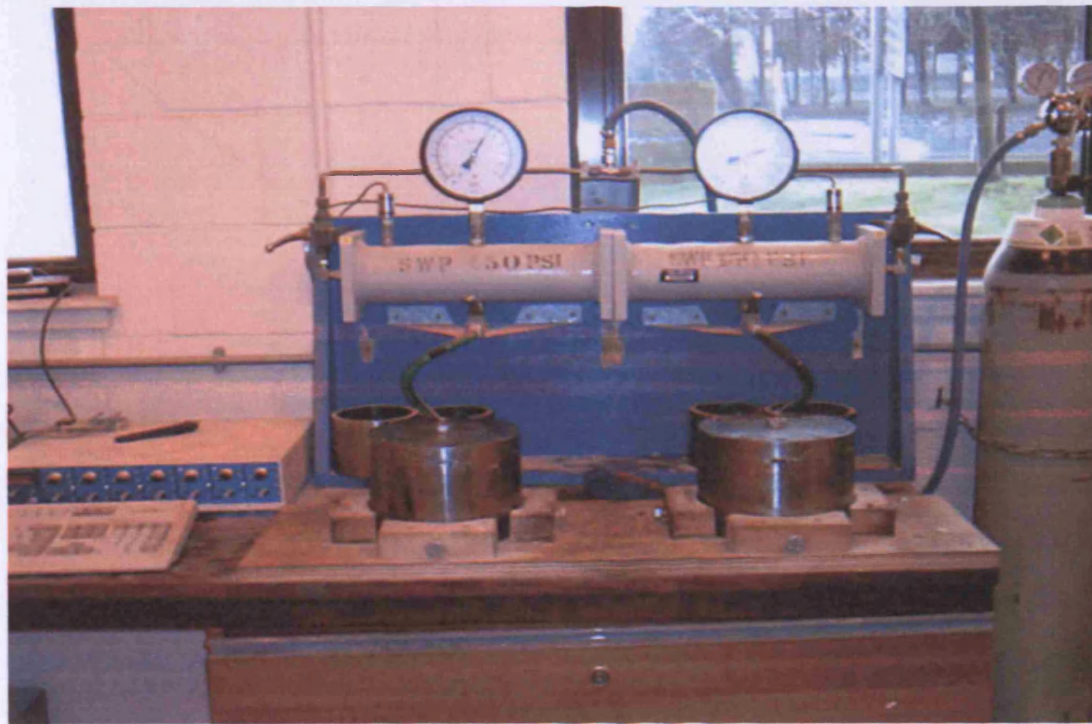
Figure 3.3 Permeability test in progress.

Lydon (1993) suggests three simple measures for the relative permeability of concrete. The three parameters, shown in Figures 3.4 and 3.5, are those which can be determined from a pressure–time decay curve and include:

- o The half time (expressed in minutes), or the time taken for the pressure inside the reservoir to decrease from 10 bar to 5 bar
- o The area under the graph of pressure against time
- o The gradient of the line of the plot of log pressure against time, $dlog_{10}(P) / dt$ referred to as m (Figure 3.5)
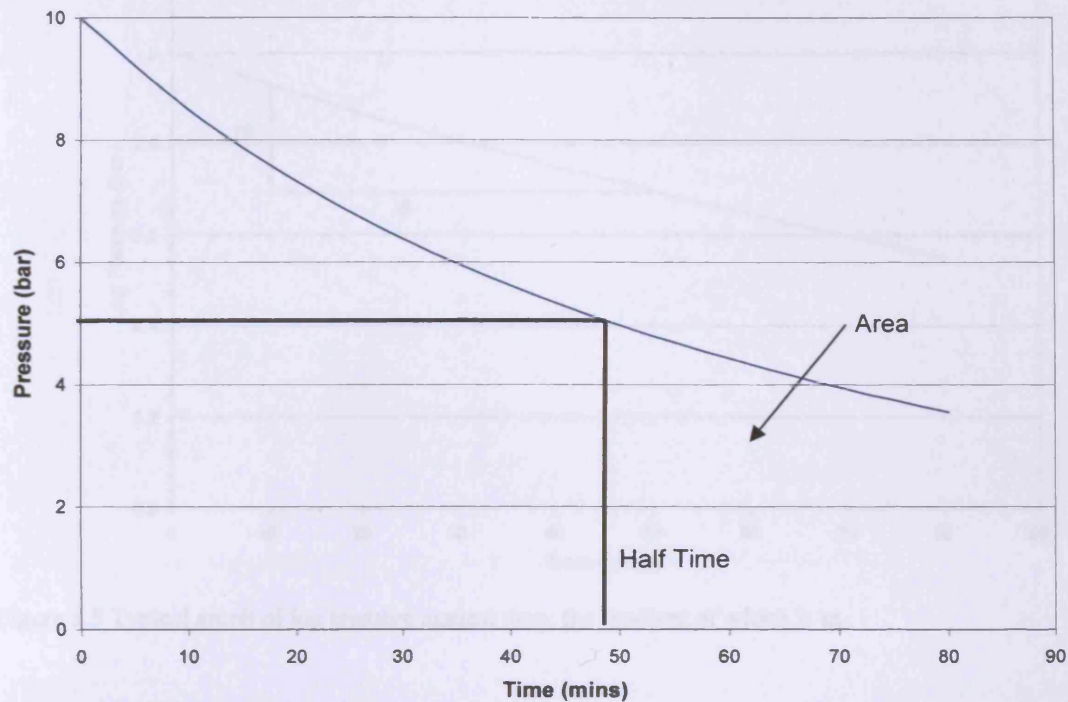
Figure 3.4 Typical graph showing the permeability parameters of pressure against time showing a half time of 48 minutes and area under the pressure-time curve

In a previous investigation by Gardner (2002), it was shown that full permeability tests performed on high-strength concrete lasted for more than 2 weeks and this time scale was considered too long. The recommendation from that study, was for the use of the half time and the gradient of the graph of log pressure against time as a measure of permeability. The data required to identify these parameters are obtained from the decrease of pressure from 10 to 5 bar. This has the advantage that the tests did not have to be continued beyond 5 bar, resulting in much reduced testing period.
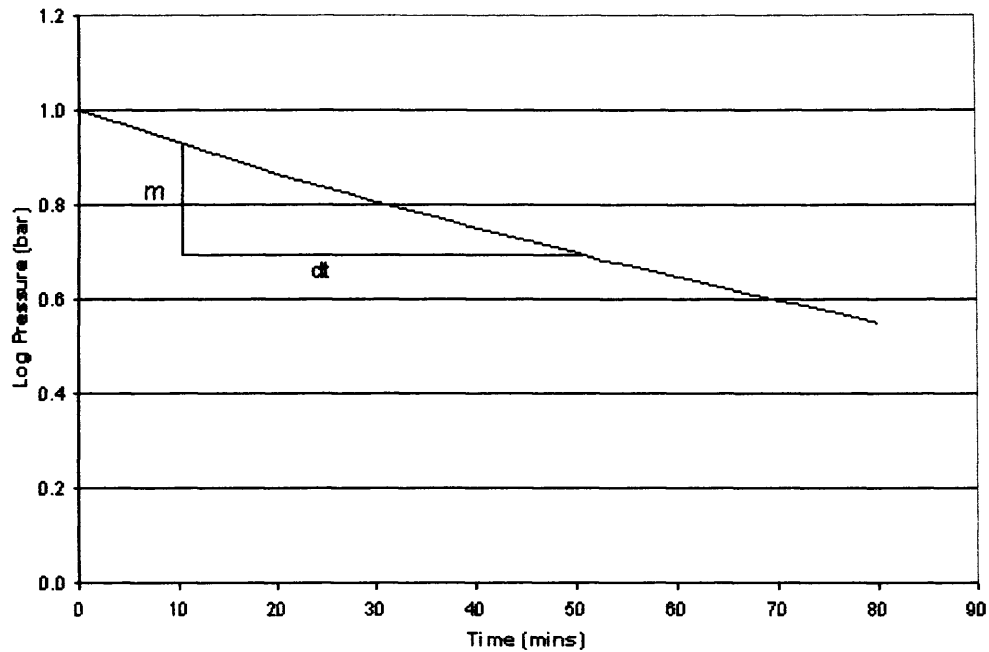
Figure 3.5 Typical graph of log pressure against time, the gradient of which is m.

Martin (1986) carried out a series of relative permeability tests and produced a series of $\log_{10}$ plots from which the value for 'm' could be found. These values for 'm' were then assigned to the original decay curves taken from the tests. This produced a series of curves, Figure 3.6, and through overlaying subsequent decay curves their value for 'm' could be recognised.

This research has been presented, on many occasions, to individuals from outside the University and people in management, who require results in a format that they can understand. For this reason, the reporting of a value for 'm' in respect to permeability would be meaningless to some people, whilst the concept of time is something that most understand. Therefore, of these three methods the measurement of the half time was the favoured approach to reporting results.
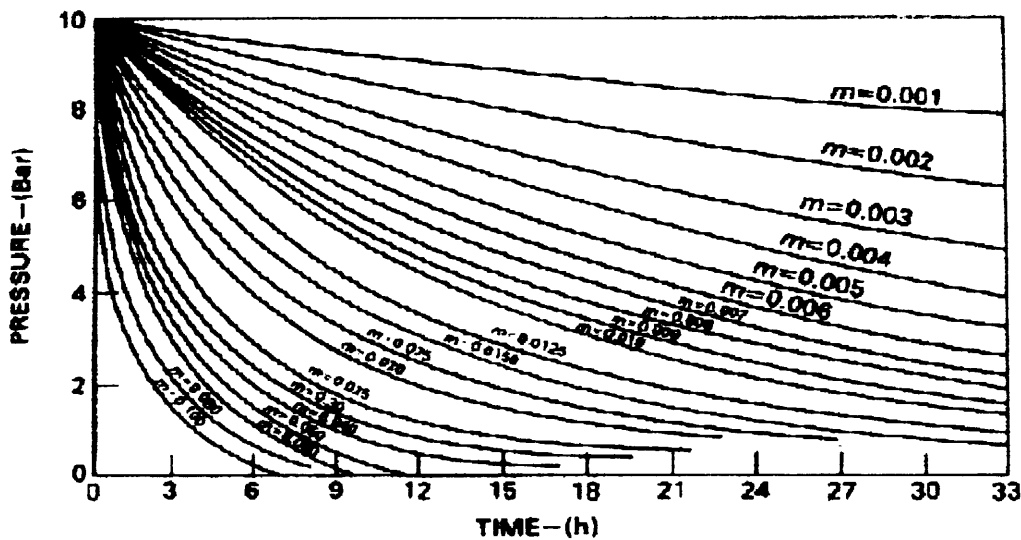
Figure 3.6 Martin's exponential decay curves for different values of m (Martin 1986)

3.5 Physical analysis

3.5.1 Determination of loss on ignition

The determination of loss on ignition (LOI) was carried out by the method given in BS EN 196-2:2005. The analyses were carried out at Cardiff University, School of Engineering laboratories.

3.5.2 Determination of specific surface

The specific surface was determined using the air permeability method (Blaine method) as described in BS EN196-6:1992 Methods of testing cement – Part 6: Determination of fineness. These analyses were carried out at the laboratories of Lafarge cement, Aberthaw, by the Author.

3.5.3 Determination of particle morphology

The scanning electron microscope

The Scanning Electron Microscope (SEM) has proved to be a very important tool for the study of size and shape of material particles. Its high magnification power and depth of focus allows for the observation of surface contours, topography and the interaction between the smaller and larger particles. Preparation of the samples required a process of 'sputter coating'.

Sputter coating is an ultrathin coating of electrically-conducting material, deposited either by high vacuum evaporation or by low vacuum sputter coating of the sample. This is done to prevent the accumulation of static electric fields at the specimen due to the electron irradiation required during imaging. Such coatings include gold, gold/palladium, platinum, tungsten and graphite. Another reason for sputter coating, even when there is more than enough conductivity, is to improve contrast, a situation more common with the operation of a FESEM (field emission SEM). When an osmium coater is used, a layer far thinner than would be possible with any of the previously mentioned sputtered coatings is possible (www3.2).

Unlike the transmission electron microscope (TEM), see section 3.5.4, where electrons of the high voltage beam form the image of the specimen, the scanning electron microscope (SEM) produces images by detecting low energy secondary electrons. These are emitted from the surface of the specimen due to excitation by the primary electron beam. In the SEM, the electron beam is rastered across the sample, with detectors building up an image by mapping the detected signals with beam position. Generally, the TEM resolution is about an order of magnitude greater than the SEM resolution; however, because the SEM image relies on surface processes rather than transmission it is able to image bulk samples and has a much greater depth of view and so can produce images that are a good representation of the 3D structure of the sample. Observations were made at 30Kv using a Jeol JSM 6300 SEM, Figure 3.7, by Mr Ravi Mitha at the Cardiff University School of Engineering laboratories.

(a)   (b)

Figure 3.7 Image of a) the Jeol JSM 6300 scanning electron microscope b) the display unit as used in this research

The procedure for applying the sputter coating is as follows:

- o A small amount of sample is spread onto a clean sheet of paper
- o Studs for use in the SEM are labelled and double sided adhesive tape is applied to one end
- o The stud is placed onto the sample until a light coating of the sample covers the adhesive tape
- o The stud is then blown to remove any large or loose particles
- o The studs are placed in a Bal-tec SCD 005 Sputter coater
- o The lid is positioned and a the vessel and vacuum is achieved inside
- o On production of the vacuum the cell is filled with Argon gas
- o The samples are then flashed with gold at a power setting of 30mA for 150 seconds
- o The application of gold minimises the effect of charging which would cause interference with the image.

3.5.4 Determination of particle size distribution

The determination of particle size distribution was carried out to the method given in BS EN 196-6:1992 Methods of testing cement – Part 6: Determination of fineness (sieve method). The analysis was carried out to fulfil the requirements of BS EN 197-1, at the laboratories of Lafarge cement, Aberthaw, by the Author.

3.5.5 Determination of compressive strength

The determination of strength was carried out to the method given in BS EN 196-1:2005 Methods of testing cement – Part 1: Determination of strength. The analysis was carried out at the laboratories of Lafarge cement, Aberthaw, by the resident technical staff.

3.5.6 Particle size distribution

The materials were graded for particle size distribution using a Malvern Mastersizer X equipped with a 2mW helium neon laser having a beam diameter of nominally 1mm. The Mastersizer was attached to a computer with the Malvern software loaded and the required information, related to the materials being tested, was input.

Samples were suspended in water and placed in a reservoir from which suspensions were pumped to a measurement cell where the partial scatter light from a 2mW He/Ne laser was focused. The scattering of the light was focused through a lens and picked up by a detector located behind.

Instrument preparation

This research used water as the fluid, as the relative densities of the materials were low enough to allow the water to transport the material through the system without clogging the pipes. The pipes connecting the reservoir to the Mastersizer and

the measurement cell were renewed and the lenses, measurement cell and presentation tank checked for impurities and cleaned if required. The required lens was selected and mounted together with the measurement cell in front of the detector. De-ionised water was slowly poured into the flow cell, so as to avoid the production of bubbles, and allowed to circulate around the system.

Computer preparation

The initial configuration of the software was set up by Mr Paul Malpas of the School of Engineering, Cardiff University. On opening the Malvern program, an "Easy button line" was used to progress the set up in the correct order. Each step was progressed for every new sample. The set up consists of Setup hardware, Setup Analysis and Presentation selection.

- o Setup Hardware requires the identification of the lens being used. This research used the 45, 100 and 300mm lenses
- o Setup analysis requires that the particle density be input
- o Presentation selection requires that the refractive index of 1.5295 for the fluid (used to suspend the sample distilled water in this case) be input
- o All other settings remain at default.

The system then runs its own setup program configuring the computer with the laser apparatus. When the 'Measure' window appeared the sample was placed into the flow cell using small quantities. Aids for the dispersion of the material in the reservoir included a cell stirrer and an ultra-sonic stirrer both set at mid power to avoid the production of air into the water. Material was added to the flow cell and ceased when the 'Obscuration' measure on the computer showed approximately 20% (with a range of -2% and +5%). At this point the scanning was started and results collected. Eight increments of a single sample were made by continuously cycling around the system. The number of measurement sweeps prior to each calculation was the default setting of 2000.

If the laser sizer had not already been used it was allowed to warm up to working temperature for 20 min before the experiments were undertaken. After each sample measurement on the laser sizer its flow cell, the pump and the suspension system were flushed several times using tap water prior to being filled with de-ionised water.

3.6   Chemical analysis

3.6.1   Leco Furnace for measuring sulphur and carbon

This analysis was carried out using a Leco SC-144DR furnace, Figure 3.8 below, by Mr Ravi Mitha at the Cardiff University School of Engineering laboratories. The SC-144DR carbon and sulphur analyser is a software controlled instrument designed to determine the carbon and sulphur content in a wide variety of organic materials such as coal, coke and oils, as well as some inorganic materials such as soil, cement and limestone, by combustion and non-dispersive infrared detection. The method is outlined below.

- o 0.35g of sample is weighed into a nickel boat container
- o The furnace is turned on and the computer set to record the sample
- o The furnace operates at a constant 1350^0C and when prompted the sample was slid into the furnace and the door closed
- o The sulphur and carbon contents are measured and the results recorded on the computer
- o At ten minutes the measurements are complete and the sample removed from the furnace
- o This was repeated with a second sample and the results compared for any erroneous results and errors. The average of the two was used for the result

When the analysis begins, the sample is placed in a pure oxygen environment typically regulated at 1350^0C. The combination of temperature and oxygen flow causes the sample to combust. All sample materials go through an oxidative ion process which causes carbon and sulphur bearing compounds to break down and free

the carbon and sulphur. The carbon then oxidises to form CO_2 and the sulphur forms SO_2. From the combustion system the gases flow through two anhydrone tubes to remove moisture, through a flow controller that sets the flow of sample gases to 3.5litres / minute, and then through the infrared (IR) detection cell. The carbon IR measures the concentration of carbon dioxide gas whilst the sulphur IR measures the concentration of the sulphur dioxide gas. The computer reads the cell output nine times a second by an interval linearization equation and the result, corrected by calibration and for sample weight, is the total weight percent of carbon and sulphur.
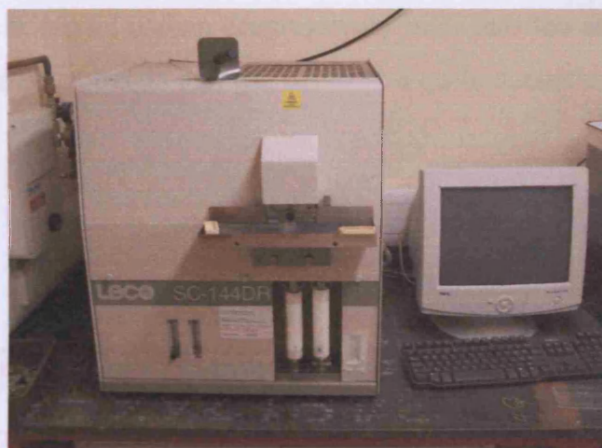
Figure 3.8 Image of the Leco SC-144DR furnace as used in this research

3.6.2   X-ray diffraction (XRD)

The instrumentation used for this analysis was a Phillips X-Ray defractometer with a PW3830 Generator, Figure 3.9, and was operated by Mr Ravi Mitha at the Cardiff University School of Engineering laboratories.
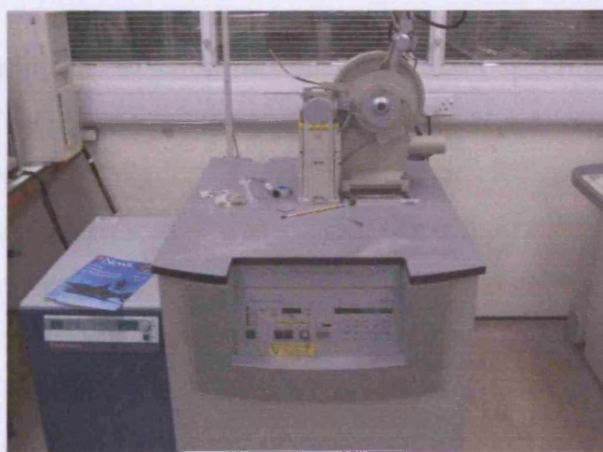
Figure 3.9 Image of the Phillips X-Ray defractometer with a PW3830 Generator
as used in this research

X-ray diffraction is a non-destructive analytical technique used to identify and quantify the various crystalline forms, known as phases, of compounds present in powdered and solid samples. It is not an imaging technique. X-rays have the proper wavelength (in the Ångström range, ~10^{-8} cm) to be scattered by the electron cloud of an atom of comparable size. Based on the diffraction pattern obtained from X-ray scattering off the periodic assembly of molecules or atoms in the crystal, the electron density can be reconstructed. Additional phase information must be extracted either from the diffraction data or from supplementing diffraction experiments to complete the reconstruction. A model is then progressively built into the experimental electron density, refined against the data and the result is a quite accurate molecular structure (www3.3).

combined
waveform

wave 1

wave 2

Constructive interference
Two sinusoidal waves in phase

Destructive interference
Two sinusoidal waves 180° out of phase
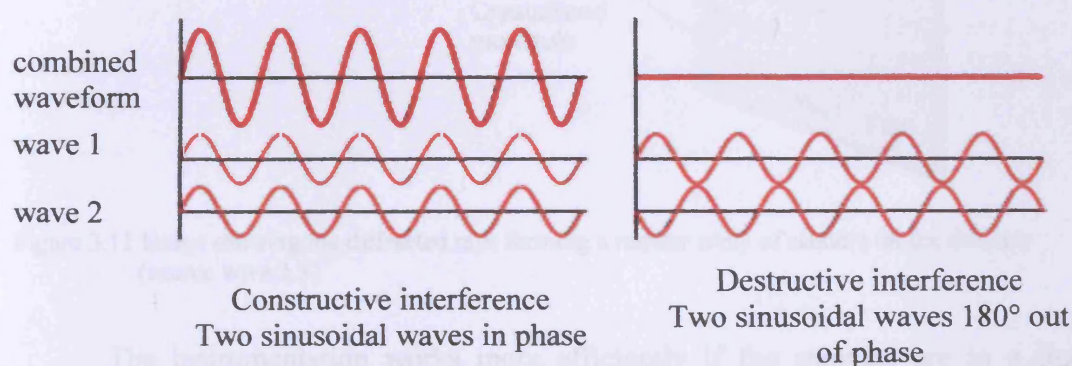
Figure 3.10 Image showing the effect of destructive interference as compared to constructive interference

An X-ray striking an electron produces secondary spherical waves emanating from the electron. This phenomenon is known as elastic scattering, and the electron is known as the *scatterer*. A regular array of scatterers produces a regular array of spherical waves. Although these waves cancel one another out in most directions through destructive interference, Figure 3.10, they add constructively, Constructive interference, in a few specific directions, determined by Bragg's law (www3.4):

$$2d\sin\theta = n\lambda$$

Here d is the spacing between diffracting planes, θ is the incident angle, n is any integer, and λ is the wavelength of the beam. When they land on a piece of film or other detector these specific directions appear as spots on the diffraction pattern called reflections, Figure 3.11. Thus, X-ray diffraction results from an electromagnetic wave (the X-ray) impinging on a regular array of scatterers (the repeating arrangement of atoms within the crystal).
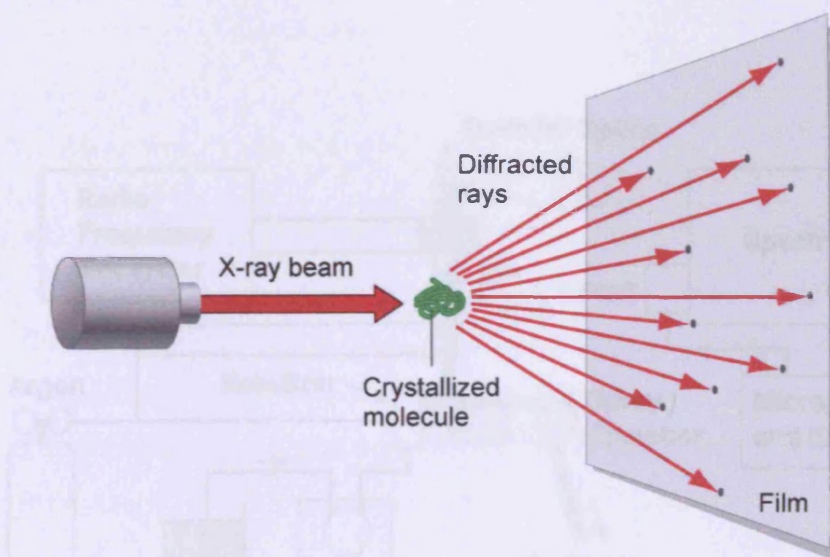
Figure 3.11 Image showing the diffracted rays forming a regular array of scatters on the detector (source www3.5)

The instrumentation works more efficiently if the samples are in a finely ground state, as these samples are already in powdered form no supplementary grinding was required. The identification of the phases is achieved by comparing the x-ray diffraction pattern, diffractogram, produced with an internationally recognised library of reference patterns, High score expert supplied by Panalytical, containing patterns for more than 70,000 phases. The details of the process used for this research are:

- o An amount of the sample was placed in the sample holder.
- o The sample is compacted, covered and lightly tapped to align the particles in the sample
- o The sample holder is placed into its holder in the XRD and closed.
- o The door is opened to allow the x-rays to bombard the sample
- o The computer program is then run using the power setting 35kV, 40mA

3.6.3   Inductively Coupled Plasma- Optical Emission Spectrometry

Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) is a very powerful multi-element analysis tool for 'trace' (ppb – ppm) and 'ultra-trace' (ppq – ppb) elemental analysis. Figure 3.12 presents a diagram of the main components of the ICP-OES.
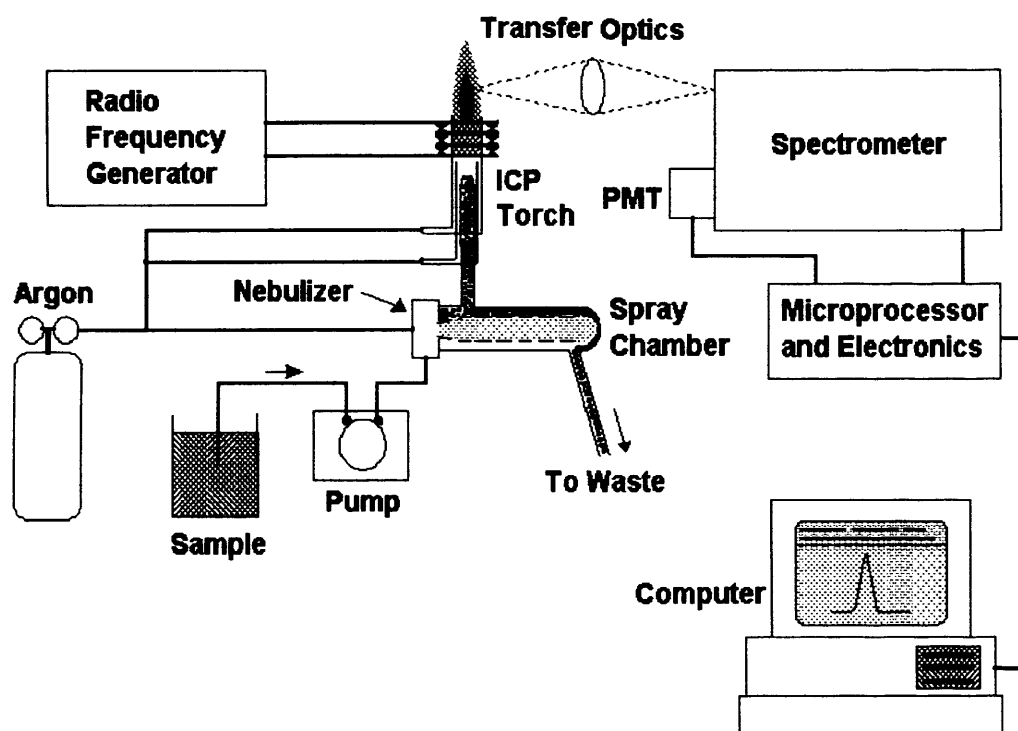
Figure 3.12 Major components and layout of a typical ICP-OES instrument (Source www3.6)

In ICP-OES, the sample is usually transported into the ICP as a stream of liquid sample. Inside the instrument the liquid is converted into an aerosol, a very fine mist of sample droplets, through a process known as nebulization. Nebulization is a critical step, as the sample must be delivered to the plasma in a form that the plasma could reproducibly desolvate, vaporise, atomise, ionise and excite. A typical nebulizer is shown in Figure 3.13. In this nebulizer the solution is introduced through a capillary tube to a low pressure region created by a gas flowing rapidly past the end of the capillary. The low pressure and high speed gas combine to break up the solution into an aerosol.
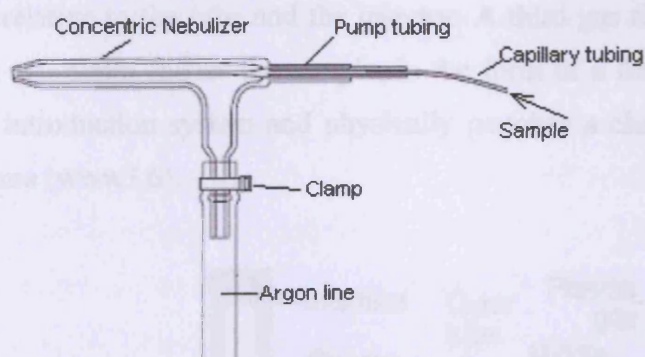
Figure 3.13 Image showing the concentric nebulizer used for ICP-OES

Once the aerosol has been created it must be transported to the torch so it can be injected into the plasma. Because only very small droplets in the aerosol are suitable for injection into the plasma the aerosol must first pass through a spray chamber, Figure 3.14. Spray chambers are designed to allow droplets of around 10μm or smaller to pass through to the plasma. This constitutes around 1 - 5% of the sample with the remaining 95 - 99% being drained into a waste container.
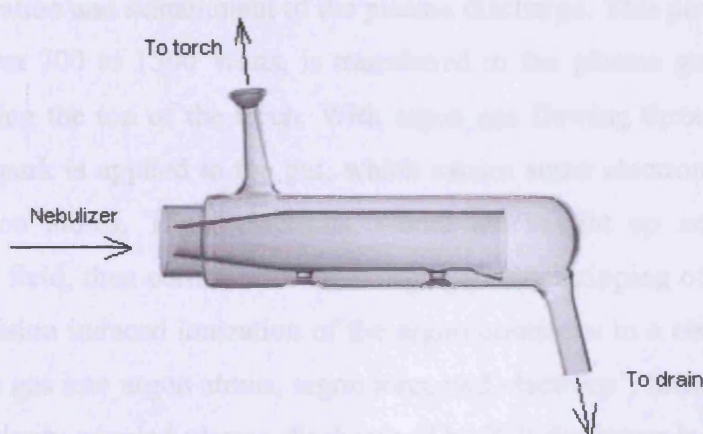
Figure 3.14 Image showing the spray chamber which filters the aerosol from the nebulizer

The ICP torch consists of 3 concentric quartz glass tubes. In Figure 3.15, these are shown as the outer tube, middle tube, and sample injector. The torch can either be one-piece, with all three tubes connected, or it can be a demountable design in which the tubes and the sample injector are separate. The gas (usually argon) used to form the plasma (plasma gas) is passed between the outer and middle tubes at a flow rate of 12–17 l/min. A second gas flow, the auxiliary gas, passes between the middle tube

and the sample injector at 1 l/min, and is used to change the position of the base of the plasma relative to the tube and the injector. A third gas flow, the nebulizer gas, also flowing at 1 l/min carries the sample, in the form of a fine-droplet aerosol, from the sample introduction system and physically punches a channel through the centre of the plasma (www3.6).
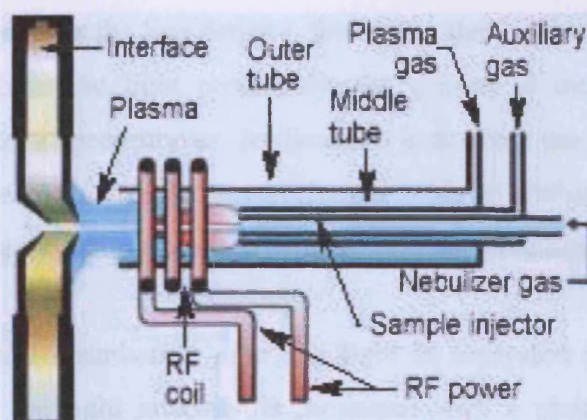
Figure 3.15 Image showing the torch assembly used for ICP-OES (source www3.6)

The radio frequency (RF) generator is the device that provides the power for the generation and sustainment of the plasma discharge. This power, typically ranging from about 700 to 1500 Watts, is transferred to the plasma gas through a load coil surrounding the top of the torch. With argon gas flowing through the torch, a high-voltage spark is applied to the gas, which causes some electrons to be stripped from their argon atoms. These electrons, which are caught up and accelerated in the magnetic field, then collide with other argon atoms, stripping off still more electrons. This collision induced ionization of the argon continues in a chain reaction, breaking down the gas into argon atoms, argon ions, and electrons', forming what is known as an inductively coupled plasma discharge. The ICP discharge is then sustained within the torch and load coil as RF energy is continually transferred to it through the inductive coupling process (Boss and Fredeen 2004).

The sample aerosol is then introduced and immediately collides with the electrons and charged ions in the plasma and is itself broken down into charged ions. The various molecules break up into their respective atoms which then lose electrons and recombine repeatedly in the plasma, giving off radiation at the characteristic wavelengths of the elements involved.

The next step is the differentiation of the emission radiation from one element from the radiation emitted by other elements and molecules. This is carried out through the use of a diffraction grating. This is simply a mirror with closely etched lines on its surface. When light strikes a grating it is diffracted at an angle that is dependant on its wavelength and the line density of the grating. In general, the longer the wavelength and the higher the line density, the higher the angle of diffraction will be. To separate polychromatic light predicably, the grating is incorporated in an optical instrument called a spectrometer. Its function is to form the light into a well defined beam, disperse it according to wavelength with a grating and focus the dispersed light onto an exit plane or circle where the optical detector sits.

Within the optical chamber(s), after the light is separated into its different wavelengths (colours), the light intensity is measured with a photomultiplier tube (PMT) or tubes physically positioned to view the specific wavelength(s) for each element line involved. The PMT is a vacuum tube which contains a photosensitive material called the photocathode that ejects electrons whenstruck by light. These electrons are accelerated towards a dynode which when struck releases two to five secondary electrons. These electrons then strike a second and a third dynode which releases further electrons each time. The final step is the collection of the secondary electrons by the anode. As many as 10^6 secondary electrons may be collected as a result of a single photon strike on the photocathode. The electrical current measured at the anode is then used as a relative measure of the intensity of the radiation reaching the PMT. The intensity is then compared to previously measured intensities of known concentrations of the elements, and their concentrations are then computed by interpolation along the calibration lines (Boss and Fredeen 2004).

To achieve the accurate results that the ICP- OES can deliver the preparation and digestion of the samples is paramount. Two methods of sample preparation have been used for this research namely Fusion Flux and Acid Digestion and a description of each process follows:

1. **Fusion Flux method**: performed by Mr Ravi Mitha at the Cardiff University School of Engineering laboratories. The main steps are:

   o 0.1g of the material was weighed onto a platinum crucible

   o 0.6g of lithium metaborate was added to form a bead

   o 10 drops of lithium iodide was added to the sample to prevent sticking

   o The crucible was supported in the Claisse Fluxer (M4)

   o The propane gas burner was lit beneath the crucible

   o The crucible was rotated as the heat was applied achieving approximately 1050° C

   o On achieving a molten state the mixture was dropped into a beaker containing nitric acid at 2% concentration

   o The solution was stirred with magnetic stirrers on a heated block for approximately 30 minutes

   o The solution was poured into conical sample jars and made up to 100ml with de-ionised water

2. **Acid Digestion using a microwave**: Performed by Mr Ravi Mitha at the Cardiff University School of Engineering laboratories. The main steps are:

   o 0.1g of sample was weighed into a clean dry polytetrafluoroethylene (PTFE) microwave tube.

   o 2ml of hydrofluoric acid (HF) was added to the microwave tube, covered and allowed to stand overnight.

   o 6ml of aquaregia (a 50/50 mix of nitric acid (HNO_3) and hydrochloric acid (HCl)) was added to the microwave tube and allowed to stand for 30 minutes

   o The microwave tube was then heated in the microwave for 30 minutes and allowed to cool for 20 minutes

   o 6ml of saturated boric acid ($B(OH)_3$) was added to the tube to neutralise the HF

   o The mixture was re-heated in the microwave for a further 15 minutes and allowed to cool for 20 minutes

- o Samples for testing were made up to 50ml using de-ionised distilled water
- o The maximum temperature in the microwave was set at 200^0C with a maximum pressure of 40 bar

Calibration and use of the ICP

The calibration of the Perkin Elmer Optima 2100 DV ICP was carried out by Mr Ravi Mitha prior to running the tests. The procedure was as follows:

- o A commercial spectroscopic standard was run containing each of the required elements. Dilutions of the standard were made using distilled water at 0.1ppm, 1.0 ppm, 10 ppm and 100 ppm
- o These dilutions were run through the ICP together with a blank sample, of de-ionised water only, to check for errors in the analysis
- o A correction coefficient accuracy of 1.0 is expected, this analysis gave an accuracy of 0.999986
- o One sample of each digestion method was analysed
- o On completion of calibration the samples were analysed

Conversion of returned information to Oxides

The ICP returns a numerical amount for the element content which then requires converting to an oxide. To get the percentage of the element in the sample the following formula is used:

$$R \times V / W \times 10000 = P \%$$

Where:

R = result from the analysis (mg/L)

V = liquid volume after digestion (ml)

W = weight of the sample digested within the liquid (g)

This result is multiplied by the ratio of its element mass to the relative oxide mass. For example using aluminium oxide Al_2O_3:

$$(((2 \times Al) + (3 \times O)) / (2 \times Al)) \times P = \text{percent of oxide in sample}$$

Where Al and O are the atomic masses (g/mol)

The full analysis results are shown in Appendix 3.

3.6.4   Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through it. An image is formed from the electrons transmitted through the specimen, magnified and focused by an objective lens and appears on an imaging screen. The image can be magnified to identify individual particles and an elemental analysis carried out using an Energy Dispersive Analysis of X-rays (E.D.A.X) technique.

The apparatus used for the analysis was a Tecnai 12 TEM, shown in Figure 3.16, operating at 80kV supplied by F.E.I. and Phillips Company used in conjunction with the Tecnai User Interface software and the E.D.A.X. micro-analysis system software.
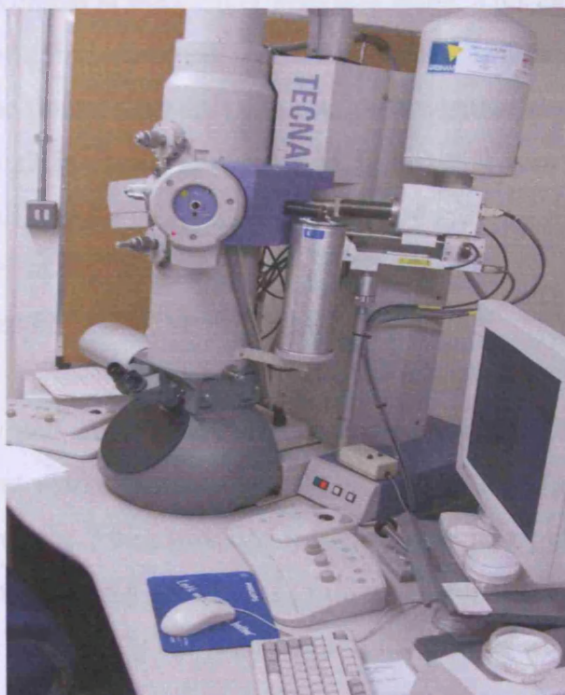
Figure 3.16 Image showing the Tecnai 12 TEM as used in this research

The samples were prepared by Mr Ravi Mitha at the Cardiff University School of Engineering laboratories. The main steps are outlined below:

- A tiny amount of the sample is placed in a test tube
- To this several drops of de-ionised water are added
- To ensure that there are no clusters in the sample it is subjected to an ultra-sonic bath until no visible clusters are seen
- De-ionised water is heated in a beaker to boiling point
- Carbon coated mica is floated in the water until the carbon separates and floats to the surface
- Gold gilded grids with 150 mesh are coated with the carbon
- The sample is dropped on to the carbon using a fine pipette
- This is left until all the moisture has evaporated and only the sample remains on the mesh
- The samples are then ready for use with the Electron Microscope

3.7 Inter-grinding

Inter-grinding of the material is a process whereby the cement replacement material is added to the cement at the clinker grinding stage. This can achieve benefits such as the production of a finer material, a shorter grinding time and control over the elemental make-up of the finished product. To establish whether any physical benefits could be achieved through inter-grinding a CEM II material was produced using a laboratory based ball mill grinder in an attempt to reproduce a representative material that would be produced at the cement works. The grinding of the materials was carried out using a Labtec ESSA, Vibratory Puckmill LM1-P

The constituents and quantities required to produce a CEM I cement were acquired from the cement works at Aberthaw. Table 3.7 gives the exact quantities of each material used to produce 7.6kg of CEM I, this amount being chosen so as not to overload the ball mill and keep the amount of grinding required to a minimum. When adding the fly ash to the blend only the total mass of the clinker was reduced to allow for this.

Table 3.7
Quantities required for the inter-grinding of the fly ash

Limestone	Gypsum	Grinding agent	Total clinker	27% replacement		33% Replacement		Total
				Clinker	Fly ash	Clinker	Fly ash	
(kg)	(kg)	(kg)	(kg)	(kg)	(kg)	(kg)	(kg)	(kg)
0.243	0.342	0.006	7.015	5.121	1.894	4.700	2.315	7.600

The clinker and limestone were first reduced in size by crushing using firstly a jaw crusher followed by a gyratory crusher. This was done to decrease the overall grinding time as the larger elements took a considerable amount of time to reduce in size. The materials were then accurately weighed and placed in a plastic container large enough so as not to lose any material from the top. If the material was to remain in the container for any length of time a lid was attached to avoid contamination. The ball mill was loaded with approximately 60 steel balls varying in size between a maximum of 30mm and a minimum of 25mm and the material added. The ball mill, shown in Figure 3.17, had a diameter of 390mm and ran at a speed of 143rpm. The lid was securely fitted to the mill and the grinding started.
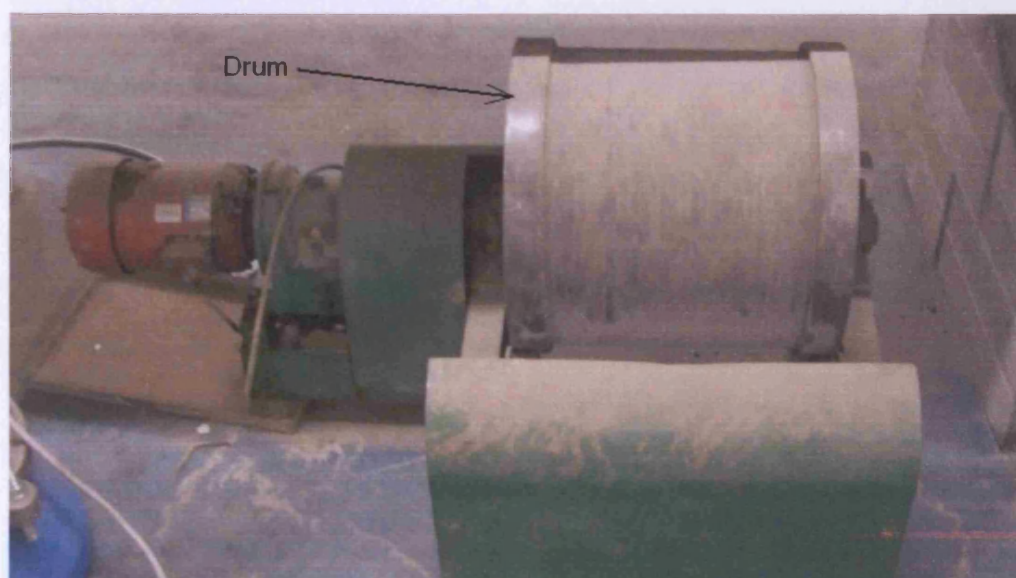
Figure 3.17 Image of the Ball mill used for the grinding of materials to produce CEM I
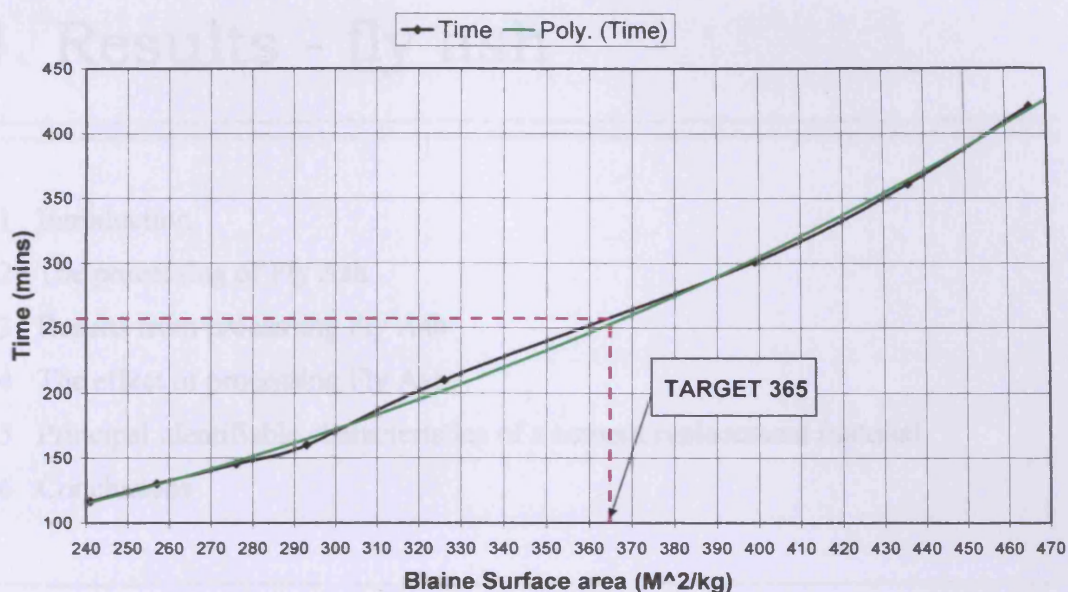
Figure 3.18 Determination of grinding time from plotting the Blaine fineness of the cement to the time in the ball mill

To achieve a grinding time which sufficiently replicated the CEM I produced at the cement works, a trial grinding was undertaken. The grinding for this trial was stopped at regular intervals and a sample removed for sizing using the Blaine method. After surpassing the required fineness of $365m^2$/kg a couple of times a graph, presented in Figure 3.18, was produced of the Blaine fineness plotted against the time taken to achieve this fineness. At $365m^2$/kg the associated grinding time was plotted as 255 minutes. To confirm this a control CEM I was ground in the ball mill for 255 minutes and the resulting material checked for fineness using the Blaine method. It was found that the results were within $5m^2$/kg and hence the time selected was deemed adequate for the successful reproduction of a CEM I cement.

4. Results - fly ash

4.1 Introduction

4.2 The processing of Fly Ash

4.3 Results from processing Fly Ash

4.4 The effect of processing Fly Ash

4.5 Principal identifiable characteristics of a cement replacement material

4.6 Conclusions

4.1   Introduction

This chapter deals with the analysis of a Fly Ash (FA) which the partner company, Minimix Concrete, has sourced locally at Aberthaw, South Wales. Minimix wishes to blend this FA with its Ordinary Portland cement (OPC) to produce a CEM II cement and needs to know that firstly, it conforms to the standards; second, performs within the concrete and third, that it is cost effective. This third part is not dealt with in this thesis but the cost analysis model produced and used by the Author for the purpose of analysing costs can be seen in Appendix 4. The supplied FA, the Raw FA, was then subject to an Electrostatic separation process, Processed FA, and an air swept classification process, Classified FA, and the analysis completed again. This was carried out to identify the physical and chemical changes which occurred due to the processing and the benefits achieved.

The chapter begins with a look at the controls used and provides values against which the test materials can be measured. The chapter continues by looking at the use of fly ash as a cement replacement and the effect that processing the fly ash producing a finer ash has on the concrete produced. The research studies the materials' performance, chemical and physical characteristics and tries to identify the characteristics which either enhance the concrete in which it is used or impair the concrete from achieving its full potential.

Further materials are then introduced as possible cement replacement materials and their physical and chemical properties scrutinised to ascertain which aspects of a material provides the perfect condition for a cement replacement material.

4.1.1 Errors

Due to the high estimate of samples required and the number of concrete mixes necessary to provide these samples it was decided from the outset to standardise the mixing and testing procedure. It was hoped that maintaining a routine would reduce errors and provide a narrow spread of results; however, potential sources of errors need to be identified.

The materials used were obtained and stored in a room with climate control, thus ensuring that the cement remained useable with no change to its properties for example moisture ingress causing the cement to harden. The cement (Ordinary Portland Cement Ready Mix (OPCRM)) was supplied from one manufactured batch direct from the cement works (Lafarge Aberthaw) and stored in sealed containers within the laboratories at the University. The aggregate proved to be a problem due to the quantities required and a number of deliveries were necessary during the period of mixing. Although the aggregates remained within the grading as required by the British Standards (BS EN 12620) there is room for variability within the aggregate size having a possible effect on the aggregate grading within each mix.

Achieving the correct slump was fundamental to obtaining accurate compressive strength results. This research relied on the fact that when the coarse aggregates were soaked for an exact period of time the moisture content would standardise for each mix. Periodical random moisture content checks showed little difference in the 14mm to 20mm aggregate between tests with the 6mm to 10mm being the most inconsistent. Both the sand and dust were tested prior to each set of tests, as these materials could not be brought to an exact moisture content through soaking. Having been dredged from the Severn estuary, the sand was saturated; however, being stored indoors ultimately dried the material, whilst the dust being stored indoors at the quarry

showed little difference in moisture content prior to mixing. The total amount of sand which would be used for a day's mixing was weighed and blended so that a representative figure for the particle grading and moisture content for the sand could be achieved prior to concrete mixing. Three samples of sand were used to determine the moisture content and, after checking for any anomalies within the moisture content, the average taken. A similar approach was use for the dust. The determination of the moisture content was carried out using the following formula:

Wet weight = A

Dry weight = B

Moisture content = A-B / B x 100

The range of moisture contained within each of the aggregates is presented in Table 4.1. Finally, the same equipment was used at the University to measure all the quantities required, to mix the concrete, to compact the concrete in the moulds, cure the samples and test the hardened properties of the concrete for every mix produced.

Table 4.1
Range of moisture contents of the aggregates as measured during this research

Material	Moisture content (minimum)	Moisture content (Maximum)
Coarse aggregate 20mm and 14mm	2.2	2.2
Coarse aggregate 6mm and 10mm	3.2	3.6
Dust	1.0	1.0
Sand	3.1	4.3

4.1.2   Control mixes

To establish a measure for the viability of any potential material, control mixes were required. These control mixes were taken from the designs of the company partner, Minimix concrete, and for ease seven designs were initially selected:

1) Low cement content 140kg/m^3

2) High cement content 450kg/m^3

3) 5 intermediate cement contents of 200, 250, 300, 350 and 400kg/m^3

These designs are given in Table 4.2 below whilst the full compliment of mix designs used for this research can be seen in Appendix 1.

Table 4.2
Component materials required to produce 1m^3 concrete as used in this research

Batch weights for 1m^3 (kg)							
Material	Cement content (kg/m^3)						
	140	200	250	300	350	400	450
Cementitious material	140	200	250	300	350	400	450
Coarse aggregate 20mm	407	403	400	404	393	393	397
Coarse aggregate 14mm	407	403	400	404	393	393	397
Coarse aggregate 10mm	184	182	169	185	181	164	152
Coarse aggregate 6mm	184	182	169	185	181	164	152
Dust	500	490	465	438	425	415	411
Sand	388	380	387	348	336	308	287

Different types and classes of cement are produced for various purposes. BS EN 197-1:2000 catalogues a number of cement specifications together with any restrictions on their use. The following cements were chosen as controls for this study as being the most commonly supplied from the partner company:

1) CEM I (OPC)

2) CEM III/A (Blended OPC and Ground Granulated Blast Furnace Slag (GGBS) in the ratio 50/50)

The mixes were produced adding enough free water to achieve a mid range slump of typically 70mm. This falls within the S2 classification as set out in BS EN 206:1-2000, with a range of between 50 and 90mm with a tolerance of +- 20mm. Although some discrepancy is to be expected between each mix due to the nature of concrete and the tester's slumping technique, every effort was made to achieve the 70mm slump.

Admixture to aid workability, whilst reducing the addition of free water, was added to the mix in the quantity (as recommended by the supplier) of 0.4% by mass of the cement content.

BS EN 206 has a requirement that the designed compressive strength of concrete be recorded at 28 days; this has therefore been used to establish the suitability of the material as a cement replacement within this research as within industry.

CEM I - Ordinary Portland cement control

Figure 4.1 presents the compressive strength results at 28 days for three CEM I control mixes of identical designs. These mixes contain 100% Ordinary Portland cement (OPCRM) at 300kg/m^3 cement content containing no cement replacement material. The mixes were produced to study the variability encountered between identical mix designs repeated at varying times. This information will highlight the range of strengths achieved within a single mix which can be allowed for in the research samples. This means that samples recording a low result will not necessarily be removed from the research if they fall within a range higher than the control. In practice this variability in compressive strength is dealt with by the Quality Scheme for Ready Mixed Concrete (QSRMC). This standard uses a statistical analysis of a running test regime to apportion a mean strength to a selected mix design and then reduce this strength by a margin which ensures the required strength is always achieved. For this research the compressive strength achieved has a bearing only as a comparison to subsequent mixes and not, at this point, as a commercial product in the sense that QSRMC regulations are required to be followed.

OPC Compressive results

Time (days)	1	2	7	28	56
mix 1	19.4	31.2	35.8	45.9	55.6
mix 2	19.4	30.0	35.0	51.0	56.0
mix 3	18.3	29.2	34.7	49.5	54.0
Average	19.0	30.1	35.2	48.8	55.2
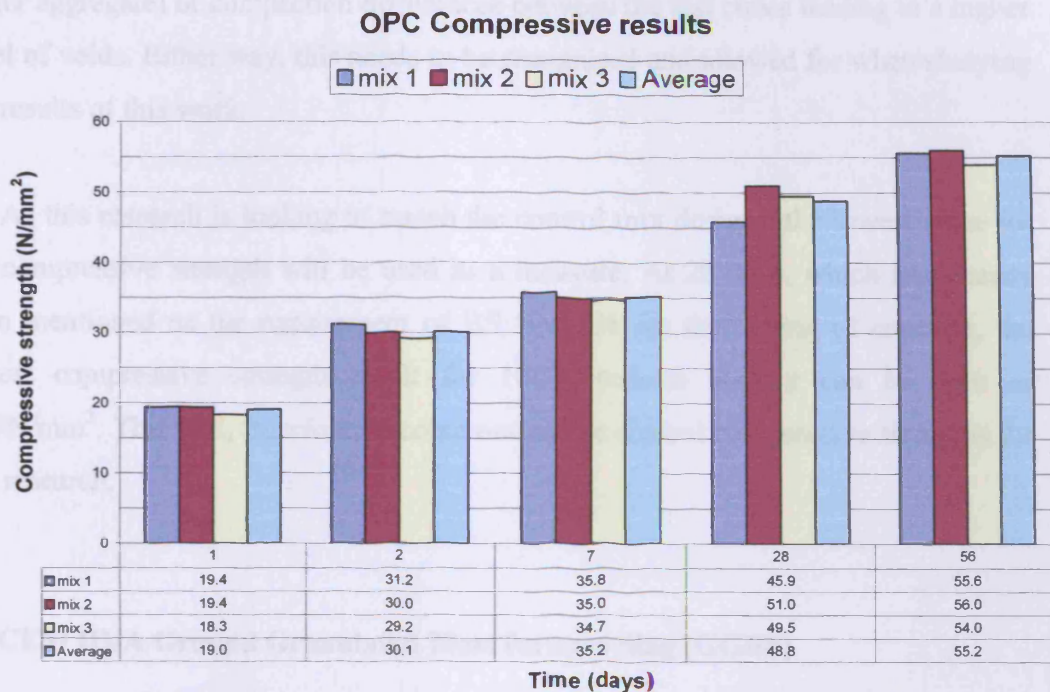
Figure 4.1 Variation in compressive strengths between three identical concretes as a function of time curing - cement content 300kg/m^3

A large number of factors affect the strength of ready mixed concrete making it a highly variable product. A coefficient of variation for the compressive strength of concrete is typically between 10 per cent and 20 per cent (Sear L 2003). As this is a laboratory mix it should be expected that the higher control available would achieve a variability in strength lower than 10 per cent.

It can be seen from Figure 4.1 that there is a variation in strength between each of the mixes at different time periods. Figure 4.1 shows that there is a strength variation between the weakest and strongest of 1.1N/mm^2 at 7 days giving a variability from the average of 2.8 per cent. The strength difference increases to 5.1N/mm^2 at 28 days but drops to 2N/mm^2 at 56 days. This gives a strength variability of 5.9 per cent and 2.2 per cent respectively.

It can also be seen that not one of the mixes is continuously the weakest or strongest throughout and that the compressive strength increase varies between each of the mixes at 7, 28 and 56 days. This difference may be due to the concrete make up actually placed into the moulds (well graded as opposed to a higher percentage of

larger aggregate) or compaction differences between the test cubes leading to a higher level of voids. Either way, this needs to be recognised and allowed for when studying the results of this work.

As this research is looking to match the control mix designs, the lowest value for the compressive strength will be used as a measure. At 28 days, which has already been mentioned as the requirement of BS EN 206 for the testing of concrete, the lowest compressive strength result for 100% cement content can be seen as $45.9N/mm^2$. This will, therefore, become one of the control compressive strengths for this research.

CEM III/A Ground Granulated Blast furnace Slag (GGBS)

The second control being used throughout this research is a 50/50 blend of GGBS and OPC, as this is one of the most commonly used Supplementary Cementitious Materials (SCMs) in industry (Scrivener et al. 2008).

GGBS cements have been in use for a reasonably long period due to the overall economy in their production as well as their improved performance characteristics in aggressive environments. Also, the use of pozzolans as additives to cement, and more recently to concrete, is well accepted in practice. GGBS is one such pozzolanic material (termed by a few as a supplementary or complimentary cementitious material) which can be used as a cementitious ingredient in either cement or concrete composites. Research work to date suggests that these supplementary cementitious materials improve many of the performance characteristics of the concrete, such as strength, workability, permeability, durability and corrosion resistance (Babu et al. 2000). This blended cement has been chosen as a control due to the fact that the company partner supplies this as common practice. The majority of the concrete supplied now contains GGBS.

As with the OPCRM tests, a number of concrete mixes were produced using an identical mix design and their 28 day compressive strengths compared to find a minimum and maximum value. Unlike the OPCRM mix, a selection of cement

contents was also introduced. This was to assess the effect that a cement replacement may have on compressive strength as the cement content increases or decreases. The mix designs chosen have cement contents of $140kg/m^3$, $300kg/m^3$ and $450kg/m^3$, the material quantities for each of these mix designs as used in this research are shown in Table 4.2 above. The mix comprised 50 per cent GGBS and 50 per cent OPCRM.
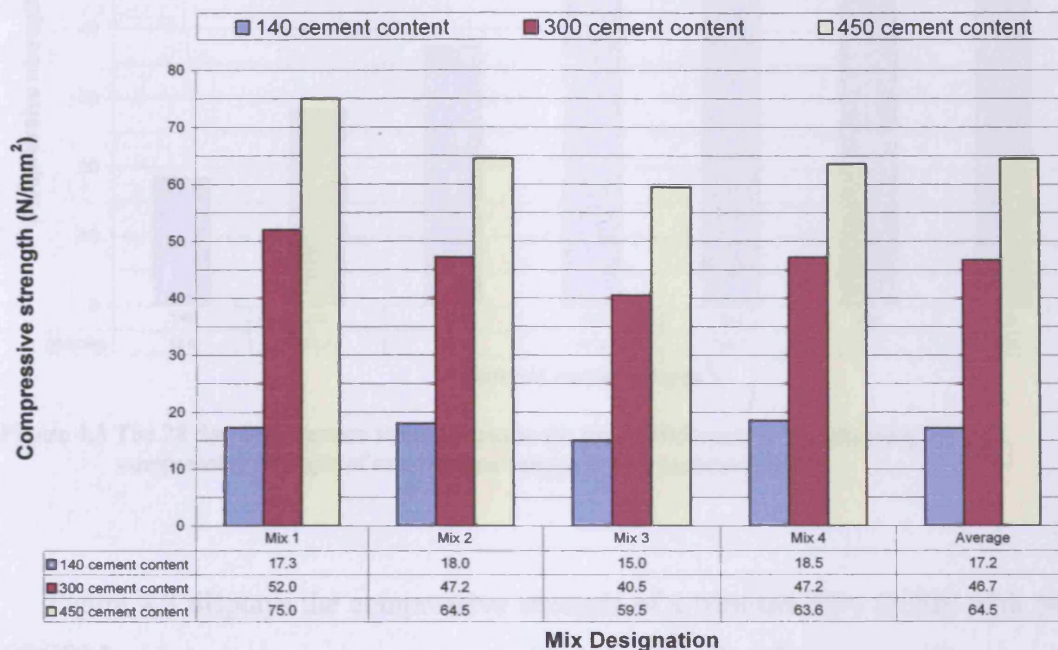
Figure 4.2 The 28 day compression strength results for the GGBS control mix showing the variation in strength through identical mix designs at different cement contents

Figure 4.2 presents the results of the compressive strength tests on the GGBS control samples. It can be seen from the chart that the there is a wide range of results from each mix. The $140kg/m^3$ mix shows a difference between the weakest and strongest mix as $3.5N/mm^2$ with a 12 per cent deviation from the average. The $300kg/m^3$ mix shows an $11.5N/mm^2$ difference with a 13 per cent deviation from the average, whilst the $450kg/m^3$ mix has the highest variation between the weakest and strongest mix at $15.5N/mm^2$ the deviation from the average being 14 per cent. The per cent deviation for each of these mixes is much higher than for the OPCRM mix but within the maximum of 20 per cent as provided by Sear (Sear L 2003).
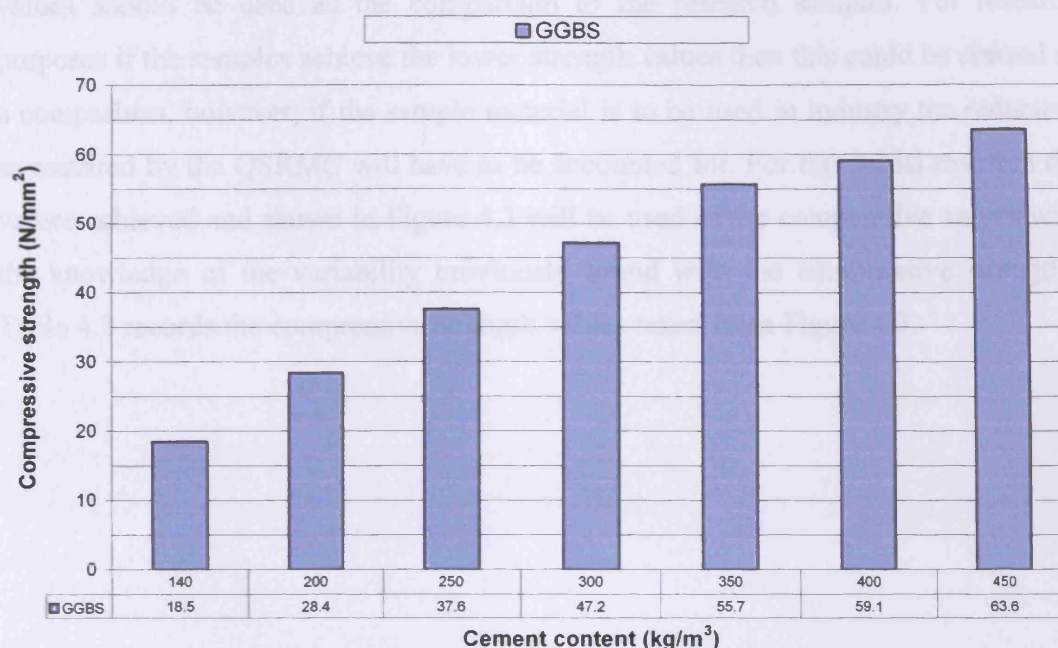
Figure 4.3 The 28 day compression strength results for the GGBS control mix showing the
compressive strength of mix designs using varying cement contents

Figure 4.3 displays the compressive strength of a blended 50% GGBS with 50%
OPCRM mix at varying cement contents. It can be seen that the compressive strengths
for the 140kg/m^3, 300kg/m^{3}and the 450kg/m^3 are similar to the average compressive
strengths shown in Figure 4.2. The variations are 7 per cent for the 140kg/m^3, 1 per
cent for the 300kg/m^3 and 3 per cent for the 450kg/m^3 mix.

Table 4.3
GGBS control mix minimum strengths achieved at the varying cement contents to be used as
comparisons to research materials.

Cement content (kg/m^3)	Target compressive strength (N/mm^2)
140	18.5
200	28.4
250	37.6
300	47.2
350	55.7
400	59.1
450	63.6

From this information a decision has to be made on which compressive strength values should be used as the comparison to the research samples. For research purposes if the samples achieve the lower strength values then this could be classed as a comparison, however; if the sample material is to be used in industry the reduction as required by the QSRMC will have to be accounted for. For this initial research the values achieved and shown in Figure 4.3 will be used as the comparative values with the knowledge of the variability previously found with the compressive strengths. Table 4.3 records the compressive strength values taken from Figure 4.3.

4.2   The Processing of fly ash

Electrostatic separator

Fly ash received directly from the power plant is a very unstable material. One consequence of high carbon is that it adversely affects workability while variable carbon content leads to erratic behaviour with respect to air entrainment (Neville, 1995). One method of reducing the carbon content is through the use of an electrostatic separator. Electrostatic separation technology is relatively new and there are few commercial applications worldwide. It, therefore, presents a unique opportunity to look at the effect that the processing of a fly ash has on its use as a cement replacement.
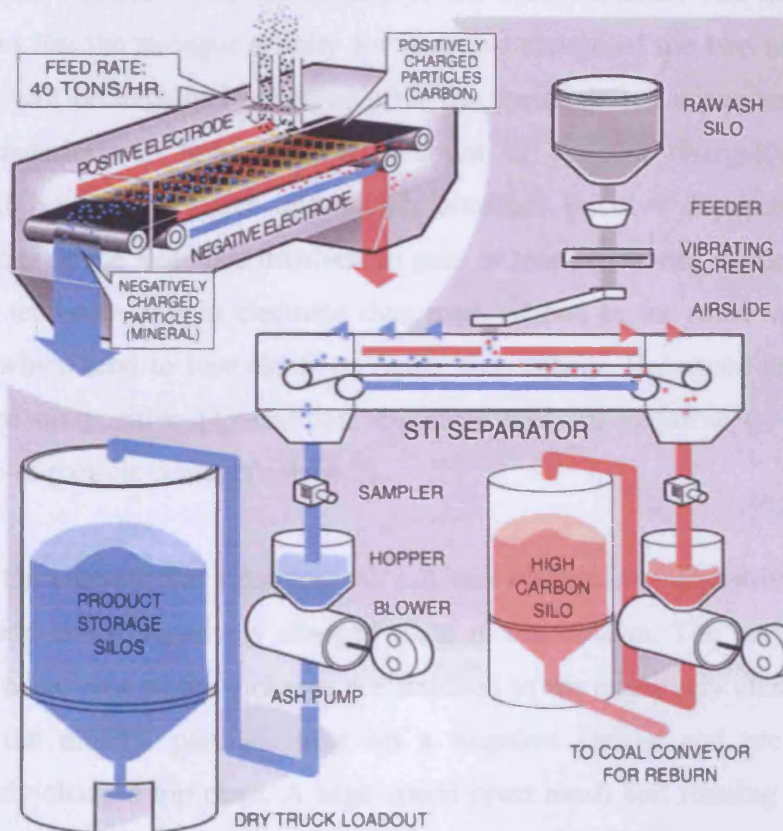
Figure 4.4 Schematic of the separation process (www4.2)

The electrostatic separator used for this research was of the type supplied by Separation Technology Incorporated (STi), USA. illustrated in Figure 4.4. The process uses positive and negative charge to separate the carbon rich material from the mineral with continuous sampling and adjustment to achieve the targeted carbon content.

Operation

Fly ash was introduced into the separator from the storage silo above. The material was fed into the thin gap between two parallel planar electrodes. The particles are triboelectrically charged. Triboelectric charging is when two different materials are pressed or rubbed together, the surface of one material will generally steal some electrons from the surface of the other material. The material that steals electrons has the stronger affinity for negative charge of the two materials, and that surface will be negatively charged after the materials are separated. (Of course the other material will have an equal amount of positive charge)(www4.1). Which material becomes negative and which becomes positive depends on the relative tendencies of the materials involved to gain or lose electrons. Some materials have a greater tendency to gain electrons than most others, in the same way that there are others which tend to lose electrons easier than others. Unburned carbon particles in ash take on positive (+) charges; minerals take on negative (-) charges through particle-to-particle contact (www4.2).

On entering the separator, the ash was subjected to a positively charged plate at the top and a negatively charged plate at the bottom. The carbon rich particles having taken on a positive charge are attached to the negatively charged bottom plate whilst the mineral particles take on a negative charge and are attached to the positively charged top plate. A high speed open mesh belt running the length of the separator, in a clockwise direction, scrapes both the top and bottom plates. The ash is collected in the mesh and dropped into storage silos at either end, carbon rich at one end mineral at the other. Access to allow safe sampling of the material is located at the ends of the belt so as monitoring of the material properties can be carried out at intervals during the operation. The separator used during this research is shown in Figure 4.5.
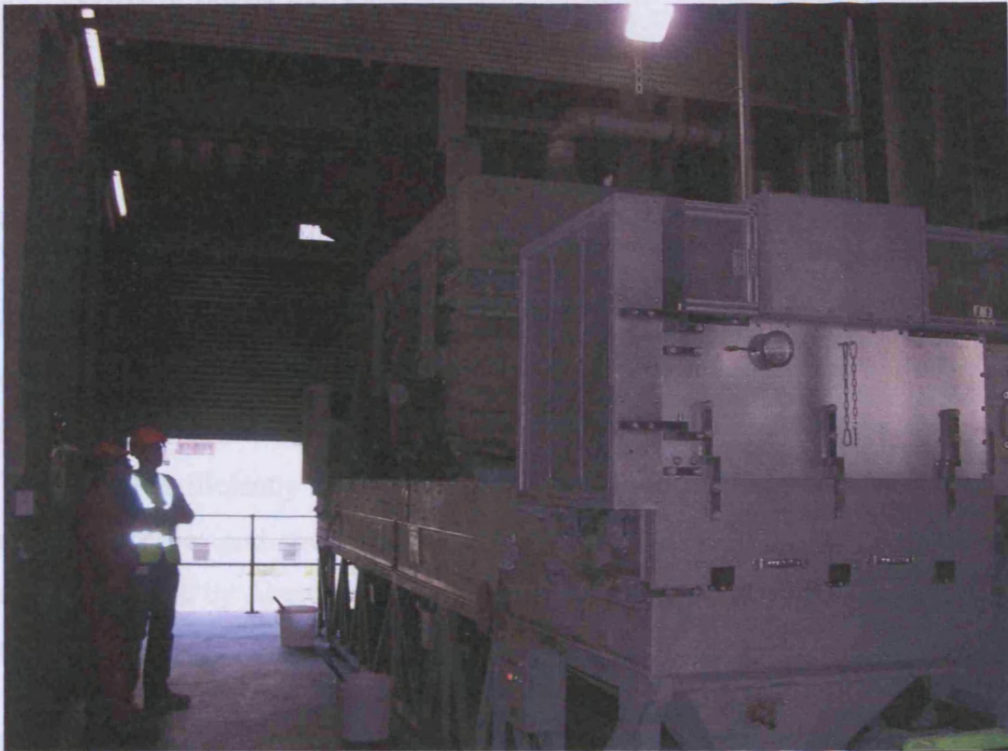
Figure 4.5 Separator in use at the Longannet power station in Scotland

Air swept classifier

The air swept classification is performed by a forced vortex classifier designed to disperse, then classify, fine particles into coarse and fine fractions. High energy dispersing air enters the rotor radially around the entire outer edge at the dispersion tips, while feed particles enter the 360 degree dispersing air zone through an inlet in the rotor ring. In the classification zone, particles are acted upon by outwardly directed centrifugal force and an inwardly directed drag force. Air carries the dispersed fine particles spirally inward to the central fine fraction outlet. Coarse particles move outward around the rotor periphery to the coarse fraction outlet. Entrained fines are recycled from the coarse cyclone collector back to the classifier. The desired cut off point is selected by adjustment of the airflow rate, rotor speed or both (www4.3).

4.3   Results from processing Fly Ash

As mentioned in Section 2.8, fly ash in its various forms has been known as a useful cementitious material for hundreds of years. One of the primary concerns with its use has been the variation in source quality, fineness of the material and carbon content, all of which affect the quality of mortar and concrete. Through the use of a new electrostatic processing unit, devised and supplied by Separation Technologies Incorporated (STi), it is hoped that the fineness and carbon content of the fly ash can be controlled sufficiently to result in a consistently high quality fly ash giving concrete properties and strengths at least comparable to that of GGBS. The fly ash used was supplied by Aberthaw Power Station in its raw form which was then subject to electrostatic processing.

(a)   (b)

Figure 4.6 Images taken at the STi processing plant Longannet in Scotland a) computer controlled
            process showing feed rate, weights, delivery routes and final storage location, b) sampling
            of the final processed fly ash taken from the separator for analysis

Approximately 60 tonnes of raw fly ash was transported in two tankers from Aberthaw to Longannet, Scotland, to be fed through the electrostatic processor. This is a relatively new process with only seven of these systems operational in the world, six in North America and one in Scotland. The process was attended by the Author who oversaw the processing operation. The whole process was computer controlled with regular sampling of the product to ensure compliance to requirements (Figure 4.6a and 4.6b). This process separated out the larger particles, which tend to consist

of mainly carbon, and the finer more useful material. The set up of the STi plant for the purpose of this research yielded 62 per cent "processed ash" as a usable product with the required loss on ignition. Figure 4.7 shows the processed ash, the raw ash and the waste ash with loss on ignition values of 3.7%, 19.04% and 44.39% respectively.
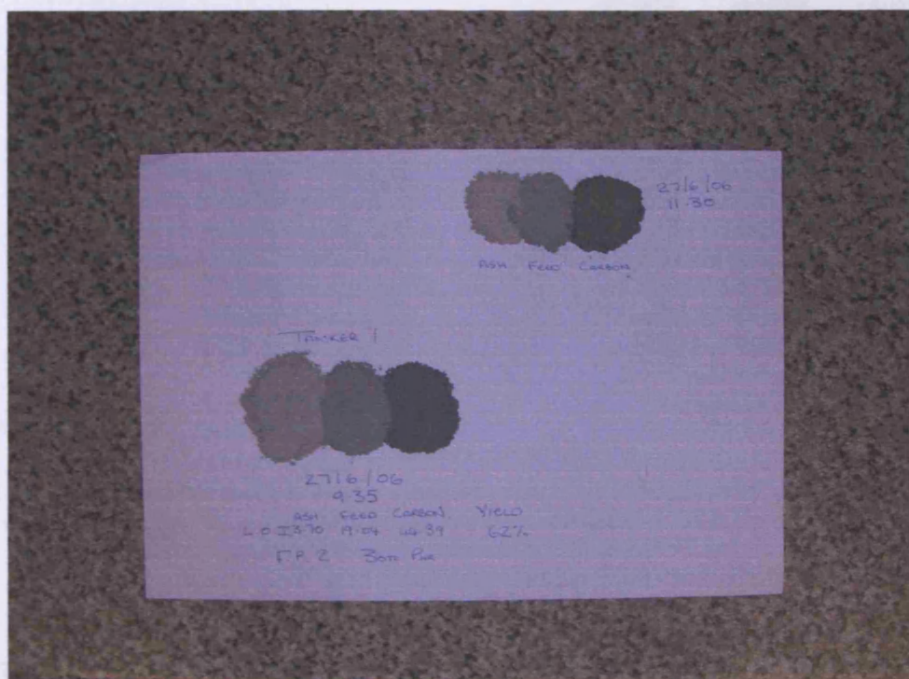
Figure 4.7 Image comparing the three products within the separation process, the processed ash, the raw feed ash and the waste, high carbon, ash.

27 per cent processed fly ash and 73 per cent OPCRM

The levels of fly ash used to replace the OPCRM for these tests were 25%, 27%, 30%, 33% and 35% on a mass basis. At these percentages the blended cement would be categorise as a CEM II B-V and hence conform to BS EN 197 which restricts the percentage of fly ash used to between 21 and 35 per cent. As a starting point 27% was used to get a feel as to how the fly ash would perform. Figure 4.8 compares the 28 day compressive strength of the processed fly ash to the GGBS control at cement contents of 140, 200, 250, 300, 350, 400 and 450 kg/m^3.
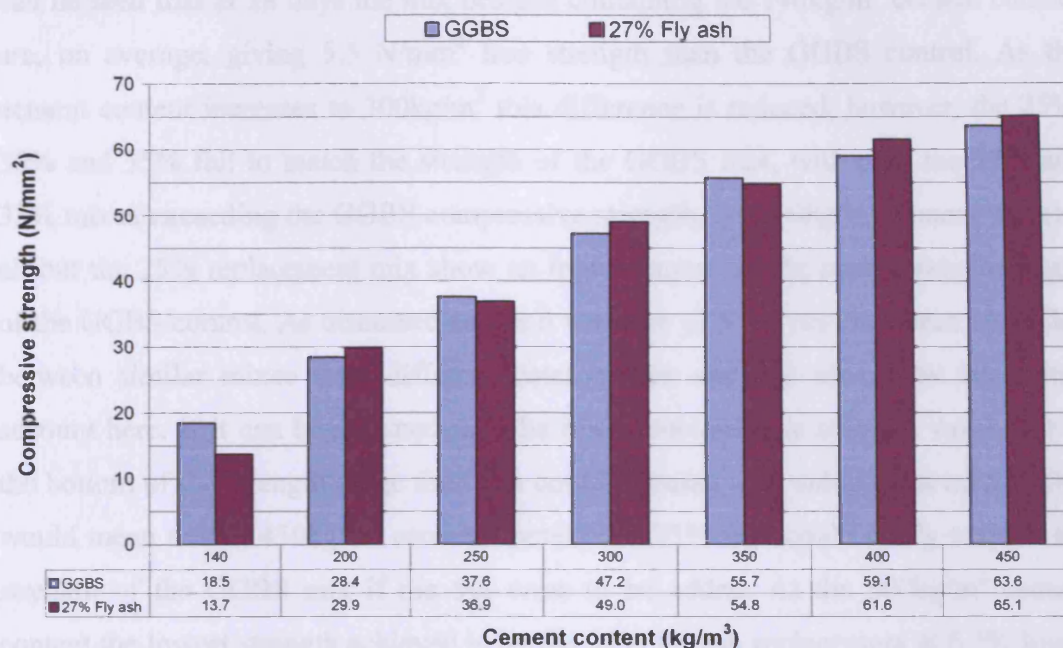
Figure 4.8 28 day compressive strength results using STI Processed fly ash at 27% fly ash to 73% OPCRM compared to a blended 50% GGBS 50% OPCRM

Overall the cement blended with 27% processed fly ash and 73% OPCRM gave positive results when compared to the GGBS control mixes at 28 days. The 200kg/m³, 300kg/m³, 400kg/m³ and 450kg/m³ cement contents exceed the compressive strengths of their respective GGBS controls whilst the mixes containing the 250kg/m³ and 350kg/m³ cement contents failed to achieve the strengths of the GGBS controls. However the results remain within 5% of each other. The mix containing the 140kg/m³ cement content failed to achieve the compressive strength of the GGBS control and showed a 25% difference in strength.

Processed fly ash at various replacement levels

Following on from the positive results gained at the 27% replacement level, the trials of the processed fly ash progressed to cover the selected replacement levels within the classification of the CEM II B-V group as discussed above. At this point the focus was placed on only three cement contents 140kg/m³, 300kg/m³ and the 450kg/m³.

The results of the 28 day compressive strength tests are presented in Figure 4.9. It can be seen that at 28 days the mix designs containing the 140kg/m³ cement content are, on average, giving 5.5 N/mm² less strength than the GGBS control. As the cement content increases to 300kg/m³ this difference is reduced, however, the 25%, 30% and 35% fail to match the strength of the GGBS mix, with only the 27% and 33% mixes exceeding the GGBS compressive strength. At 450kg/m³ cement content, all but the 25% replacement mix show an improvement on the compressive strength of the GGBS control. As discussed earlier a variance of 5 per cent has been identified between similar mixes from different batch mixes and this should be taken into account here. If it can be assumed that the lower compressive strength values are at the bottom of the strength range then this could increase with subsequent mixes. This would mean that at 450kg/m³ cement content the 25% mix could easily surpass the strength of the GGBS mix if the 5% were to be added. At the 300kg/m³ cement content the lowest strength achieved is by the 30% fly ash replacement at 6.5% lower than the GGBS control. An increase by 5% would however reduce the margin between the fly ash and GGBS to 0.72N/mm². The 140kg/m³ having a 5.9N/mm² lower compressive strength means at 31% this is well outside the 5% allowance, and with all the results being similar it shows that the lower cement content is having a significant effect on the rate of strength gain.

	GGBS	25%	27%	30%	33%	35%

Cement content (kg/m³)	140	200	250	300	350	400	450
GGBS	18.5	28.4	37.6	47.2	55.7	59.1	63.6
25%	12.6	0.0	0.0	44.6	0.0	0.0	62.8
27%	13.7	29.9	36.9	49.0	54.8	61.6	65.1
30%	12.9	0.0	0.0	44.1	0.0	0.0	67.6
33%	13.1	0.0	0.0	47.9	0.0	0.0	66.2
35%	12.9	0.0	0.0	46.7	0.0	0.0	64.6
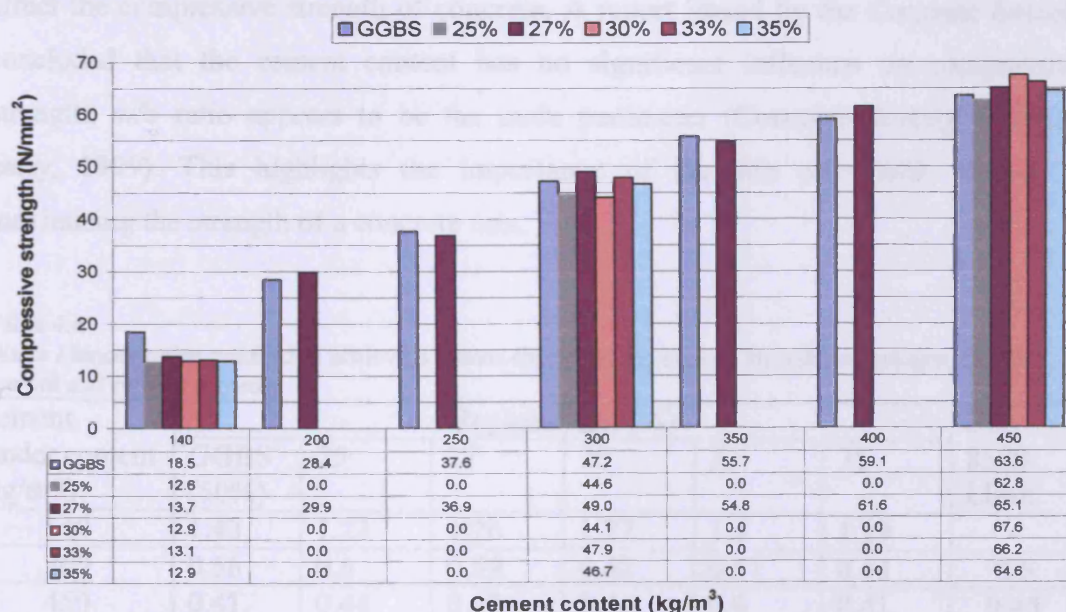
Figure 4.9 28 day compressive strength results comparing the processed fly ash blended with OPCRM at varying levels to the GGBS controls

Previous research has shown that it would be expected to see a drop in 28 day compressive strength as the fly ash content increases (Sear 2007, Siddique 2004). Figure 4.9 should therefore show that at 25% replacement a stronger mix is achieved than the other fly ash mixes. However, in all cases there is an increase in strength at some point above the 25% replacement. For example, at 450kg/m^3 cement content the strength increases from 62 to 65 to 67 N/mm^2 as the amount of FA increase from 25% to 27% to 30%. At replacement levels above 30% the strength is reduced but these reduced values still remain higher than for the 25% mix.

4.2.1   Water / Binder ratio

The water / binder ratio (w/b) is an important factor for two main reasons. First, it is well documented that the w/b ratio has a direct effect on the compressive strength of concrete, i.e. the higher the ratio the more water has been added and the weaker the concrete will be (Balendran et al. 1995, Lydon 1982, Lewis 2003). Second, the British and European standards have set limits for certain mix designs to ensure that durability requirements are met. As discussed in Chapter 2, Lydon (1982) suggested that the water / cement ratio (water / cement ratio is used when 100% OPC has been used, therefore without a replacement material) is one of the main variables which can affect the compressive strength of concrete. A report issued by the Concrete Society concluded that the cement content has no significant influence on compressive strength; w/b ratio appears to be the main parameter (Concrete Society Working party, 1999). This highlights the importance of the w/b ratio with respect to maximising the strength of a concrete mix.

Table 4.4

Water / binder ratios required to achieve a 70mm slump for the various fly ash percentages, GGBS control and cement contents

Cement	Replacement (%)						BS
binder content (kg/m3)	GGBS (50%)	25	27	30	33	35	8500 Limit
140	1.43	1.22	1.26	1.27	1.3	1.19	-
300	0.56	0.6	0.59	0.62	0.57	0.53	0.6
450	0.41	0.44	0.42	0.4	0.4	0.41	0.45

Table 4.4 shows the w/b ratios for the three main cement contents used for the processed fly ash comparison with GGBS and the associated British Standard limit. It is well recorded (Owens, 1979) that the partial replacement of CEM I by fly ash will result in a reduction in water demand with a consequent increase in strength. This increase in strength partially offsets the lower early strengths associated with the delayed reaction of the fly ash. Table 4.4 shows that the mixes containing the lower cement content, of $140kg/m^3$, achieve a lower w/b ratio than the GGBS control at all replacement levels. This, however, does not relate to the compressive strengths as none of these mixes reach the compressive strength of the GGBS control. At this level of cement content there is no British Standard limit as the cement content is regarded as too low to meet any durability requirements. At $300kg/m^3$ cement content the 27% fly ash replacement achieves the highest compressive strength yet the w/b ratio exceeds that of the GGBS control. The 30% fly ash mix is higher than the British Standard limits at 0.62, which could explain the dip in the compressive result at this position whilst at $450kg/m^3$ cement content the 30% fly ash mix, having the lowest w/b ratio, out performs all the other mixes in that group. At $450kg/m^3$ cement content the results begin to follow the expected pattern with the lower w/b ratios achieving the greater compressive strengths and the higher w/b ratio at the 25% replacement, achieving the lowest. The 27% replacement shows a higher w/b ratio but exceeds the GGBS control strength.

The finer the fly ash, the greater the water reducing effect and, by increasing the quantity of fly ash in the cement, the demand for water will further decrease (Owens, 1979). The results of the water / binder ratios do not follow this statement exactly as it can be seen that with the 30% fly ash replacement both the $140kg/m^3$ and the $300kg/m^3$ mixes give higher w/b ratios than their preceding fly ash mixes as does the 33% fly ash replacement at $140kg/m^3$. Therefore, judging the compressive strength on w/b alone seems to be inadequate, as it ignores other factors, particle shape and grading for example (Balendran and Pang 1995), which also have a bearing on performance.

4.2.2 Permeability results

The relative permeability test measures the rate at which nitrogen gas passes through a concrete sample. This is indicative of the rate that moisture may be absorbed into the concrete and, hence, has a bearing on the concrete's durability, the main factor determining the lifespan of the concrete and possible repair costs throughout its life. The relative permeability of the concretes was carried out using the method engineered by Lydon, (1993) described in Chapter 3. The samples were removed from the curing tank at 28 days and oven dried at 105^0C until a steady mass was achieved. On cooling the samples were tested. The 100mm cube specimens were subject to 10 bar pressure of nitrogen gas and the time taken to reduce the pressure to 5 bar was used as the measure of permeability for the sample. For this test both the lowest value and the highest value of each control have been used to establish a range for the comparison.
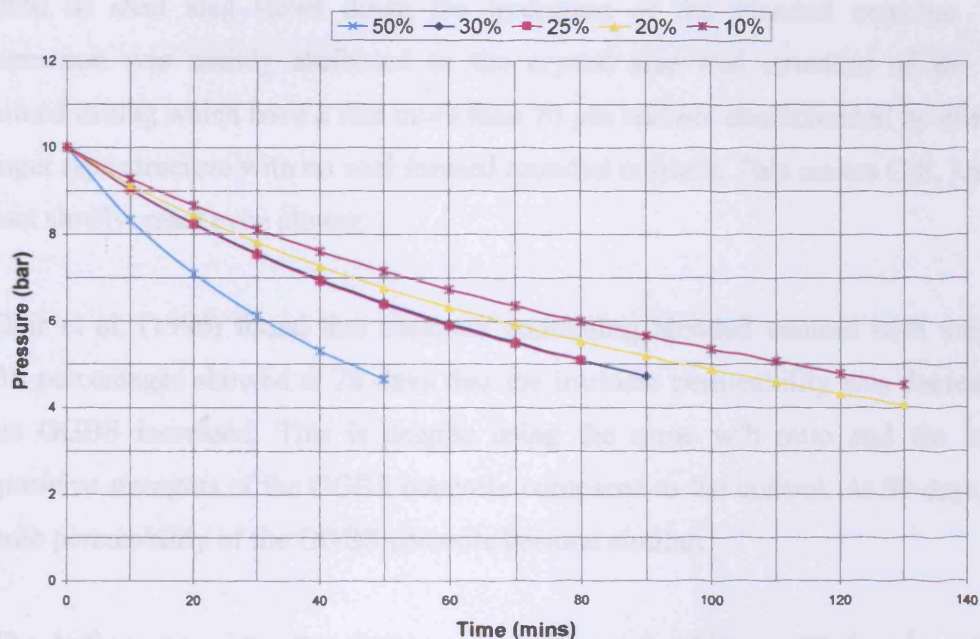
Figure 4.10 Permeability results of a blended GGBS / OPC concrete using 250kg/m^3 cement content at various replacement levels. Measure of permeability is taken at 5 bar pressure

Both the CEM I (OPCRM) and CEM III/A (GGBS) controls were tested three times using two cubes per test; therefore six results from each material were used. Both the lowest and highest results have been used for the controls to form an envelope into which the blended concrete samples should fall. Samples exceeding the highest values are less permeable and hence a better product whilst samples beneath

the lowest control are more permeable and likely to have problems associated with water penetration.

Figure 4.10 presents the permeability results of blended OPC / GGBS samples produced at the outset of the research. The samples were made using $250kg/m^3$ cement content with a variable cement replacement of 10%, 20%, 25%, 30% and 50% GGBS. It can be seen that the permeability of the samples improves as the percentage of cement replacement reduces, as the 50 per cent mix records the shortest time to achieve the 5 bar pressure.

This would appear to follow the correct course as Kourounis et al. (2007) found that "Slag cements develop lower strength, at all ages, compared to the pure cement (OPC), and the strength decrease is higher, the higher the slag content". Their research studied the pore structure of hardened cement and concluded that the addition of steel slag slows down the hydration of the blended cements. This phenomenon was mainly attributed to the crystal size and structure of the C_2S contained in slag which have a size more than 70 μm and are characterized by clusters of finger type structure with no well formed rounded crystals. This makes C_2S, known to react slowly, react even slower.

Dhir et al. (1996) found that concrete containing blended cement with varying GGBS percentages showed at 28 days that the intrinsic permeability was decreasing as the GGBS increased. This is despite using the same w/b ratio and the lower compressive strengths of the GGBS concrete compared to the control. At 90 days, the intrinsic permeability of the GGBS cements became similar.

The Author appreciates that testing a concretes permeability at 28 days is early in its life span when there is potential for carbonation, within the concrete, to increase its permeability. This research is, however, a comparison between various concretes at a point in time. It has been said (Lewis 2003) that the carbonation of fly ash is not significantly different from Portland cement-only concrete at the same grade (28 days) as its low permeability compensates for its reduced lime contents.
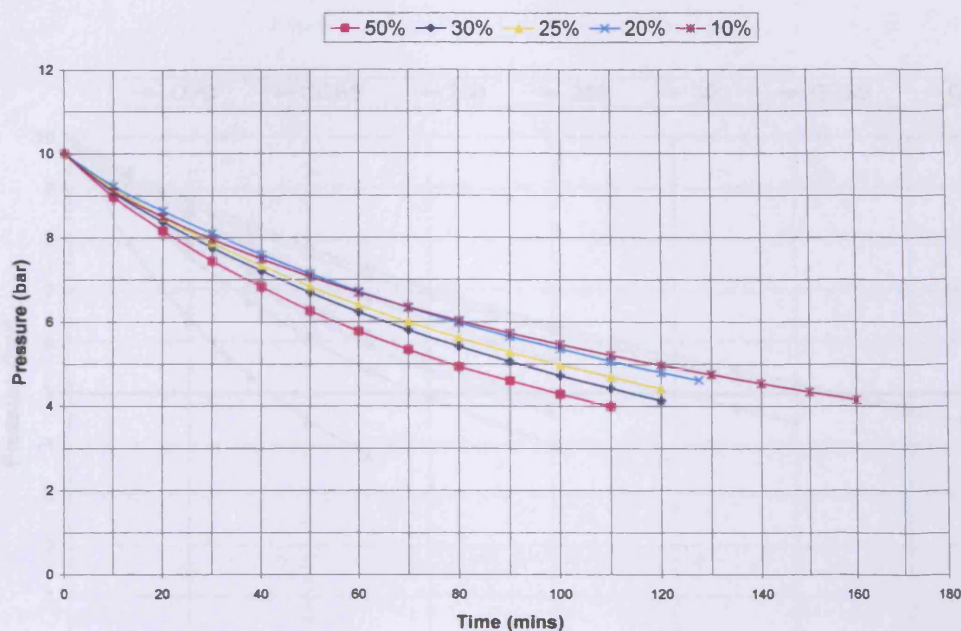
Figure 4.11 Permeability results of a blended fly ash / OPC concrete using 250kg/m^3 cement content at various replacement levels. Measure of permeability is taken at 5 bar pressure

Figure 4.11 presents the results from the series of permeability tests carried out on a blended fly ash / OPC mix. As with the GGBS, a 250kg/m^3 design mix was used with varying percentages of fly ash replacement. When compared with the GGBS results it can be seen that the concrete made using the fly ash retains the gas pressure for a longer period, making it a less permeable concrete. It is widely accepted that fly ash can reduce concrete permeability, although its magnitude is determined by the water / binder ratio and gel formation. If the physical and chemical properties of the fly ash are such that a significant reduction in the w/b ratio can be achieved without loss of workability as compared to an equivalent mix, then a reduction in permeability may be expected from the corresponding reduction in the number of large pores (BRE 1987).

Table 4.5
Water / binder ratios required to achieve a 70mm slump for the various fly ash percentages, GGBS control and cement contents

Replacement	10	20	25	30	50	BS 8500 limit
Fly ash	0.57	0.55	0.55	0.55	0.56	0.6
GGBS	0.6	0.58	0.59	0.6	0.58	0.6
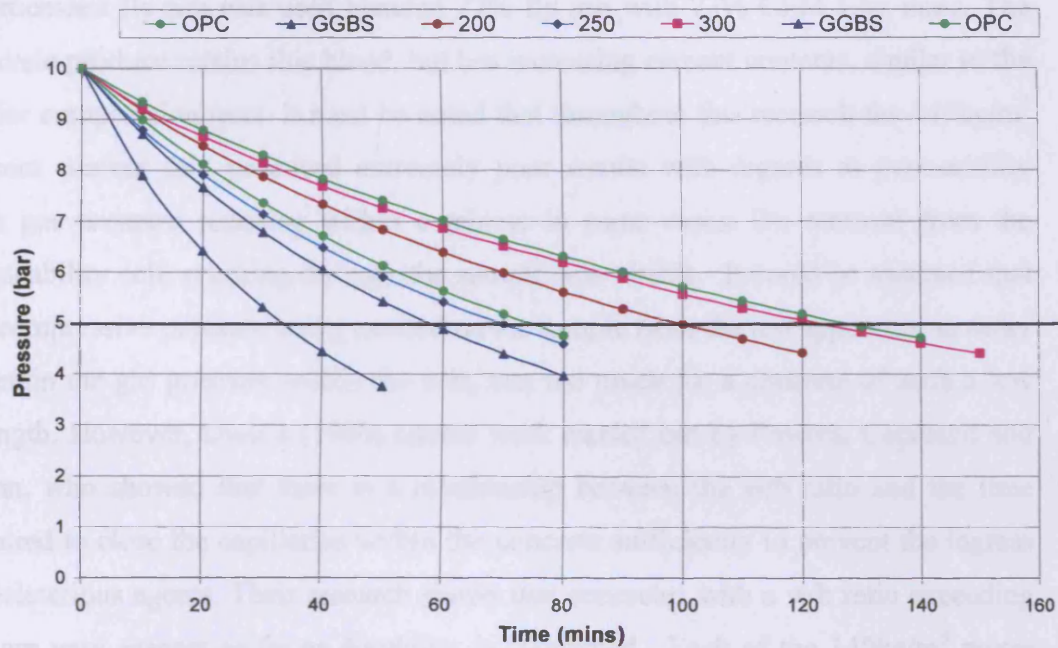
Figure 4.12 Permeability results of 27% fly ash at cement contents of 200kg/m^3, 250kg/m^3 and 300kg/m^3 as compared to the maximum and minimum values for the CEM I and GGBS controls.
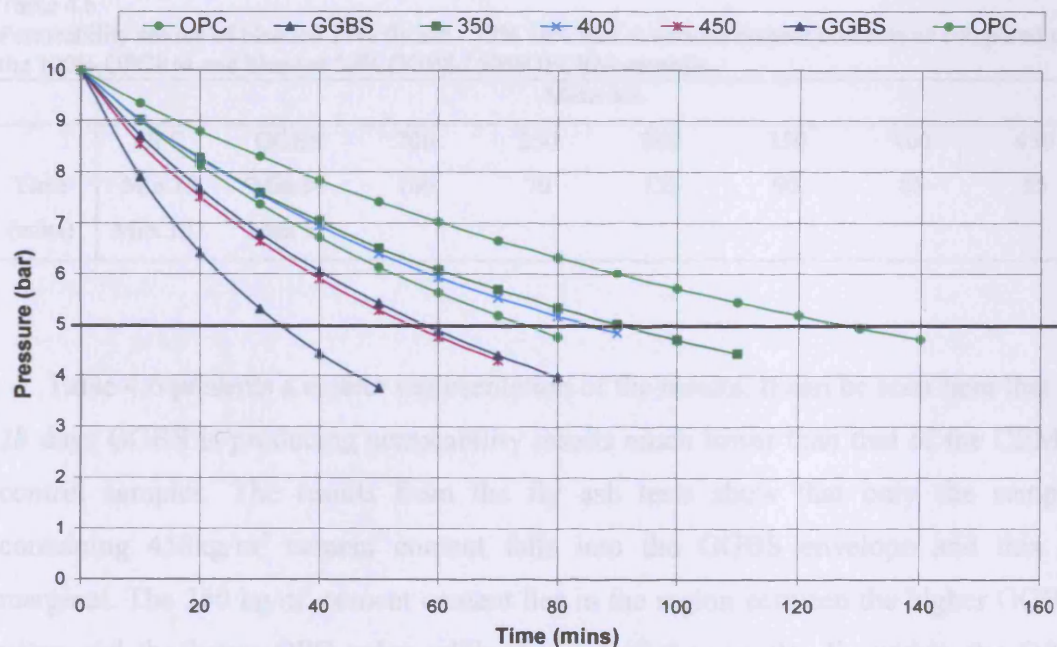
Figure 4.13 Permeability results of 27% fly ash at cement contents of 350kg/m^3, 400kg/m^3 and 450kg/m^3 as compared to the maximum and minimum values for the CEM I and GGBS controls.

Figure 4.12 and 4.13 present the results of the permeability tests taken at 28 days. A processed fly ash was used blended 27% fly ash with 73% CEM I by mass. The concrete produce retains this blend, but has increasing cement contents, similar to the earlier compression tests. It must be noted that throughout this research the $140kg/m^3$ cement content mix produced extremely poor results with regards to permeability with gas pressure reducing within a minute in some cases. On removal from the permeability cell, cracking through the sample was visible. It could be assumed that the compressive pressure being exerted on the sample from the test apparatus, in order to retain the gas pressure within the cell, was too much for a concrete of such a low strength. However, Owens (1980) quotes work carried out by Powers, Copeland and Mann, who showed that there is a relationship between the w/b ratio and the time required to close the capillaries within the concrete sufficiently to prevent the ingress of deleterious agents. Their research shows that concretes with a w/b ratio exceeding 0.6 are very suspect as far as durability is concerned. Each of the $140kg/m^3$ mixes produced within this research required a w/b ratio exceeding 0.6. This may also be the reason that concretes at this low level of cementitious material failed to produce reasonable values.

Table 4.6
Permeability results of blended 27% fly ash / 73% OPCRM at various cement contents as compared to the 100% OPCRM and blended 50% GGBS / 50%OPCRM controls

	Materials							
	OPC	GGBS	200	250	300	350	400	450
Time	Min 75	Min 34	100	70	123	90	85	55
(mins)	Max 127	Max 57						

Table 4.6 presents a clearer representation of the results. It can be seen here that at 28 days GGBS is producing permeability results much lower than that of the CEM I control samples. The results from the fly ash tests show that only the sample containing $450kg/m^3$ cement content falls into the GGBS envelope and this is marginal. The 250 kg/m^3 cement content lies in the region between the higher GGBS value and the lower OPC value while the rest of the samples lie within the OPC permeability envelope. This shows that at 28 days the fly ash samples generally fall into an acceptable range for durability. As discussed in Chapter 2, fly ash involves a

secondary reaction between active silicon dioxide (SiO_2) within the fly ash and the calcium hydroxide (CH) produced as a by-product from the cement hydration. This increases the time required to reach its full potential and is probably not realised here. However, these results show that the durability of concrete containing fly ash is not an issue.

4.2.3 Discussion

The processed ash has performed well at the replacement levels used. At 27% the use of the processed fly ash has compared well with the GGBS controls except at the lowest strength of $140N/mm^2$ where a 25% drop in strength was recorded. Concrete at this cement content is seldom supplied anymore as it is a very low grade, weak concrete. The low level of cement content and the high water / binder ratio may not be providing the alkali rich environment that the fly ash requires to become a contributing factor. Also, the lower level of fine material makes this mix a coarse looking mix and the particle grading may not produce the particle packing necessary for a strong concrete. An awareness of this is required if concrete at this cement content is to be supplied; plant trials must be produced and cement contents adjusted accordingly. Both the 33% and 35% replacement levels give good values for compressive strength. This is in line with a study carried out by Oner et al. (2004) who concluded the optimum value of fly ash is about 40% beyond which compressive strength starts to decrease.

The results of the water / binder ratios show that although in theory lower w/b ratios will produce a higher strength concrete the inclusion of fly ash may be having an effect on this. Therefore, further research is required to identify other factors involved in producing a good cement replacement.

4.4 The effect of processing fly ash

A significant part of this research was looking at the effect that the processing of a fly ash has on its use as a cement replacement. The question that needs to be asked is:-

'To what extent is processing of fly ash necessary, and what are the changes within the material that improves its performance?'

As was mentioned previously, fly ash from Aberthaw power station has been subject to an electrostatic separation (STi) process which separates the coarse and fine fly ash particles. This separation process has resulted in the production of a processed fly ash (processed), a high carbon (waste) material and the raw ash (no processing) for analysis. The processed ash was then passed through an air swept classifier which provided a fourth material in the form of a finer fly ash (classified). The raw, processed and classified materials were all individually blended with OPCRM and concrete produced using these blends. The waste material was also analysed both chemically and physically in an attempt to identify what was being removed from the fly ash during the processing of the material. This material was not used as a cement replacement because of its high carbon content and, hence, was not incorporated within any concrete produced.

Figure 4.14 Fly ash samples from the separation process (left to right) processed, raw and waste (see also Figure 4.7)

Figure 4.14 is an image showing the fly ash at three different stages, processed, raw and waste. The image shows how the material becomes lighter in colour as carbon is removed. A field inspection confirmed that the lighter material was considerably finer and less abrasive than that of the darker materials. The quality of the processed ash can be adjusted to suit the requirements of its destination; this will ultimately have an effect on the yield, however; the yield achieved will depend on the original particle size characteristics of the parent ash (Jones et al. 2006b). The yield of the processed material from the STi plant for the present research was 62%. The classification of the fly ash was performed at a later date when the Author was not in attendance. The plant can not measure the yield for this process however this may not be required as the coarser fraction of this separation can be reinstated with the processed ash as this remains a useable material and not a waste.

4.3.1   Compressive strength

	GGBS	Classified 33%	Processed 33%	Raw 33%
140	15.0	14.9	13.1	11.6
300	40.4	54.5	47.9	39.8
450	59.5	76.0	66.2	52.6
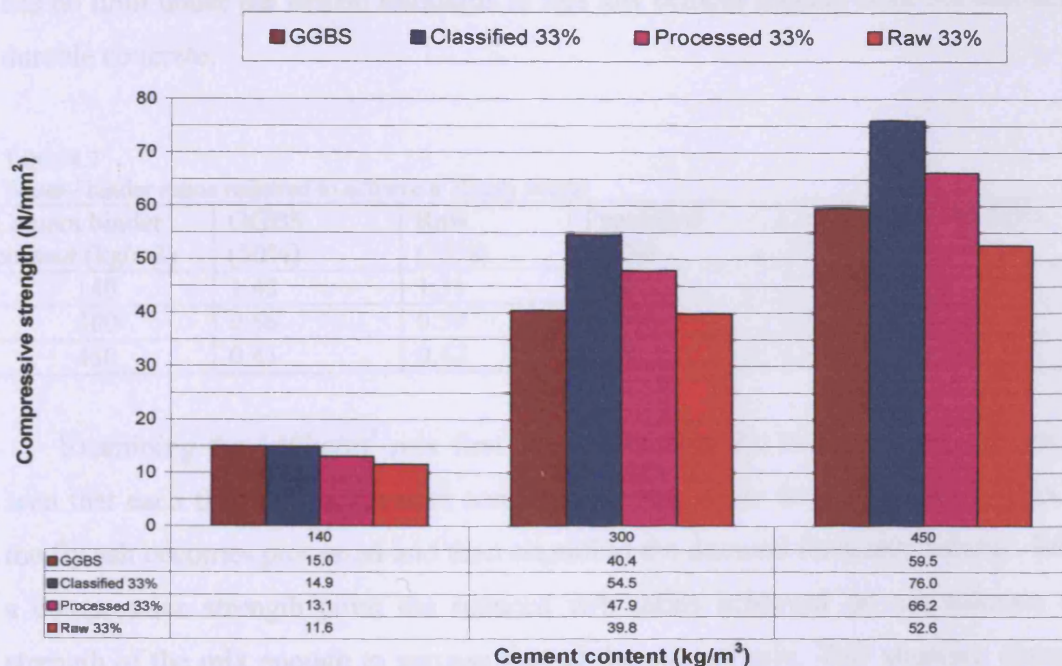
Figure 4.15 28 day compressive strength results of concrete using various blended 67% OPCRM with classified, processed and raw fly ash as compared to GGBS 50% / OPCRM 50%

Figure 4.15 presents the 28 day compressive strength results of concretes containing fly ash in its raw, processed and classified state at cement contents of 140kg/m^3, 300kg/m^3 and 450kg/m^3. The mixes have used blended 33% fly ash to 67% OPCRM

by mass, this replacement percentage being based on the positive results gained from the previous trials (Section 4.2). The graph shows that there are no compressive strength benefits from the inclusion of the raw ash into the blend. When the fly ash has been processed the compressive strength shows improvement above the 140N/mm^2 concrete strength. By classifying the fly ash a further strength gain is realised comparable to GGBS blended concrete at low cement contents but surpasses this at the higher cement contents.

4.3.2 Water / Binder ratio

Table 4.7 presents the results of the w/b ratios for the various fly ash grades, the GGBS control and the British Standard maximum for designated concretes to BS 8500-2:2002. As discussed previously the water is the required amount to achieve a slump of 70mm. It is clear that the w/b ratios for the fly ash reduce as the material becomes finer. This is the case at all cement contents. The 140kg/m^3 cement content has no limit under the British standards as this low cement content does not produce a durable concrete.

Table 4.7
Water / binder ratios required to achieve a 70mm slump

Cement binder content (kg/m3)	GGBS (50%)	Raw (33%)	Processed (33%)	Classified (33%)	BS 8500 Limit
140	1.43	1.31	1.30	1.23	-
300	0.56	0.59	0.57	0.48	0.6
450	0.41	0.47	0.40	0.37	0.45

Examining the 140kg/m^3 mix first as compared to the GGBS control, it can be seen that each fly ash mix requires considerably less water then the control. Also, as the fly ash becomes processed and then classified the demand for water reduces. From a compressive strength point the reduced w/b ratios achieved do not enhance the strength of the mix enough to surpass that of the control mix. This situation changes as the cement content increases. At 300kg/m^3 cement content only the mix containing the classified fly ash improves on the w/b ratio, whilst the others show a slight increase. The higher w/b ratios do not, however, stop the fly ash from competing with the control with the weaker raw fly ash mix being less than 1% lower in strength. All of these mixes remain within the British standards requirement. At 450kg/m^3 cement

content the control is only superseded by the raw fly ash mix. This mix is not only above the British standards required limit but also 12% weaker than the control mix. Both the processed and classified mixes show a reduction in w/b ratio and an increase in strength against the control.

4.3.3 Physical analysis

Grading

It has been discussed in Chapter 2 about the importance that the material fineness has on the reactivity and strength development of the cementitious material (Erdogdu and Turker 1998, Lee et al. 1999). BS EN 450-1:2005 recognises two categories of fly ash fineness which are expressed as the mass proportion in percent of ash retained when wet sieved on a 0.045mm mesh sieve. The categories and associated limits are presented below:

- o Category N: The fineness shall not exceed 40% by mass, and it shall not vary by more than ±10 percentage points from the declared value.
- o Category S: The fineness shall not exceed 12% by mass. The ±10 percentage points fineness variation limits are not applicable.

Figure 4.16 presents the grading curves produced by the Malvern Mastersizer X, as discussed in Chapter 3, for the three fly ash samples and the waste high carbon material compared to the controls of OPCRM (CEM I) and GGBS. The graph is presented to show that the finer the material the further left the grading line will be, a vertical grading curve indicates a lot of material at that fineness whilst a more horizontal curve would indicate a more even spread of sizes.

The graph in Figure 4.16 shows that the processing of the fly ash has removed the coarser fraction, as the waste is to further to the right of the graph. Also, the raw material is to the right of the processed which indicates that the processed ash has become finer than its parent raw ash. Classifying the ash has produced a finer ash again as the grading curve moves to the left of the processed ash.
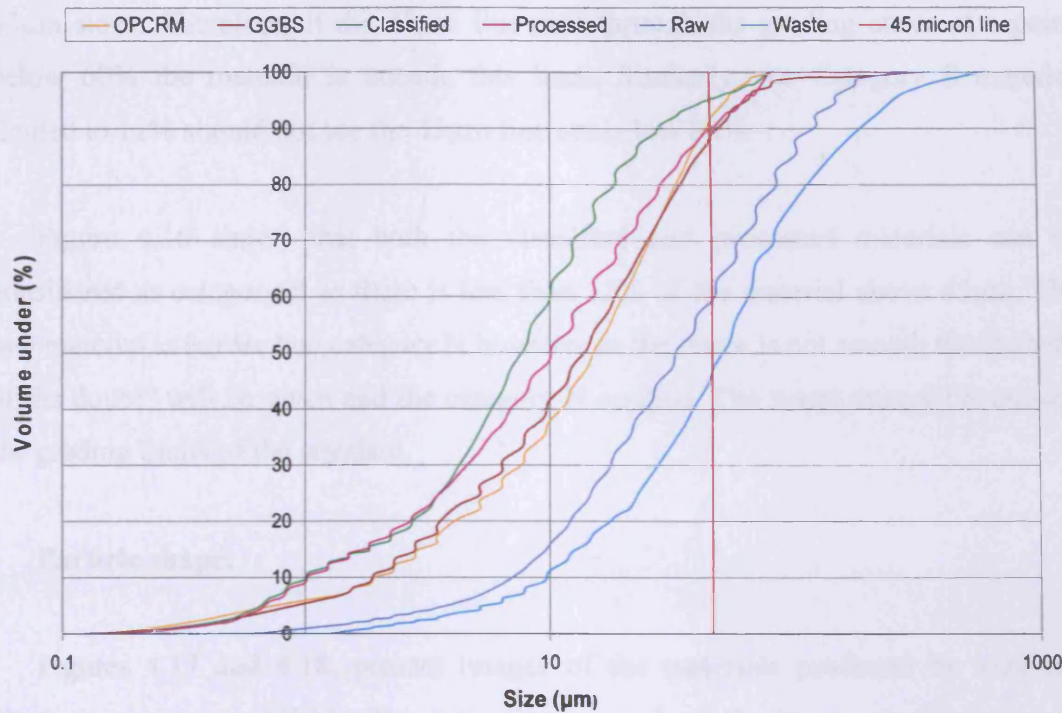
Figure 4.16 Particle size distribution results from the Malvern Mastersizer X for the Raw, Processed and Classified fly ash with the GGBS and OPCRM as controls. The 45μm measure is shown in red

It can be seen from Figure 4.16 that the controls are of similar fineness to each other to approximately 80% of their mass, whereby GGBS becomes slightly coarser. In comparing the fly ash to the controls it can be seen that the processed fly ash is the closest match being slightly finer than both controls up to 90% of its mass. At this point the particles become coarser than OPCRM but not quite as coarse as GGBS.

Both the classified fly ash and the OPCRM contain a maximum particle size of 83μm, however the classified fly ash grading line is more vertical with a sharp bend above 90% which indicates there is less of the coarser material. The grading line of the OPCRM is not as vertical as the fly ash grading line showing that it is a more evenly graded material through all particle sizes.

Using Figure 4.16 a judgement as to the fineness category, stipulated in BS EN 450-1, that each material fits into can be made. The position of the 45μm sieve has been shown on the graph with any material to the right of this line being coarser than 45μm. A category N material should not retain more than 40% of its mass on the

45µm sieve. Therefore, if the 45µm line cuts through the grading curve at a point below 60% the material is outside this limit. Similarly, the Category S material limited to 12% should not see the 45µm line cut below 88%.

Figure 4.16 shows that both the classified and processed materials can be considered as category S as there is less than 12% of the material above 45µm. The raw material is border line category N however as the curve is not smooth the "benefit of the doubt" will be given and the category N applied. The waste material is outside the grading limits of the standard.

Particle shape:

Figures 4.17 and 4.18, present images of the materials produced by scanning electron microscopy (SEM). The scale line on each of the images is 10µm and an attempt has been made to capture a representative image of how the material is made up. It can be seen in Figure 4.17 that both the OPCRM (a) and GGBS (b) are non-spherical materials being made entirely with angular shaped particles. The majority of the particles are smaller than 10µm in both materials with only a few individual particles larger than 20µm. The GGBS is estimated to be slightly coarser agreeing with the Mastersizer data presented in Figure 4.16. (Note that the Mastersizer data percentages are on a mass or volume basis whilst the SEM observation is based on number)

(a)	(b)
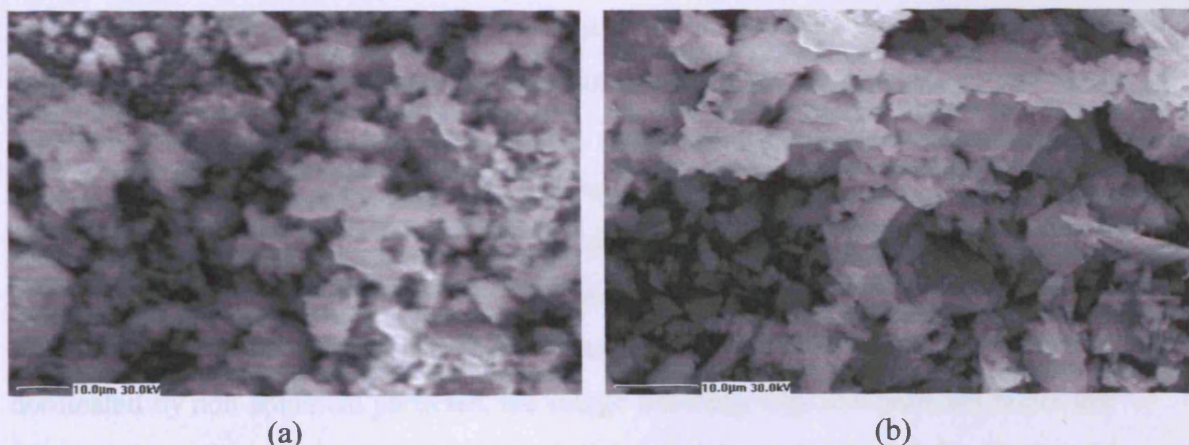
Figure 4.17 SEM images of the control materials a) OPCRM, b) GGBS

(a)

(b)

(c)

(d)
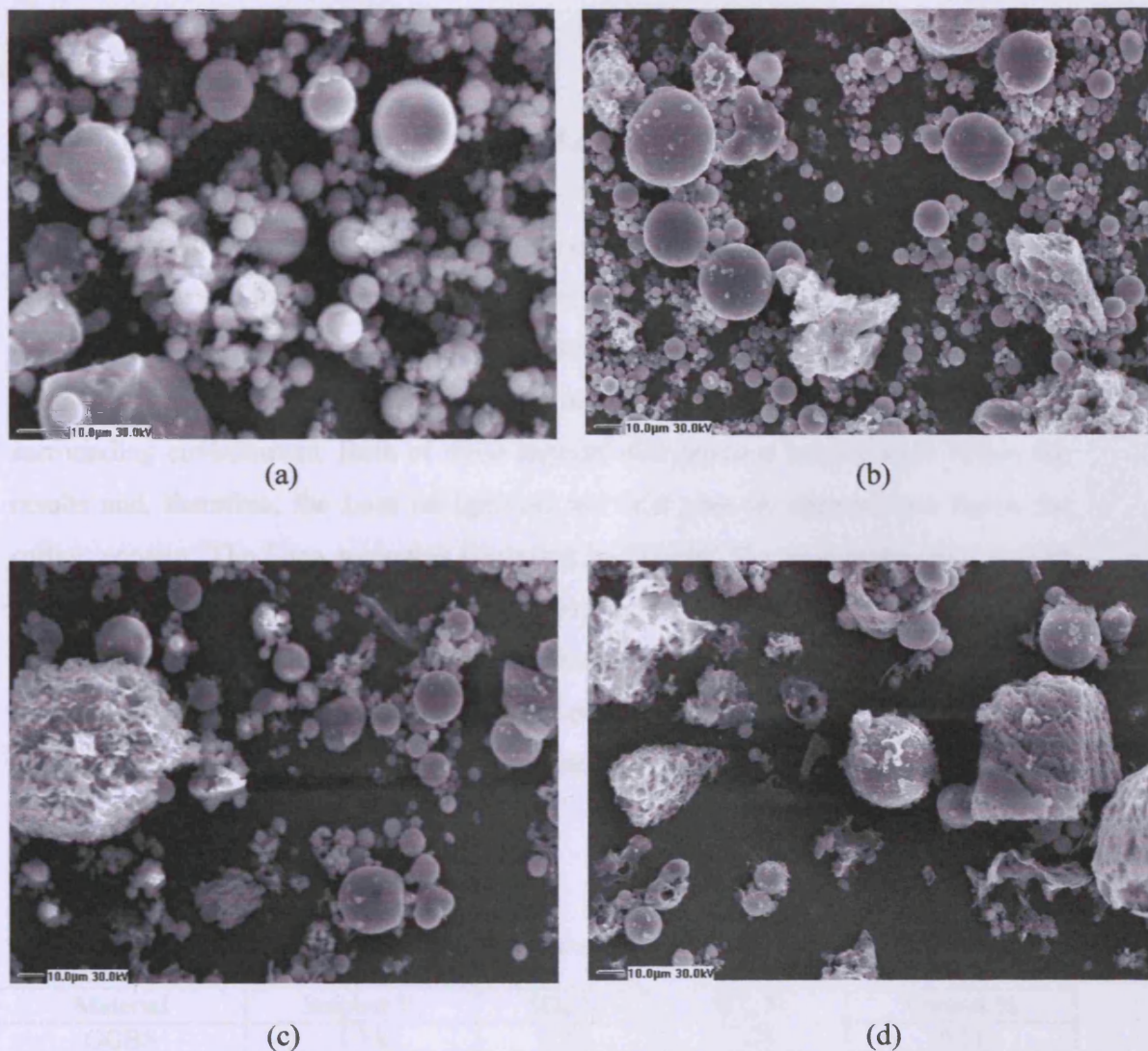
Figure 4.18 SEM images of the fly ash a) Classified, b) Processed, c) Raw, d) Waste

Images in Figure 4.18 (a) through to (d) are the fly ash samples classified, processed, raw and waste respectively. Generally, the particle shapes are spherical with a number of angular particles in amongst them. The classified fly ash has spherical particles of 10µm or less with a small quantity of larger more angular particles showing in this image. The processed fly ash again shows angular particles as part of its make up and also that the spherical particles range up to approximately 20µm. The raw fly ash continues this trend with particles ranging up to approximately 20µm however; the non-spherical particles are more prevalent. The waste sample is dominated by non-spherical particles, the image showing vary few particles under the 10µm range with the larger spherical particles being contaminated by fragments adhering to their surfaces.

4.3.4   Chemical analysis

Loss on Ignition and Leco Sulphur and carbon analysis:

It is normal for the carbon content to be ascertained from the use of Loss on Ignition. However, this method measures the weight loss of the sample which would include moisture and any organic matter in the sample. Also, on removing the sample from the furnace certain materials will begin to re-absorb moisture from the surrounding environment. Both of these aspects will produce inaccuracies within the results and, therefore, the Loss on Ignition test will give an approximate figure for carbon content. The Leco apparatus (Detailed in Chapter 3) uses a sealed unit to heat the sample at 1400°C and records the carbon emitted as a gas by the sample and expresses the result as a percentage of the weight of the sample tested. This gives a more accurate measurement of carbon content and also measures sulphur content. Table 4.8 gives the results from the Leco apparatus.

Table 4.8
Results from the Leco analysis for Sulphur and Carbon and the converted values to SO_3 and SO_4 from the calculation in Table 4.9

Material	Sulphur %	SO_3 %	SO_4 %	Carbon %
GGBS	1.74	4.33	5.20	0.11
Raw FA	0.31	0.78	0.93	18.38
Processed FA	0.25	0.63	0.75	3.43
Classified FA	0.38	0.94	1.13	2.42
Carbon FA	0.40	1.00	1.21	44.01

The results show the total quantity contained in the fly ash alone. Blending the fly ash with OPCRM will reduce this figure and hence this is the maximum amount which if below the British standards requirements will conform within the blended cement. Table 4.8 presents the results of the carbon and sulphur analysis together with the calculated SO_3 and SO_4 contents. The details of the calculation for the amount of SO_3 and SO_4 within the sample are shown in Table 4.9.

BS EN 197-1 limits the sulphate content for the production of cement. There are two limits dependant on the cement strength and cement class and are compared to the sulphate SO_4 content being expressed as a sulphite SO_3. Therefore, the figure in the SO_3 column has been used to ascertain conformity against this requirement. Table 4.10 presents the requirements of BS EN 197.

Table 4.9
Calculation of SO_3 and SO_4 quantity within the fly ash samples

Description	Mass	Percentage per sample
Sulphur atomic mass (u)	= 32.066	
Oxygen atomic mass (u)	= 15.9994	
Sulphite SO_3	= 32.066 + 3 x 15.9994 = 80.06	(Sulphur % / 32.066) x 80.06
Sulphate SO_4	= 32.066 + 4 x 15.9994 = 96.06	(Sulphur % / 32.066) x 96.06

It can be seen that the values for SO_3 in Table 4.8 are well within the limiting values required by BS EN 197-1 although the sulphate content should be calculated as the total from the various constituents of the mix. This requires that the SO_3 in both the OPC and the aggregate be taken into account when producing a blended cementitious material for concrete. The sulphate levels in the GGBS are higher than the requirements of the standard; however, as this is blended with CEM I the sulphate content for the total mass of the material would be lowered. It is for this reason that the cement manufacturers must be aware of the chemical make up of all additions to the concrete and produce their CEM I accordingly.

Table 4.10
Requirements of BS EN 197-1 regarding Sulphate limits

Property	Test reference	Cement type	Strength class	Requirements
Sulphate content (as SO₃)	EN 196-2	CEM I CEM II CEM IV CEM V	32.5 N 32.5 R 42.5 N	≤ 3.5%
			42.5 R 52.5 N 52.5 R	≤ 4.0%
		CEM III/A CEM III/B	ALL	≤ 4.0%
		CEM III/C	ALL	≤ 4.5%

Loss on ignition (LOI) is related to the presence of carbonates, combined water in residual clay minerals, and combustion of free carbon. Carbon is the most important component of LOI with the water required for workability of concrete dependant on it. The higher the carbon content of fly ash the more water is required to achieve the normal consistency (Malhotra and Ramezanianpour 1994).

BS EN 197-1 and BS EN 450-1 have strict limits on the amount of carbon cement can contain as measured by its Loss on Ignition. The procedure used for this research is detailed in BS EN 196-2:2005. The procedure states that the sample must remain in a furnace at 950^0C for 15 minutes. BS EN 450-1 2005, which defines fly ash for concrete, increases the ignition time for fly ash to 1 hour. BS EN 450-1:2005 recognises three categories of fly ash defined by their LOI value which must fall within the limits specified below:

- o Category A: Not greater than 5.0% by mass
- o Category B: Between 2.0% and 7.0% by mass
- o Category C: Between 4.0% and 9.0% by mass

BS EN 197-1:2000 states, however, that the LOI of fly ash shall not exceed 5.0% by mass. It will allow fly ash with a LOI of up to 7.0% to be accepted provided that requirements for durability, especially frost resistance, and compatibility with admixtures are met according to the appropriate standards. There are no specified limits for the blended cements CEM II, Pozzolanic cement CEM IV and Composite cement CEM V within BS EN 197-1; however, Portland cement CEM I and Blast furnace cement CEM III are restricted to a limit of 5.0% LOI.

Table 4.11
Carbon content (LOI) of the OPCRM and cement replacement materials used

Material	LOI (%)	
	BS EN 196-2	Leco (%)
OPCRM	4.9	0.6
GGBS	0.85	0.11
Raw FA	20.1	18.38
Processed FA	4.1	3.43
Classified FA	3.3	2.42
Waste FA	46.3	44.01

Table 4.11 presents the results for the LOI carried out on the controls and the fly ash using both the BS EN 196-2 2005 method (LOI) and the Leco analysis. First, it can be seen that there is a difference in results between each method. It was expected that the LOI results would be slightly higher as this method measures anything in the sample that is burnt off in the furnace whilst the Leco analysis measures only the carbon emitted from the burning.

It can be seen that the controls are within the requirements of the standard whilst the ash material varies depending on the degree processing it has received. The raw fly ash is the feed into the separator which has come directly from the power plant; its high LOI is the reason that it can not be used directly as a cement replacement. LOI contents consist of unburned carbon that is generally present in the form of cellular particles larger than 45 μm (Atis 2005). Therefore, it would be expected that the LOI would decrease as the material becomes finer.

This becomes evident from the LOI results. The classified FA is showing a carbon content lower than that of the processed fly ash, which in turn is lower than that of the Raw material, both of which fit the expected result. Comparing these results to the required European standard, BS EN 197-1, it can be said that both the processed fly ash and the fine fly ash are compliant with the standards regarding LOI.

It should be mentioned that at an ignition time of 1hour the waste material achieved a LOI of only 20%. This did not correspond to the Leco analysis or the analysis supplied by the processing plant. The LOI was repeated at an ignition time of 24 hours and the result of this is presented in Table 4.11, page 4-36. A mass balance check found the error to be 2.5%, Appendix 3.1.

Inductively Coupled Plasma Analysis (ICP)

The results of the ICP chemical analysis are shown in Table 4.12 below. The principal elements have been presented here with the full analysis, including the minors, available to view in Appendix 3. This analysis has been carried out to look at the chemical differences between the fly ash as it undergoes the refining process and to look at how they compare, or differ from, the OPCRM and GGBS controls. The elements have been converted to oxides as the sum of the oxides should come close to 100% (Moir 2003). The sum of the oxide results are all within 5% of 100% expected, with the mass balance check of the error being within 2%, Appendix 3.1. The controls have been shown for completeness.

The main elements within the fly ash samples are those of SiO_2, Al_2O_3, CaO and Fe_2O_3. The amount of silicon increases with the processing of the raw material rising from 41.7% up to 54.7%. At this point no further increase in silicon content is gained from further classification of the material. The carbon waste material contains a considerable amount of silicon at 27.5%. Silicon in its reactive form is a beneficial element of fly ash and its removal from the waste material into the processed may enhance the strength properties of the concrete (Lewis et al. 2003). This would require optimisation of the STi process varying feed rates and belt speeds etc. separating the valuable elements from the waste elements. However, should the particles have been

removed because it contains a high level of carbon, then this may negate the benefits of the silicon.

Table 4.12
The chemical analysis results from the ICP analysis of Aberthaw fly ash and the control materials

Oxide (%)	Material					
	CEM I	GGBS	Raw	Processed	Classified	Waste
Na_2O	0.2	0.2	0.5	0.5	0.5	0.3
P_2O_5	0.0	0.0	0.2	0.2	0.2	0.1
SiO_2	20.3	34.7	41.7	54.7	53.4	27.5
Al_2O_3	4.2	12.2	21.6	24.5	22.1	12.7
CaO	66.3	38.5	3.1	2.9	4.3	2.8
Fe_2O_3	2.2	0.3	4.0	3.6	3.6	3.8
K_2O	0.6	0.6	1.7	2.1	2.2	1.1
MgO	2.5	9.4	1.4	1.4	1.8	1.3
Mn_2O_3	0.1	0.7	0.2	0.2	0.1	0.2
Minors	0.1	1.7	2.6	3.7	5.7	2.7
LOI	4.90	0.85	18.38	4.07	3.25	44.01
Total (%)	101.4	99.1	95.4	97.8	97.3	96.4
$SiO_2 + Al_2O_3 + Fe_2O_3$			67.3	82.8	79.1	44.0
Na + K			2.2	2.6	2.8	1.4

The aluminium content follows a similar pattern to that of the silicon, whereby the processed material contains more than the raw and slightly more than the classified. This would seem to suggest that some of the more minor elements are found in the finer particles which are altering the elemental balance as the larger particles are removed. The calcium content drops when the material is processed but increases as the material further classified. Once again this may be due to the calcium tending to be in the finer particles. The iron content drops slightly due to the processing, but no change is recorded when the material is classified further.

Transmission Electron Microscopy (TEM)

When coal burns in a power station furnace between 1250^0C and 1600^0C, the incombustible materials coalesce to form spherical glassy droplets of silica (SiO_2), alumina (Al_2O_3), iron oxide (Fe_2O_3) and other minor constituents (Lewis 2003). The grading of the materials showed that on completion of the separation process the raw fly ash became a finer material. When this material was subject to the classification process it became finer again. It is, therefore, important to know what elements are being removed during each of these processes and any possible effect they may have

on the concrete mix. Through transmission electron microscopy (TEM) it is possible to magnify the various sized particles within each material and carry out an elemental analysis using an Energy Dispersive Analysis of X-rays (E.D.A.X) technique, details in Chapter 3.
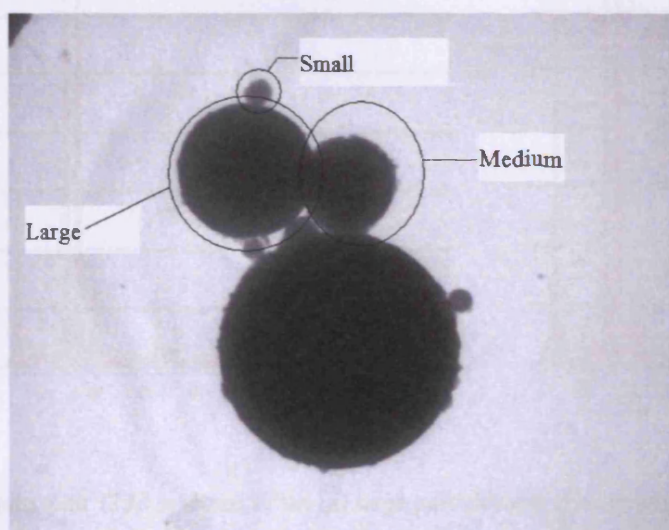
Figure 4.19 Image showing the various size groups used in the elemental analysis

The viewing area of the microscope shows two concentric circles which, at a magnification of 23,000 times, sizes them at 0.25μm and 2.0μm. The particle sizes were judged on where they fell in relation to these circles therefore:

- o Small particles <0.25μm
- o Medium particles <2.0μm and >0.25μm
- o Large particles >2.0μm

An image showing the various sizes of fly ash analysed can be seen in Figure 4.19 above.

A range of analyses were carried out on the raw fly ash at each size and the elemental results compared. Only the raw material was analysed, as it is this same material which produces the processed and the classified with the larger element removed. In general, the spectra were very similar for the particles in a given size range and typical spectra are presented as Figures 4.20 (a) and (b) and Figure 4.21(a) for the raw fly ash as large, medium and small particles.

(a)   (b)
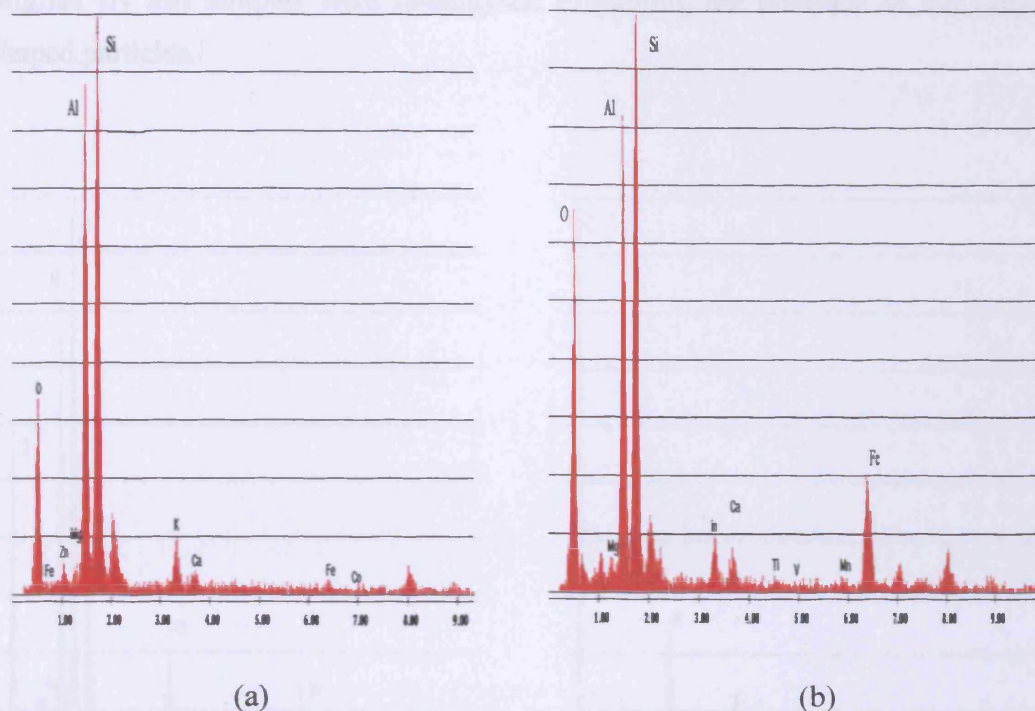
Figure 4.20 TEM analyses of the (a) large particles and (b) medium particles within the raw fly ash

It can be seen that the analysis of the large particle identifies the main elements of silicon, calcium, aluminium and iron with some other minor elements as oxygen, potassium and magnesium. The medium spherical particles, Figure 4.20b, again show that the main elements silicon, calcium and aluminium being similar to the large particles with iron giving a higher reading. The spectra for the minor elements are similar to that of the large particle the change in the element labelling being due to the software. Spectra of the small spherical particles, Figure 4.21a, show a similar pattern to that of the medium particle with peaks for all the main elements. The analysis shows an increase in the calcium peak and the addition of phosphorous to the spectra of the waste particle.

It has been shown from the Loss on Ignition and the Leco analysis that there is carbon present in the raw material, yet none has appeared on any particle analysis. The analysis was carried out on the waste material and the resulting spectra can be seen in Figure 4.21b. This analysis produced consistent results showing high carbon, some phosphorous and very little of the other elements. However, the fly ash analysis had concentrated the analysis on the spherical particles, as this is a main characteristic

of fly ash, the waste samples contained mainly irregular shaped particles and so the original fly ash samples were re-analysed examining the presence of the irregular shaped particles.

(a)   (b)
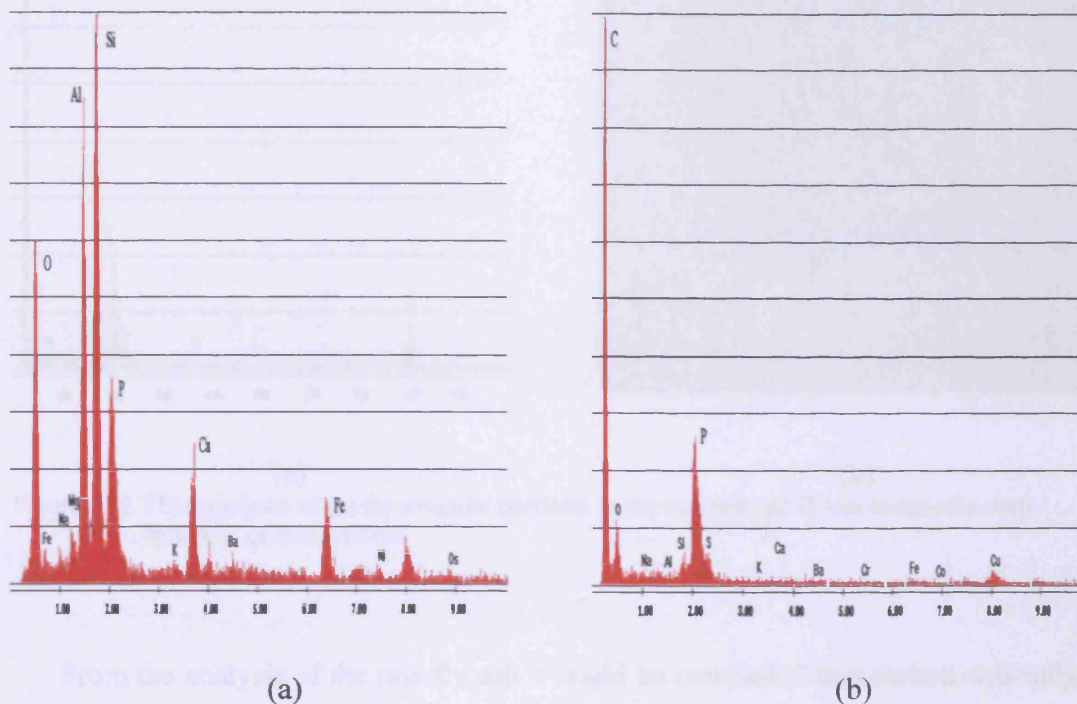
Figure 4.21 TEM analyses of the (a) Raw small spherical particles and (b) Waste material particles

It was assumed that the waste fly ash would include the larger particles containing the carbon taken from the raw material during processing. This analysis showed that the majority of particles in this material were irregular in shape (see for example Figure 4.22b). These irregular particles were larger than 4.0µm and gave the spectra typical of that presented in Figure 4.22a. It was also seen that the waste fly ash contained a large quantity of larger spherical particles but no small particles were seen. It was also noted that, although the majority of the irregular particles were similar to the spectra in Figure 4.21a, a number of these contained quantities of silicon, aluminium and iron.

(a)   (b)
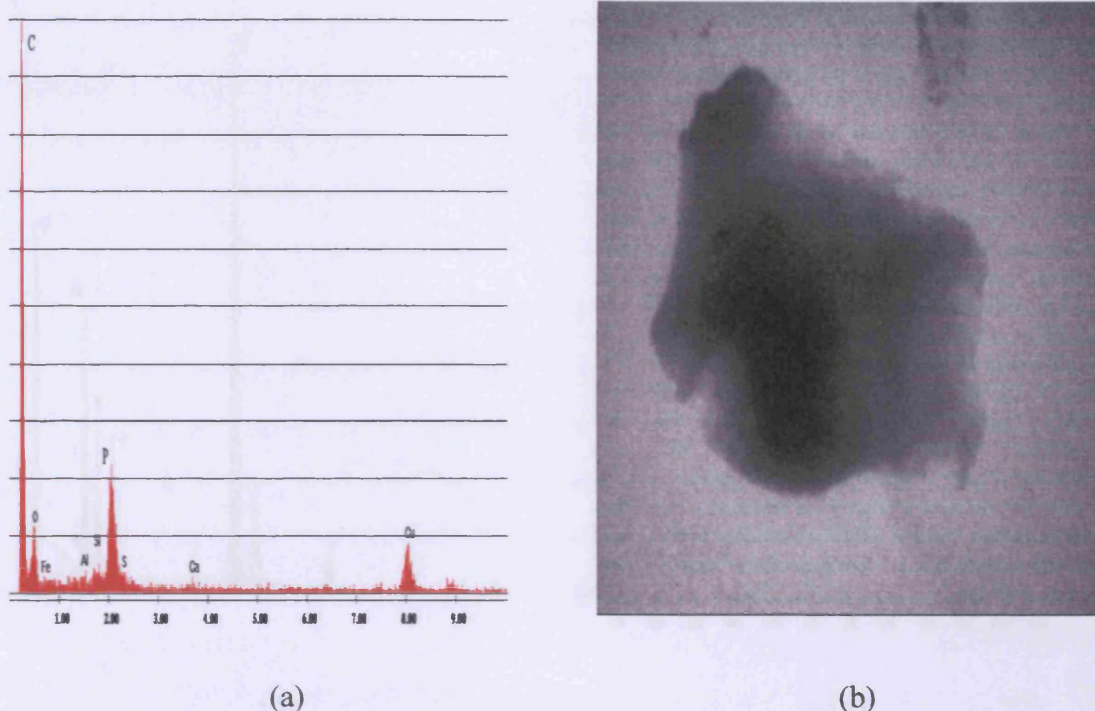
Figure 4.22 TEM analyses of (a) the irregular particles in the raw ash and (b) an image of a non-spherical carbon particle

From the analysis of the raw fly ash it could be concluded that carbon was only to be found in the irregular sized particles, as none has been seen within the spherical particles. Figure 4.23a shows the spectrum for a large spherical particle which shows a high reading for titanium an increase in vanadium and also carbon content. Conversely Figure 4.23b shows the spectrum of a non-spherical particle where it can be seen that the elements available are similar to that of a medium spherical particle as shown in Figure 4.20b. It has to be acknowledged that the positioning of the particle during the analysis can have an influence the results. Intriguing results may be produced due to the distribution of the particle, the orientation of the element within the particle, interference from neighbouring particles or simply that the particle does contain what the analysis shows. Also, it must be noted that the electron beam only penetrates the surface of the particle and does not perform a deep analysis (i.e. not to the centre of the particle). This may result in further elements, not identified through this analysis, being released during hydration of the cement.

(a)   (b)
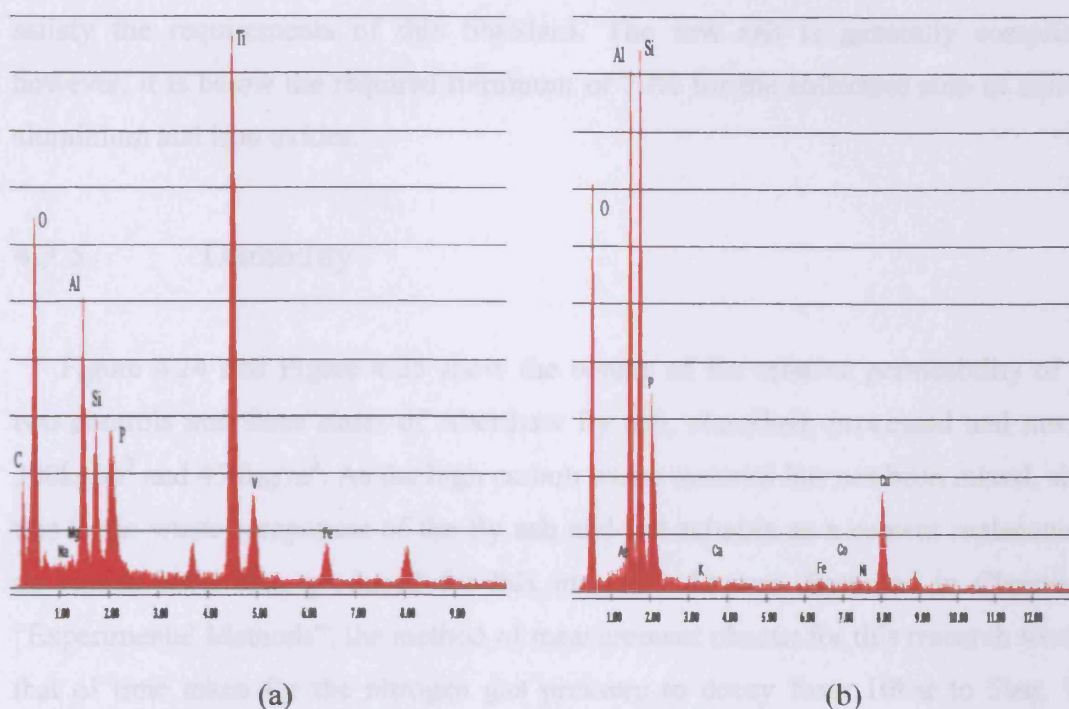
Figure 4.23 TEM analyses on the raw fly ash showing (a) large spherical particle containing carbon and (b) a non-spherical particle not containing carbon

BS EN 450 requirements

The chemical requirements as described in the British and European Standard for fly ash BS EN 450-1:2005 are shown in Table 4.13. The analysis up to and including soluble phosphate was carried out at RWE Power International Central Support Laboratories in North Yorkshire. This laboratory is set up to analyse fly ash to the accepted standard whereas the University is not; hence for speed and ease RWE were asked to perform the analysis.

Table 4.13
Fly ash analysis results and the requirements of BS EN 450

Analysis	Classified	Processed	Raw	EN 450
Chloride (Cl)	<0.005	0.007	0.011	<0.1% mass
Sulfuric anhydride (SO_3)	0.46	0.48	0.62	<3.0 % mass
Free calcium oxide	<0.02	<0.02	<0.02	<1.0 % mass
Reactive silicon dioxide	36.83	37.47	32.84	>25 % mass
Total alkalis Na + K	3.28	3.67	2.69	<5.0 % mass
Soluble phosphate (P_2O_5)	0.0003	0.0006	0.0014	<0.1 % mass
$SiO_2 + Al_2O_3 + Fe_2O_3$	79.1	82.5	67.2	>70.0%
Magnesium Oxide (MgO)	1.8	1.4	1.4	<4.0%

It can be seen from the results that both the processed ash and the classified ash satisfy the requirements of this Standard. The raw ash is generally compliant; however, it is below the required minimum of 70% for the collective sum of silicon, aluminium and iron oxides.

4.3.5   Durability

Figure 4.24 and Figure 4.25 show the results of the relative permeability of the two controls and three states of Aberthaw fly ash, classified, processed and raw, at $300kg/m^3$ and $450kg/m^3$. As the high carbon waste material has not been mixed, since this is the waste component of the fly ash and not suitable as a cement replacement, no results have been produced for this material. As was discussed in Chapter 3, "Experimental Methods", the method of measurement chosen for this research work is that of time taken for the nitrogen gas pressure to decay from 10bar to 5bar. The results are measured against the average results of the OPCRM control. The results of the fly ash samples are the average of two permeability tests. Table 4.14 records the results of the permeability test as numerical values.
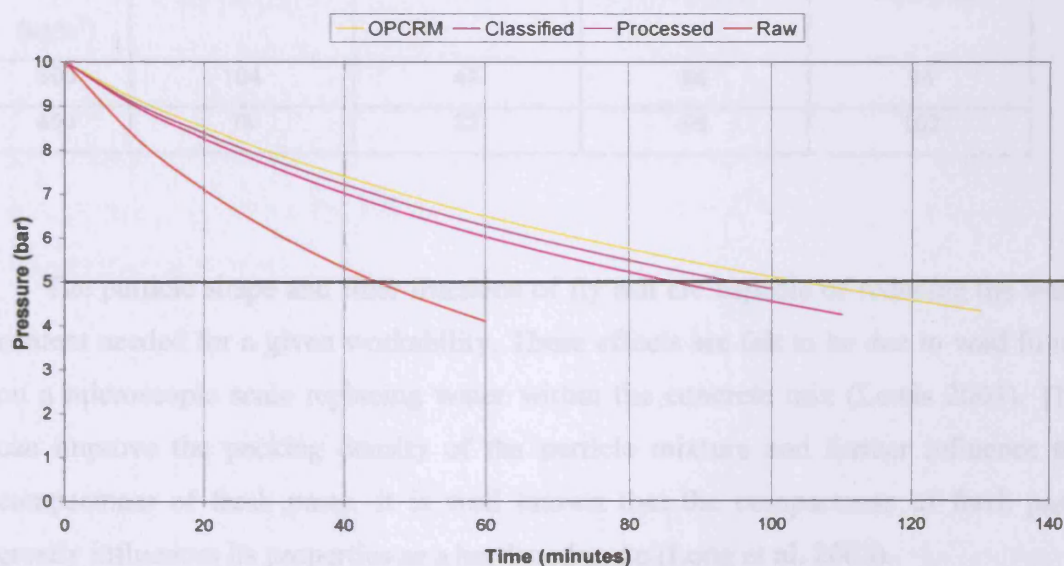
Figure 4.24 Results from the relative permeability test on $300kg/m^3$ cement content concrete 33% fly ash replacement with 67% OPCRM
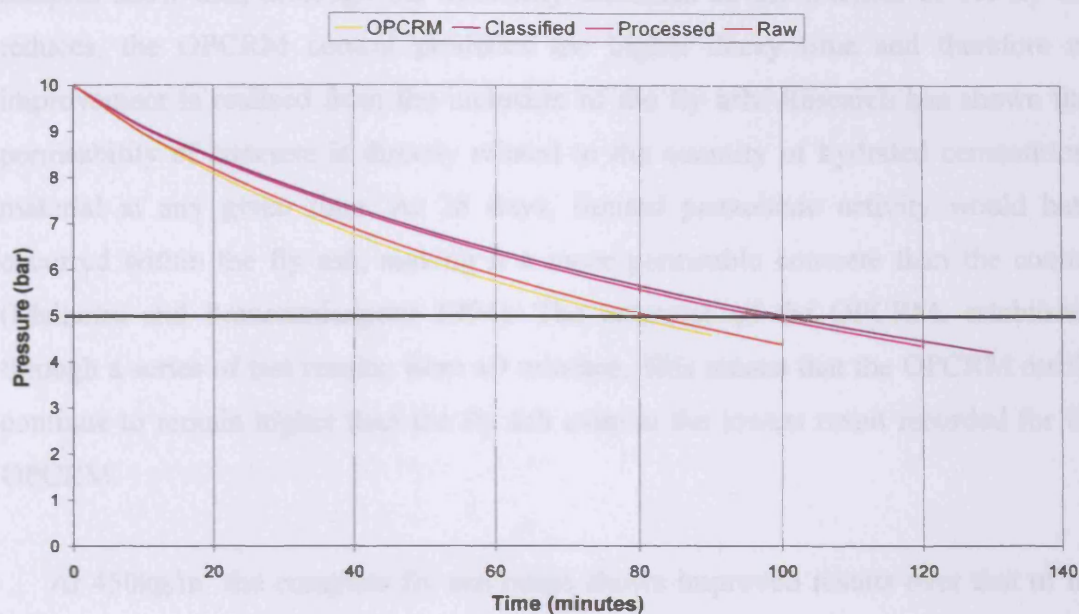
Figure 4.25 Results from the relative permeability test on 450kg/m³ cement content concrete 33% Fly ash replacement with 67% OPCRM

Table 4.14
Measure of permeability at 28 days for the fly ash in its three states of raw, processed and classified at 33% replacement with 67% OPCRM as compared to 100% OPCRM

Cement content (kg/m³)	Time (mins)			
	OPCRM	Raw	Processed	Classified
300	104	44	86	94
450	78	82	98	102

The particle shape and finer fractions of fly ash are capable of reducing the water content needed for a given workability. These effects are felt to be due to void filling on a microscopic scale replacing water within the concrete mix (Lewis 2003). This can improve the packing density of the particle mixture and further influence the compactness of fresh paste. It is well known that the compactness of fresh paste greatly influences its properties as a hardened paste (Long et al. 2003).

It can be seen from the permeability results that concrete incorporating fly ash show the improvement in durability as the decay time increases between the raw, the processed and the classified fly ash. The results from the 300kg/m³ cement content

samples show that, although the durability increases as the fineness of the fly ash reduces, the OPCRM control produces the higher decay time and therefore no improvement is realised from the inclusion of the fly ash. Research has shown that permeability of concrete is directly related to the quantity of hydrated cementitious material at any given time. At 28 days, limited pozzolanic activity would have occurred within the fly ash, making it a more permeable concrete than the control (Malhotra and Ramezanianpour 1994). The extremes of the OPCRM, established through a series of test results, were ±9 minutes. This means that the OPCRM results continue to remain higher than the fly ash even at the lowest result recorded for the OPCRM.

At $450kg/m^3$ the complete fly ash range shows improved results over that of the OPCRM control, although none betters the OPCRM at $300kg/m^3$ cement content. The range of results for the OPCRM control was ±13 minutes which at the higher decay time, 92 minutes, would surpass that of the raw fly ash and follow closely behind the processed fly ash. The raw fly ash has shown the best improvement in relation to the $300kg/m^3$ cement content mix which may highlight the variability in quality inherent with fly ash in the raw condition. The OPCRM comparison shows that the higher cement content provides the lower permeability. Research has shown that both oxygen diffusion and oxygen permeability increase with increasing cement content (Buenfeld and Okundi 1998. Dutron 1987); this agrees with the result found within this research. Overall, the concluding comment is that, from these results, incorporating the finer fly ash as a cement replacement benefits the concrete with respect to its durability.

4.3.6   Discussion

The benefits of reducing the fineness of fly ash can be seen from the increase in compressive strength and a lower permeability with respect to the other states of fly ash. These properties have benefits not only from a concrete point (i.e. a stronger more durable concrete), but from a financial aspect in that less of the expensive OPCRM can be used blended with fly ash to achieve the required 28 day compressive

strength. However, a balance has to be achieved between performance of the material and the amount of usable fly ash which will be rejected as being too coarse for the required material properties. For a general use concrete, the processed fly ash state produces an enhanced concrete, in comparison to the GGBS concrete, at replacement percentages of up to 33%. The strength and permeability are both improved, which leaves a margin for either the reduction in cement content within the mix or fine-tuning the STI electrostatic precipitator to increase the yield reducing the quality slightly but reducing wastage. The former of these requires care as certain concretes, Designated and Designed concrete, have a minimum cement or combination content which must conform to BS EN 8500-2:2002.

The ICP analysis has shown that there is very little difference between the chemical analyses of the processed ash and the classified ash. There is, however, a marked difference with the compressive strengths between the two. Therefore, the increased compressive strength must have some bearing on another aspect of the material at this level of processing. The fine-tuning of the STi process as mentioned earlier could also be used in an attempt to remove more of the silicon from the waste carbon material. It has been shown that carbon is generally localised to one type of particle and therefore could be separated from the silicon particles. This is an area that requires an in-depth study of the STi process and its capabilities.

An attempt at listing the main attributes of fly ash which may potentially enhance its use as a cement replacement material will now be made. This information will then be used to consider any future waste materials and assess the likelihood of their suitability as a cement replacement material. The advantage of this is that an initial assessment may be completed within 24 hours prior to any mixing. From this initial assessment a judgement can be made as to whether or not trials of the mortar and concrete should proceed to establish the compressive strength, etc., from which initial results take days rather than hours to achieve.

4.5 Principal identifiable characteristics of a cement replacement material

Grading

The fineness of the material is important, in that surface area exposed to the alkaline environment within the concrete should be as great as possible (Lewis 2003). As the processed fly ash has produced compressive strength results in excess of the controls, it would be fair to say that the materials which follow this grading have the prospect of being a good cement replacement. OPCRM and GGBS samples were seen to be slightly coarser than the processed fly ash, see Figure 4.26. However, it could be expected that samples with as fine as these could also make satisfactory cement replacement materials. Gradings found to be coarser then those shown here should be considered complimentary to other characteristics as, for example, if the particles demonstrate a more rounded smoother surface texture this would aid in the reduction of free water required which ultimately influences the concrete strength.
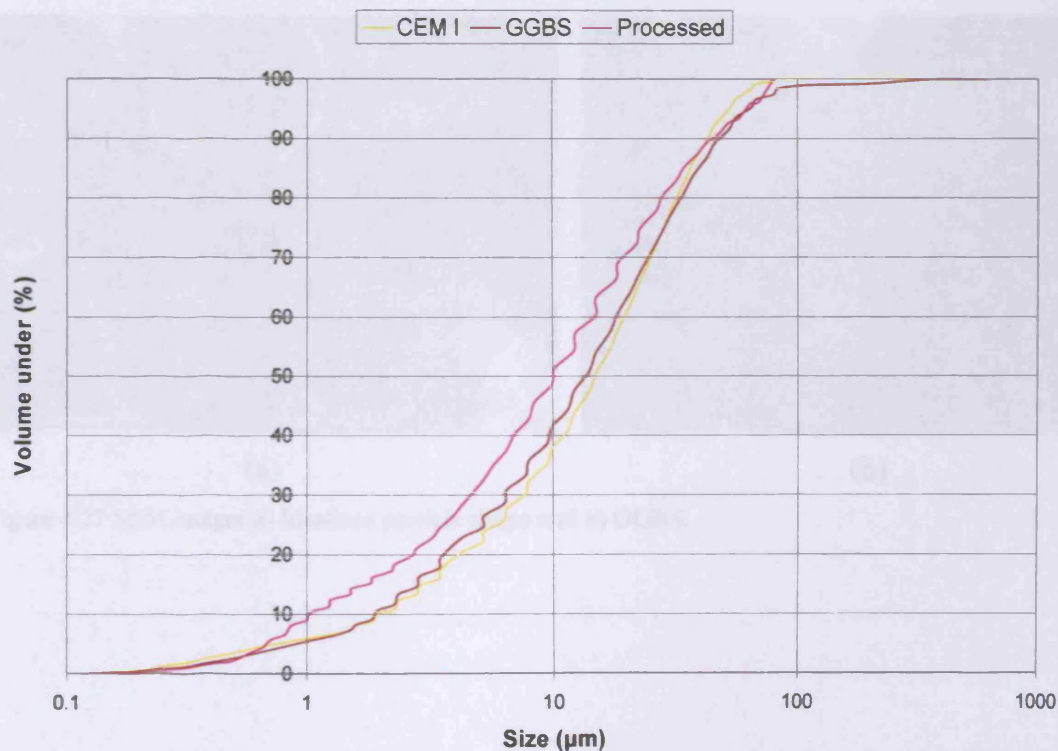
Figure 4.26 Target grading for a potential cement replacement.

Particle shape

Water in concrete has two purposes, to hydrate the cementitious particles and to allow the concrete to flow (i.e. affects consistence). The spherical shape of fly ash acts as lubrication for the particles in a concrete mix; hence, aiding the movement of the concrete leading to a reduction in the water requirement. Therefore, the ideal particle shape should be smooth and spherical see Figure 4.27a, or at least have a rounded form to help create a rolling effect between the particles. Coarser, flatter or squarer particles will have the opposite effect which will ultimately increase the water demand and reduce the concrete compressive strength. However, it can be seen from the image, Figure 4.27b, that GGBS does not follow this requirement but is never the less a successful cement replacement material. This material property is not deemed relevant by the standards as no guidelines are in place to limit a material based on is particle shape. Nevertheless, it is thought that the spherical shape of the fly ash aids the workability and, hence, reduces the water demand required to motivate the mix; this spherical shape would therefore be viewed as a beneficial characteristic.

(a)   (b)
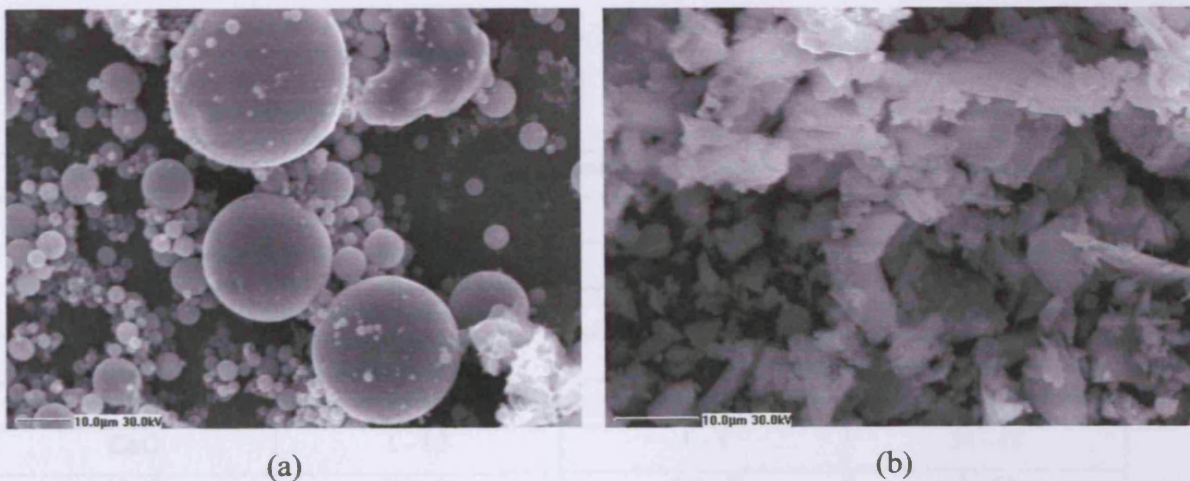
Figure 4.27 SEM images a) Idealised particle shape and b) GGBS.

Loss on Ignition

Chapter 2 discussed the effect that carbon content has on the reduction in workability within concrete. This is overcome by the addition of water which in turn leads to concrete with lower compressive strengths due to the higher water / cement ratio. There are strict limits set by the British and European standards on values for the loss on ignition within cements. As a general rule, in the present study it has been found that with fly ash the amount of water required to achieve the target slump value reduces as the LOI of the binder is reduced. Table 4.11 shows the LOI decreasing as the material is processed, whilst Table 4.7 presents the corresponding w/b ratios of the fly ash mixed as concrete. The compressive strength results have shown, Figure 4.15, the expected rise brought about due to the lowering of the w/b ratio. This would imply that the LOI is an important measure of the material's ability to perform as a cement replacement. This is reflected by the British and European standards which impose limits on carbon content.

Chemical analysis

Table 4.15
Composite cement constituents
Source Moir 2003

Reaction type	Pozzolanic		Latently hydraulic
Constituent	Siliceous fly ash	Natural pozzolana	GGBS
Typical composition	Range	Range	Range
SiO_2	38 - 64	60 - 75	30 - 37
Al_2O_3	20 - 36	10 - 20	9 - 17
Fe_2O_3	4 - 18	1 - 10	0.2 - 2
CaO	1 - 10	1 - 5	34 - 45
MgO	0.5 - 2	0.2 - 2	4 - 13
S	-	-	0.5 - 2
SO_3	0.3 - 2.5	<1	0.05 - 2
LOI	2 - 7	2 - 12	0.02 - 1
K_2O	0.4 - 4	1 - 6	0.3 - 1
Na_2O	0.2 - 1.5	0.5 - 4	0.2 - 1

The chemical analysis carried out has produced results for the processed and fine fly ash and the GGBS. It has been found that the processed and fine fly ash provides comparable, if not better, results than that of GGBS and that GGBS is an accepted cement replacement widely used in industry today. There is, however, a vast difference between the chemical analysis of the fly ash and the GGBS.

The main differences are between the silicon oxide content and the calcium oxide content. In the GGBS both silicon oxide and calcium oxide are 34% and 38% respectively, while in the fly ash the silicon oxide content is 54% and the calcium oxide 2.9%. Both of these materials work, yet the chemical make up is different. This means that waste materials looked at as part of this research, or at some time in the future, may not match the chemical make up of the fly ash yet could prove to be adequate cement replacement materials. Therefore, it is sensible to present an acceptable range of the cement constituents from which a judgement on the new materials elemental analysis can be made. Table 4.15 presents ranges for both pozzolanic and latently hydraulic materials as produced by Moir (2003) which the Author views as an adequate aid in making an initial judgement on the suitability of a new material as a partial cement replacement material.

Transmission Electron Microscopy (TEM)

This work has shown that individual particles vary with respect to their element composition. Numerous analyses were undertaken on individual particles with the establishment of an elemental composition being made on the basis of a specific elemental pattern re-occurring on several occasions (further results from this analysis can be viewed in Appendix 3). If a representative sample of the material is ensured and enough analyses are completed, then it would be expected that an accurate image of the elemental make up can be established. Materials that show separation of elements can be better manipulated to produce the required material, so a careful study of the particles at various sizes should be carried out. With respect to fly ash, knowing which particles contain carbon will influence the method used to remove it.

4.6 Conclusions

From the work carried out in this chapter the main conclusions are;

- o Applying the STi process to the fly ash is a quick and easy method of lowering the carbon content within the ash, producing a material which satisfies both British and European standards.

- o The compressive strength results of the processed fly ash at 33% replacement showed an improvement in strength over the blended GGBS. Therefore, there remains scope for adjustment of the STi process to increase the yield up from 62% which will provide an economic benefit and a reduction in waste sent to landfill.

- o No single property of fly ash can readily predict its performance in the concrete mix.

- o Reducing the particle size of the fly ash through classification provides further benefits with regards to compressive strength of the concrete containing the fly ash.

5. Results - additional candidate cement replacement materials

5.1 Introduction

5.2 Compressive strength

5.3 Physical properties

5.4 Chemical analysis

5.5 Discussion

5.6 Conclusions

5.1 Introduction

Chapter 4 established the main properties of a processed fly ash that contribute to its successful application as a cement replacement material. This chapter considers other materials, available in a form which can successfully be added as a cement replacement, to determine their effect on concrete strength when used as a cement replacement material. Their physical and chemical properties will then be examined and a comparison made to the findings in the previous chapter. The research studies the performance of materials', chemical and physical characteristics and seeks to identify the characteristics which either enhance the concrete or impair the concrete from achieving its full potential. There are four materials being studied in this section, their origins are described in Chapter 3, and are listed below:

- o Sewage Sludge Ash (SS)
- o Municipal Solid Waste Ash (MSW)
- o Fly ash (FA2) supplied from Didcot A Power station
- o A blended selection of Industrial Materials (IM)

The mix designs were produced and tested by the Author at the University using a cement content of 270kg/m^3. This amount was chosen as at that time this concrete design was the highest selling concrete at Minimix Concrete LTD and any successful material would be introduced into the company designs for economical benefit. The range of cement replacement percentages used were 10%, 20%, 25%, 30% and 50%. A target quantity of 100kg per mix was designed for, which gave more than enough concrete for the samples required and sufficient to produce a consistent mix.

This section begins by looking at the compressive strengths of the materials and how they compare to the control of a blended GGBS and OPCRM at similar replacement levels to the research materials. Physical and chemical properties are then examined and compared to the results in Chapter 4 and a discussion on the positive and negative attributes of the materials, as compared to the Processed Fly Ash, will then be presented. The mix procedure can be seen in Chapter 3.

5.2   Compressive strength

	GGBS	SS	MSW	FA2	IM
	■GGBS	■SS	■MSW	■FA2	■IM

Replacement (%)	10%	20%	25%	30%	50%
■ GGBS	51.6	50.2	51.9	49.0	47.0
■ SS	41.0	35.2	38.6	31.3	19.0
■ MSW	32.3	26.1	23.8	23.3	16.6
■ FA2	47.7	45.9	40.7	40.3	28.3
■ IM	43.6	31.2	30.4	27.7	20.0
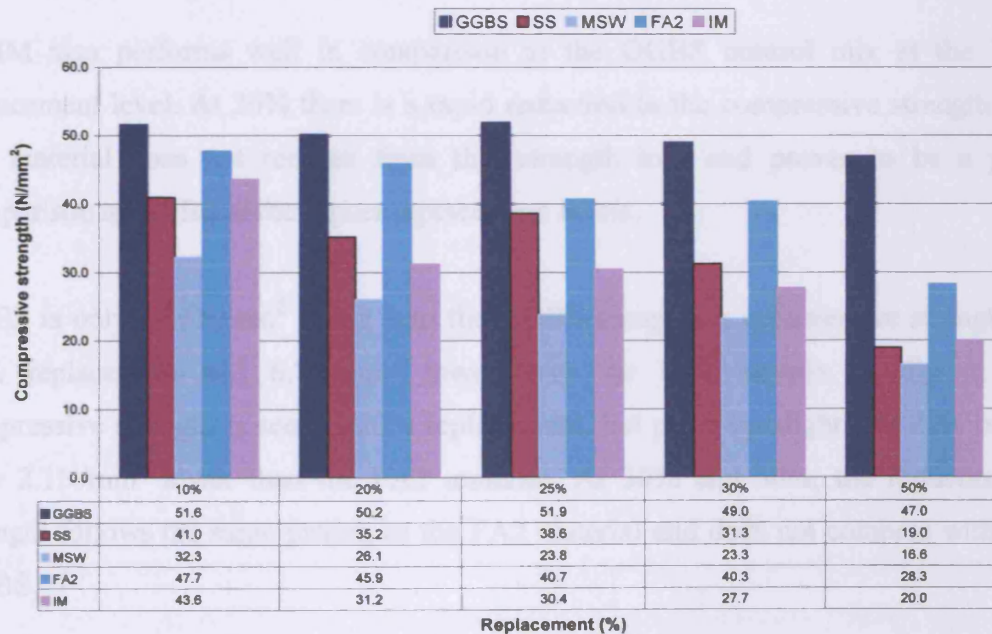
Figure 5.1 Compressive strength comparisons at 28 days of the replacement materials blended with OPCRM at various percentages and a blended mix 50% GGBS 50% OPCRM

Three GGBS control mixes using identical designs were produced as a comparison for the test samples with the average value for compressive strength used.

The spread of compressive strength results between each of the repeat GGBS mixes varied by less than $1N/mm^2$. A single concrete mix has been produced using each sample with the compressive strength being the average of three cubes crushed from this mix at 28 days. The complete set of results can be seen in Appendix 3.

Figure 5.1 presents the results from the compressive strength tests taken at 28 days. Generally, it can be seen that, whereas the GGBS mix maintains a steady compressive strength value over the complete range of replacement percentages, the other materials do not. At 10% replacement all the materials achieve their highest compressive strength, which generally decreases as the replacement percentage increases. The exception to this is the SS material which shows a slight improvement in strength between the 20% and 25% replacement levels. At 10% replacement FA2 is achieving good results which are maintained at 20% and continues to perform well up to 30% where at only $8.7N/mm^2$ weaker than the GGBS is still a strong mix. At 50% the compressive strength of FA2 drops considerably; however, it does remain the best of the test samples having the highest compressive strengths at each replacement percentage.

IM also performs well in comparison to the GGBS control mix at the 10% replacement level. At 20% there is a rapid reduction in the compressive strength and this material does not recover from this strength loss and proves to be a poor comparison to GGBS at the higher replacement levels.

SS is only $10.6N/mm^2$ lower than the GGBS sample on compressive strength at 10% replacement and $6.7N/mm^2$ lower than the FA2 sample. A dip in the compressive strength is seen at 20% replacement, but picks up slightly at 25% being only $2.1N/mm^2$ lower than the FA2 material. At 30% and 50%, the reduction in strength follows the same pattern as the FA2 material and does not compete with the GGBS.

MSW provides the worst case at all replacement levels. The strengths achieved do not compare favourably with the GGBS and are generally well below the other materials being researched.

Water / Binder ratio

The water / binder ratio (w/b) is one of the controlling factors when dealing with the strength of concrete. The British standard BS 8500 -2:2002 has a requirement for a maximum w/b ratio when producing a designated concrete (Table 8 in the standard). This maximum is dependant on cement content and maximum aggregate size. The mixes produced here contain 270kg/m^3 cement content and have a maximum aggregate size of 20mm. Table 8 considers cement contents in multiples of 20kg/m^3 and, hence, 270kg/m^3 does not appear on this table. In this case it would be reasonable to interpolate between the 260kg/m^3 figure and the 280kg/m^3 figure and argue that this should be the correct w/b ratio to use or the smaller value could be used and err on the side of caution. At 280kg/m^3 the maximum specified w/b ratio is 0.60 for a maximum size aggregate of 20mm, whereas at 260kg/m^3 with a maximum aggregate size of 20mm the ratio is 0.65. Therefore, the figure used to test compliance with the standards will be the lower value of 0.6 w/b ratio. Table 5.1 presents the water / binder ratios measured for each of the mixes completed on each material.

Table 5.1
Water binder ratios of the various blended cements at increasing replacement levels

	Replacement %				
Material	10	20	25	30	50
GGBS	0.60	0.56	0.58	0.6	0.58
SS	0.59	0.53	0.54	0.52	0.51
MSW	0.67	0.67	0.65	0.62	0.51
FA2	0.57	0.53	0.48	0.51	0.55
IM	0.66	0.70	0.76	0.73	0.71
BS EN 8500 limit			0.60		

The GGBS has been included in Table 5.1 to show that the mix used complies with the standard at all replacement levels. The majority of the SS material produces results well below the limit, with values ranging between 0.5 and 0.59. It can be seen that as the replacement level increases the w/b ratio decreases. MSW does not produce such positive results, with all but one ratio being above the limit. The results for MSW show a maximum of 0.67 and it can be seen that, as with the SS material, as the replacement percentage increases the w/b ratio reduces until at 50% replacement the w/b ratio is 0.51 being well below the limit. FA2 produces good results all within

the limit and achieving the lowest w/b ratio of 0.48 at 25% replacement. The results for the FA2 fall as the replacement increases until, at 30%, an increase can be seen which continues on to the 50% replacement level. The IM material produces the highest w/b ratios with the lowest result measuring 0.66 whilst subsequent results exceed 0.7.

The influence of the water-cement ratio and cement content on the compressive strength is well documented with the compressive strength decreasing with a higher water-cement ratio (Schulze 1999); therefore, the less water in the mix, the stronger and less porous the concrete. When comparing the results to the compressive strengths, it can be seen that the materials requiring the higher water demand, MSW and IM blends, both produce low compressive strength results.

FA2 shows a decrease in water demand until the 25% replacement level. From this point the water demand increases and it is the only material which shows this behaviour. This may be attributed to the amount of material being introduced into the mix as a result of the differences in particle densities. The particle density of fly ash is typically $2300kg/m^3$, which is significantly lower than OPC at $3120kg/m^3$. Table 5.2 reports the specific gravities of the materials used in this research as determined using the method laid out in BS EN 196-6:1992 Methods of testing cement (National annex NC - Method of testing cement for density).This method determined the density of cement by displacement of a non-reactive liquid (pure water) in a pyknometer. Two separate determinations, on different portions of the sample, using two calibrated pyknometers achieved the average figure used in this research. Therefore, for a given mass of OPC a direct mass substitution of fly ash will give a greater volume of cementitious material. Table 5.2 shows that the density of the fly ash is lower than that of the OPC. However; density alone does not explain the trend for FA2, as SS has a lower density than FA2.

Table 5.2
Specific gravity of the controls and the researched materials

Material	OPCRM	GGBS	SS	MSW	FA2	IM
Specific gravity (kg/m^3)	3268	2942	1705	2496	2207	2734

5.3   Physical properties

Material grading
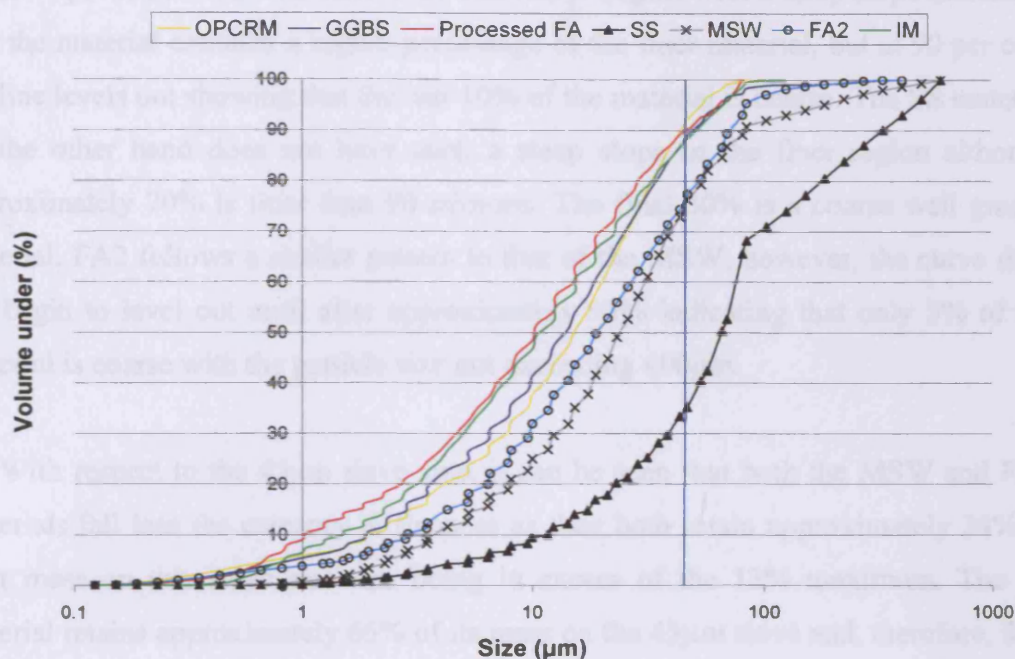
Figure5.2 Particle grading results of the OPCRM, GGBS and Processed fly ash as compared to the SS, MSW, FA2 and IM cement replacement material

Figure 5.2 presents the results from the particle size analysis whilst Figure 5.3 has been derived from it focusing on the OPCRM, Processed fly ash and IM. Chindaprasirta et al (2009) found that the reduction in fineness of a fly ash resulted in higher compressive strength, lower total porosity and capillary porosity than when a coarser fly ash was used. EN 450-1 (2005) requires that the finer classification of fly ash, Category S, shall not retain more than 12% of its mass on a 45μm sieve, the coarser Category N shall not exceed 40%. In Chapter 4 it was discussed that a successful cement replacement should have grading characteristics similar to that of the OPC control as this retained less than the 12% limit. The vertical line shown in both Figures 5.2 and 5.3 show the position of the 45μm sieve, the amount passing is found by reading across to the percentage axis at the point that the grading line cuts through it. The retained amount is the amount passing per cent deducted from 100%.

It can be seen from the Figure 5.2 that the coarsest material is the SS containing particles of a size in excess of 490µm, whilst the maximum particle size for OPC is 100µm. The next coarsest material is the MSW, also having a maximum particle size in excess of 490µm. The difference between these two materials is the total content of the finer particles within the materials. The MSW begins with a steep slope indicating that the material contains a higher percentage of the finer material, but at 90 per cent the line levels out showing that the last 10% of the material is coarse. The SS material on the other hand does not have such a steep slope in the finer region although approximately 70% is finer than 90 microns. The final 30% is a coarse well graded material. FA2 follows a similar pattern to that of the MSW; however, the curve does not begin to level out until after approximately 95% indicating that only 5% of the material is coarse with the particle size not exceeding 400µm.

With respect to the 45µm sieve size, it can be seen that both the MSW and FA2 materials fall into the category N fineness as they both retain approximately 24% of their mass on this sieve size this being in excess of the 12% maximum. The SS material retains approximately 65% of its mass on the 45µm sieve and, therefore, falls outside the limit for category N and outside of the scope for fly ash. IM, however, retains approximately 12% of its mass on the 45µm sieve and, therefore, can be classified as category S. The IM is the finest material of those researched being of a similar fineness to both the processed fly ash and the OPCRM.

Figure 5.3 removes the data from the materials previously discussed and the GGBS control so as to focus on the finer materials of OPC, processed fly ash and the IM material. It can be seen that the grading of the IM falls between the grading of both the OPC control and the processed fly ash although the IM does contain a small percentage of coarser particles around 120µm. It was discussed in Chapter 4 that the ideal cement replacement should have a grading within this range and IM is the only material which fits into this.
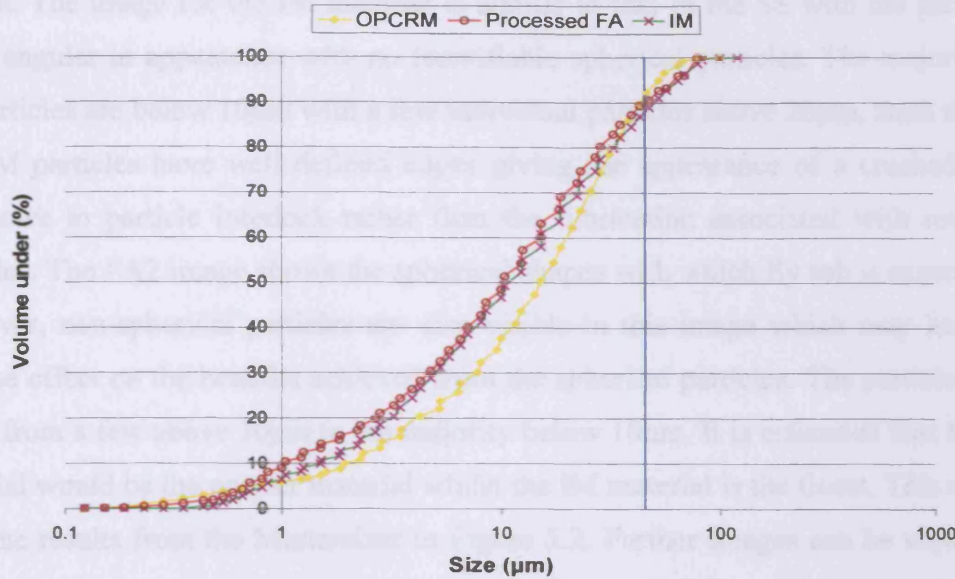
Figure 5.3 Material particle grading focusing on the finer materials of OPC, processed fly ash and the IM material

Particle shape

Figure 5.4 presents the particle images as viewed through the scanning electron microscope. It was discussed in section 4.5 that the idealised particle shape would be spherical or at least smooth and rounded, which would act as a lubricant, allowing the concrete constituents to move with a lower resistance. However, Bullard and Garboczi (2006) reported that spherical shapes have the minimum possible ratio of surface area to volume; the greater the departure from sphericity, the greater this ratio becomes. Therefore, compared to spherical particles, the kinetics of hydration at early ages may be enhanced for pastes formed from non-equiaxed particles. So a spherical particle may enhance the "ball bearing effect", which in turn reduces the w/b, ratio but non-spherical particles promote early hydration.

It can be seen from the images that SS is a very angular material containing no recognisable spherical shaped particles at any particle size. The majority of the particles are below 50μm with a few individual particles larger than 100μm. MSW is also an angular material, but the smaller particles and those particles which are not clumped together give a rounded appearance. All the particles in this image are below

100µm. The image for the IM material is similar to that of the SS with the particles being angular in appearance with no identifiable spherical particles. The majority of the particles are below 10µm with a few individual particles above 20µm. Both the SS and IM particles have well defined edges giving the appearance of a crushed rock conducive to particle interlock rather than the lubrication associated with rounded particles. The FA2 image shows the spherical shapes with which fly ash is associated. However, non-spherical particles are also visible in this image which may have an adverse effect on the benefits achieved from the spherical particles. The particle sizes range from a few above 30µm to the majority below 10µm. It is estimated that the SS material would be the coarser material whilst the IM material is the finest. This agrees with the results from the Mastersizer in Figure 5.2. Further images can be viewed in Appendix 3.

(a)

(b)

(c)

(d)
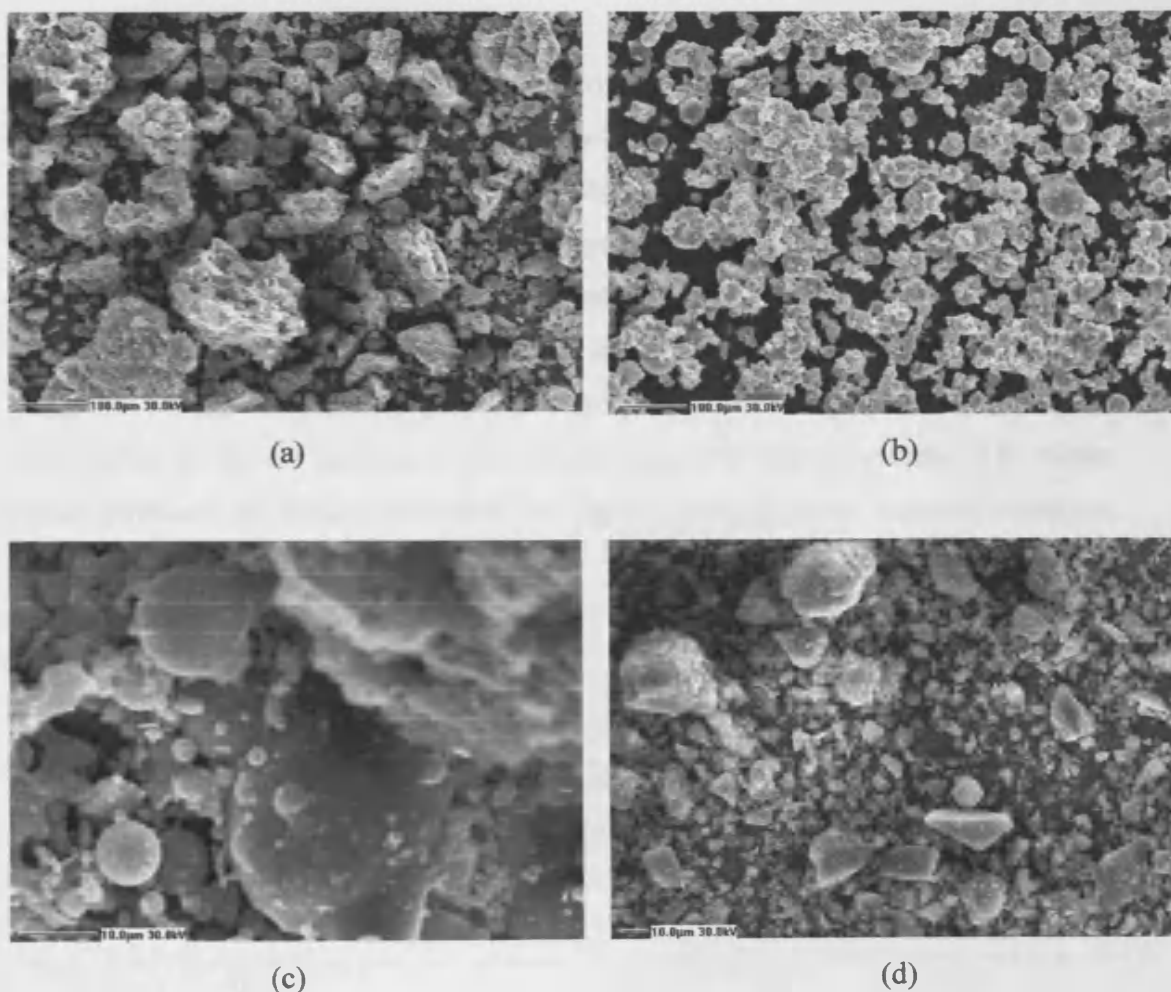
Figure 5.4 SEM images showing the particle shapes of the replacement materials a) SS, b) MSW, c) FA2, and d) IM

Loss on ignition and sulphur analysis

As previously reported, the highest limiting value for SO_3 in cement is 4.0% (3.5% in lower strength cements). The results for the materials in this research are presented in Table 5.3 and give the values for sulphur, SO_3 and SO_4. It can be seen that the SO_3 values for SS, FA2 and IM are within the limits for the British and European standards. The value for the MSW material is more than double the limiting value. As was mentioned previously, this value may be taken as a sum total of the blended material and not just as an individual value. Therefore, this material may not be problematic unless it is blended at a high volume. However, the suggested limits for SO_3, presented in the previous section, placed a limiting range of 0.3% to 2.5% for a siliceous fly ash, <1.0% for a natural pozzolan and 0.005% to 2% for GGBS. This now puts MSW outside any of these acceptable ranges.

BS EN 197-1:2000 requires that cement types CEM I and CEM III have a loss on ignition value smaller than 5.0% but does not state a value for CEM II cement. The standard deals with other materials separately to the cement therefore the carbon content of each material would be restricted prior to its addition to the CEM I. As SS, MSW and FA2 are all ashes the maximum value given in the standard is 7%. The IM sample does not have a category within BS EN 197 so for this research the limiting value will be taken as that of the fly ash. The carbon contents in Table 5.3 show very little carbon in the SS material with a small amount in the IM sample. The higher values produced are in the MSW with the highest being the FA2 material. However, both are within the 7% limit.

Table 5.3
Results for Sulphur and Carbon analysis - Leco

Name	Sulphur %	SO_3 %	SO_4 %	Carbon %
SS	0.53	1.33	1.6	0.28
MSW	3.87	9.65	11.58	4.70
FA2	0.32	0.79	0.95	5.65
IM	0.71	1.77	2.13	1.23

Table 5.4 presents the loss on ignition values as achieved using the British standard test method to BS EN 196-2:2005. This method subjects a sample with a known weight to be heated to 950° C for 15 minutes then re-weighed the difference between the two weights being the carbon content. The Leco test uses a method which analyses the atmosphere within the apparatus and records the amount of carbon detected which is then expressed as a percentage. The main issue with the British Standard test is that any inorganic material within the material plus any water content within the sample is removed due to the heat and taken into the calculation. Therefore, the result is a percentage of everything that was burnt off during the firing of the material.

It can be seen from the comparisons of the data in Tables 5.3 and 5.4 that the losses on ignition vary considerably between the Leco test and the British standard test in all but the FA2 results. Where the Leco analysis permits all the materials to be used, being below the limiting value of 7%, the British Standard method does not. The loss on ignition carried out to BS EN 196-2:2005 prohibits the use of both MSW and IM as having too high a value however the SS material remains within the acceptable limit.

As the British standards method is the industry standard for the determination of the carbon content, this is the figure which should be used when reporting on the material.

Table 5.4
Carbon content (LOI) of the replacement materials

Material	LOI (%)	Leco (%)
SS	2.82	0.28
MSW	34.67	4.70
FA2	5.69	5.65
IM	9.08	1.23

5.4 Chemical analysis

Inductively Coupled Plasma Analysis (ICP)

Tables 5.5 and 5.6 present the results from the ICP chemical analysis. It was proposed in Section 4.5 that the comparison from the chemical analysis should lie within a range of values rather than just achieve a singe value. Tables 5.5 and 5.6 show the chemical analysis results of the research materials along with the proposed idealised chemical ranges. The calculations used to produce the table are shown in Chapter 3 with the full analysis results in Appendix 3.

Table 5.5
Nature of composite cement constituents (Moir 2003)
as compared to the chemical analysis of SS and MSW

Oxide (%)	Acceptable ranges			Material	
	Siliceous fly ash	Natural pozzolana	GGBS	SS	MSW
SiO_2	38 - 64	60 - 75	30 - 37	32.40	6.06
Al_2O_3	20 - 36	10 - 20	9 - 17	13.82	1.12
Fe_2O_3	4 - 18	1 - 10	0.2 - 2	9.39	0.64
CaO	1 - 10	1 - 5	34 - 45	12.67	34.43
MgO	0.5 - 2	0.2 - 2	4 - 13	2.19	0.55
P_2O_5				4.22	0.11
K_2O				1.90	4.34
Na_2O				0.46	2.08
Mn_2O_3				0.24	0.04
Minors				11.50	19.09
LOI	2 - 7	2 - 12	0.02 - 1	2.82	34.67
Total (%)				91.62	103.12
Al + Si + Fe	>70			55.62	7.82
Na + K	<5.0			2.36	6.42
Ca + Mg / Si			>1.0	0.46	5.77

It can be seen that the amount of silicon and aluminium within SS places this material in the GGBS class. The other elements are, however, not compliant with this classification. The silicon value is fairly high, although not as high as required by the fly ash classification, and the calcium low; therefore, it would be expected that this material will act as a pozzolanic material. The loss on ignition is within the range specified for the pozzolanic material but the sum of the oxides for Al + Si + Fe does not achieve the specified value for a fly ash of 70%.

When considering the MSW material, it can be seen that the high level of calcium and iron place this under the GGBS category. The most important element on which the chemical reaction in cement relies, silicon, is in short supply. At only 6%, this value falls well short of any of the suggested values and, together with the low aluminium and iron contents, remains well below the required minimum of 70% for the sum of these elements within fly ash.

Table 5.6
Nature of composite cement constituents (Moir 2003)
as compared to the chemical analysis of FA2 and IM

Oxide (%)	Acceptable ranges			Material	
	Siliceous fly ash	Natural pozzolana	GGBS	FA2	IM
SiO_2	38 - 64	60 - 75	30 - 37	53.92	40.00
Al_2O_3	20 - 36	10 - 20	9 - 17	27.47	10.17
Fe_2O_3	4 - 18	1 - 10	0.2 - 2	2.05	0.92
CaO	1 - 10	1 - 5	34 - 45	6.37	20.99
MgO	0.5 - 2	0.2 - 2	4 - 13	2.08	11.28
P_2O_5				0.27	0.06
K_2O				0.53	0.92
Na_2O				0.14	0.40
Mn_2O_3				0.07	0.39
Minors				6.29	1.98
LOI	2 - 7	2 - 12	0.02 - 1	6.76	9.08
Total (%)				105.94	96.19
Al + Si + Fe	>70			83.44	51.09
Na + K	<5.0			0.67	1.32
Ca + Mg / Si			>1.0	0.14	0.81

Table 5.6 compares the remaining two materials, FA2 and IM, to ascertain whether either falls into a standard category. FA2 is a fly ash material and it would be expected that this will follow the requirements of the siliceous fly ash. There are only two slight differences between the material and the requirements, these being Fe_2O_3 which is slightly lower in FA2 and the MgO which is slightly higher. The sum of the oxides for Al + Si + Fe at 83% is above the minimum 70% and sum of the alkalis at 0.67% is lower than the maximum 5.0%. This then falls into the classification of a siliceous fly ash.

IM is a blend of industrial waste materials mixed in a way as to try and emulate an ideal cement replacement material. A number of blends were available to test, but this blend was used as it had shown positive results in a previous study on mortar. As with the other three materials in this study, the IM material conforms to some of the requirements of each of the classifications but does not give a clear preference. The silicon content conforms to the range of the siliceous fly ash but this is where the conformity ends. The aluminium, iron and magnesium conform to the requirements of the GGBS, but the calcium lies midway between the two specifications. Both the sums of Al + Si + Fe and (Ca + Mg)/Si are below the requirements of their respective specification; however, the sum of the alkalis conforms to the requirements of fly ash.

Transmission Electron Microscopy (TEM)

The particles of each material have been observed by the TEM using identical settings, magnification and sizing of the particles as small, medium and large:

- o Small particles <0.25μm
- o Medium particles <2.0μm and >0.25μm
- o Large particles >2.0μm

An image showing these various sizes can be seen in Section 4.34, Figure 4.19. The TEM was used in an attempt to identify the elemental differences between the various sizes of particles within each material. By establishing this it will be possible to determine whether the removal of a certain size particle would make a difference to

the material's performance as a cement replacement. The results from the analysis of
the materials are now discussed:

Figure 5.5 TEM particle analyses on a large SS particle.

Figure 5.6 TEM particle analyses on a medium SS particle
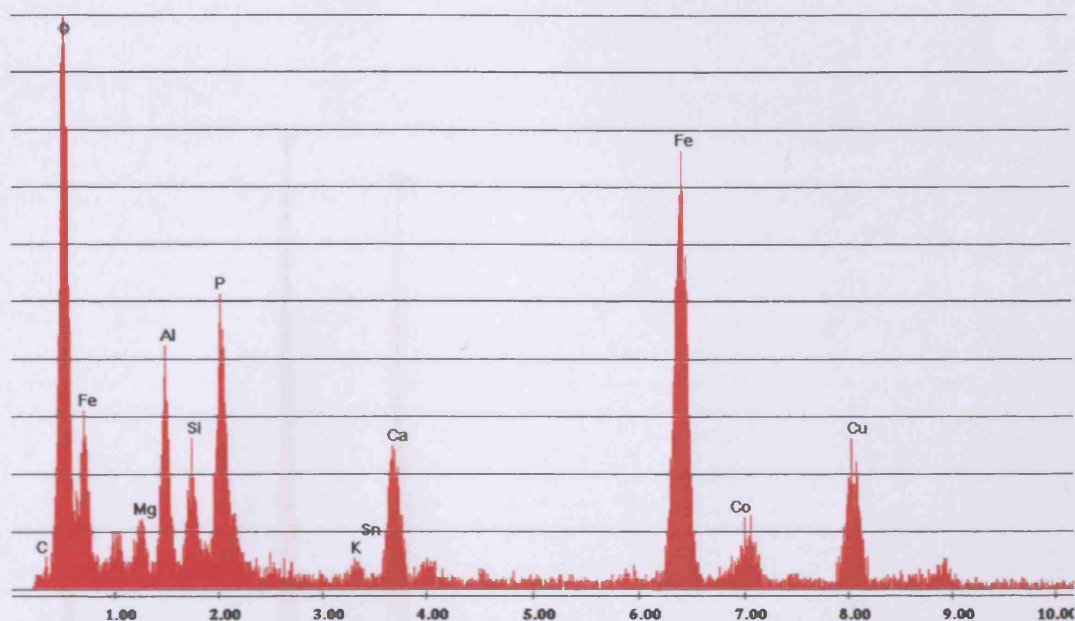
Figure 5.7 TEM particle analyses on a small SS particle

SS: The analyses of the large, medium and small particles for the SS material are shown in Figures 5.5, 5.6 and 5.7 respectively. The analysis on the three particle sizes shows that generally the elemental make up is consistent throughout with the same elements appearing at each size. The differences are that the large particle displays titanium which the other particle sizes do not; the medium sized particle shows a significant increase in silicon, potassium and calcium over the large and small particles and the small particle displays a large proportion of iron.
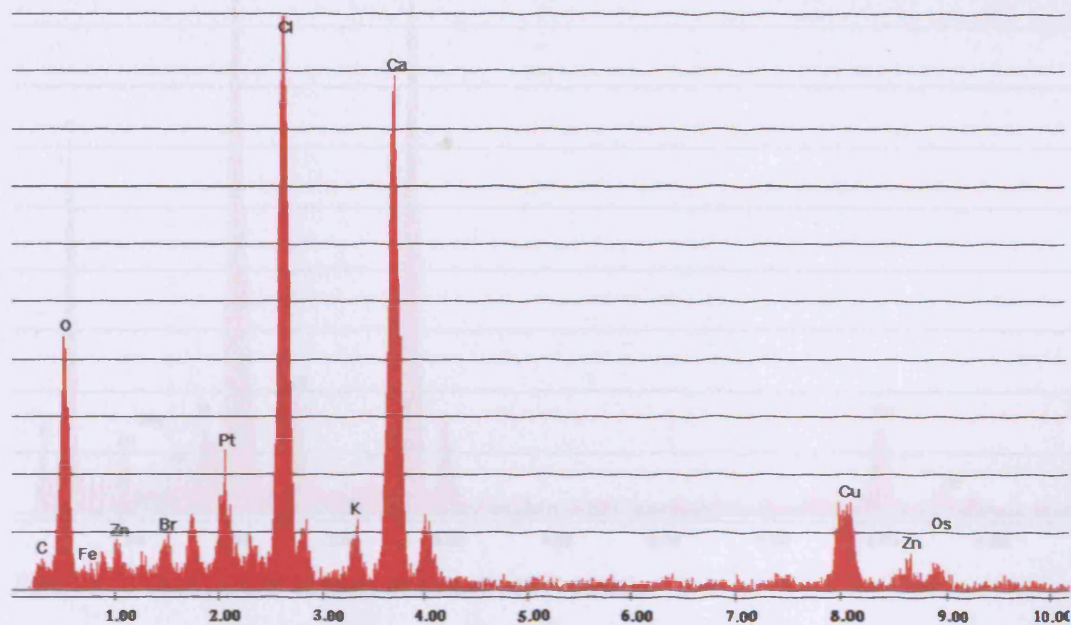
Figure 5.8 TEM particle analyses on a large MSW particle
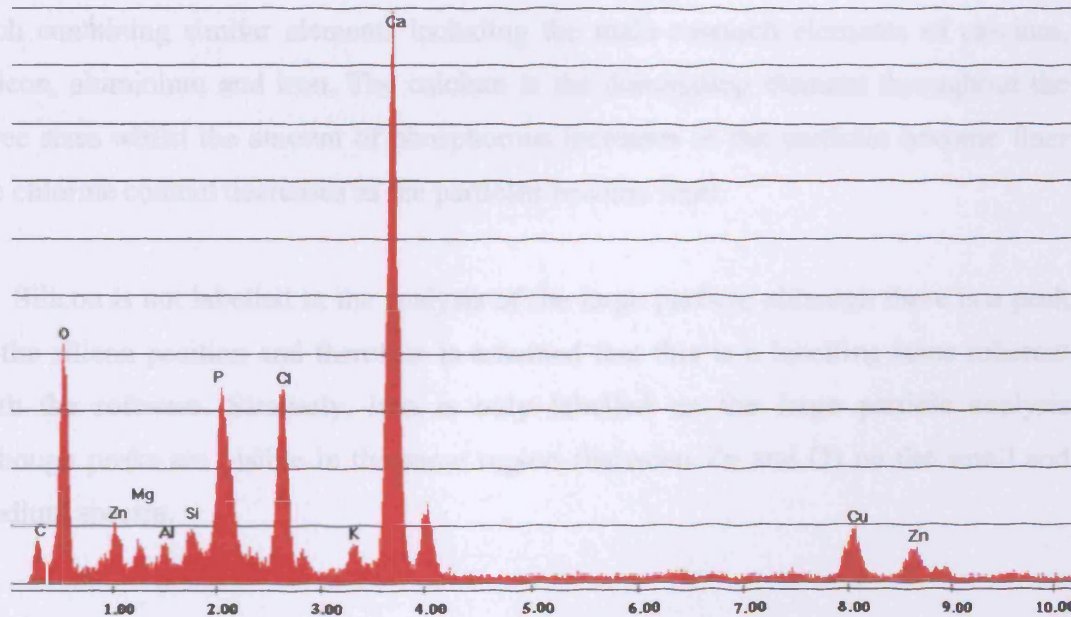
Figure 5.9 TEM particle analyses on a medium MSW particle
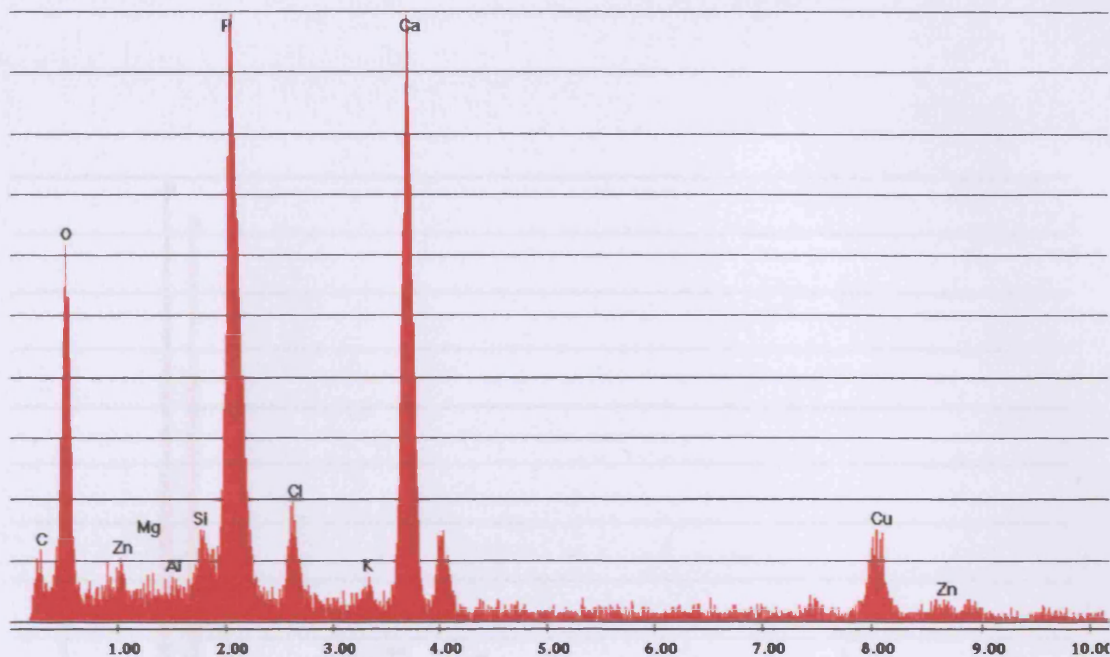
Figure 5.10 TEM particle analyses on a small MSW particle

MSW: The analyses of the large, medium and small particles for the MSW material are shown in Figures 5.8, 5.9 and 5.10 respectively. As with the SS material the analysis of the three particle sizes generally shows consistency throughout with each containing similar elements including the main research elements of calcium, silicon, aluminium and iron. The calcium is the dominating element throughout the three sizes whilst the amount of phosphorous increases as the particles become finer the chlorine content decreases as the particles become finer.

Silicon is not labelled in the analysis of the large particle although there is a peak in the silicon position and therefore is assumed that this is a labelling issue inherent with the software. Similarly, iron is only labelled on the large particle analysis although peaks are visible in the same region (between Zn and O) on the small and medium spectra.
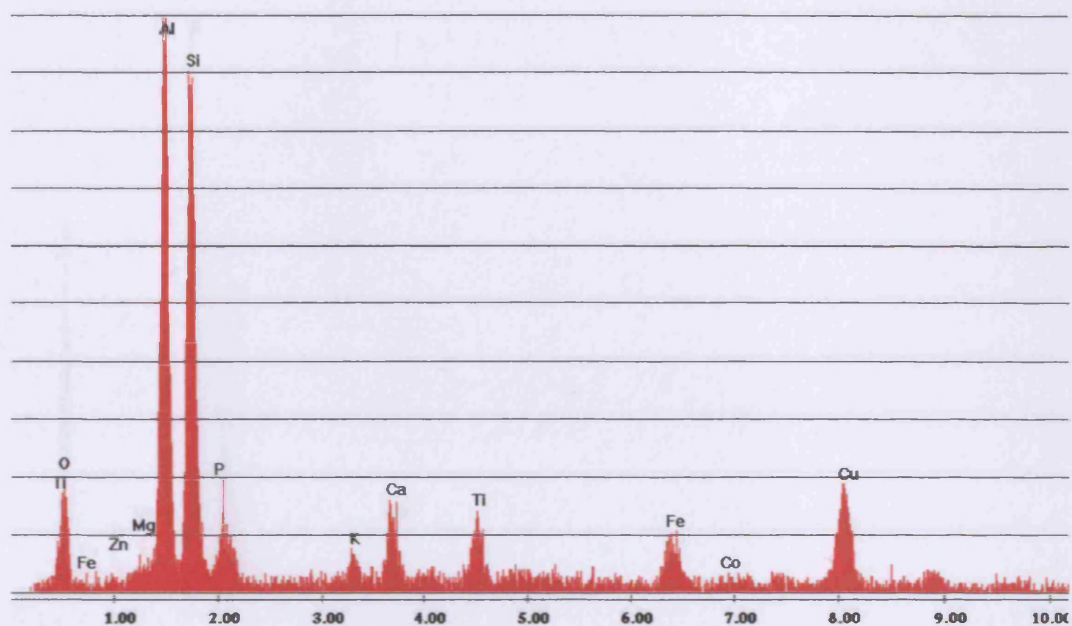
Figure 5.11 TEM particle analyses on a large FA2 particle
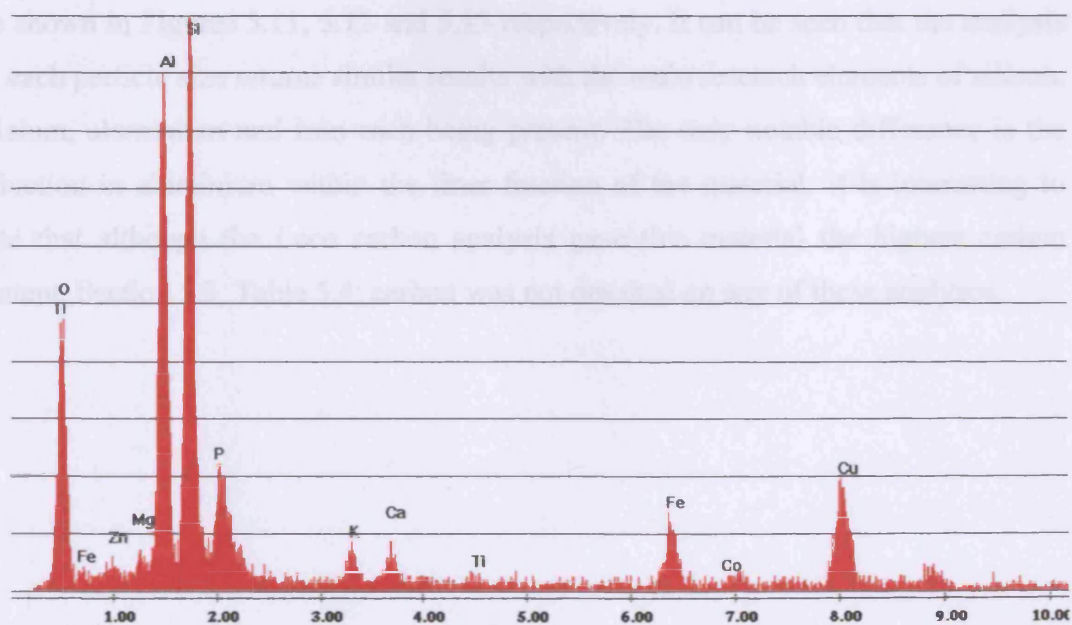
Figure 5.12 TEM particle analyses on a medium FA2 particle
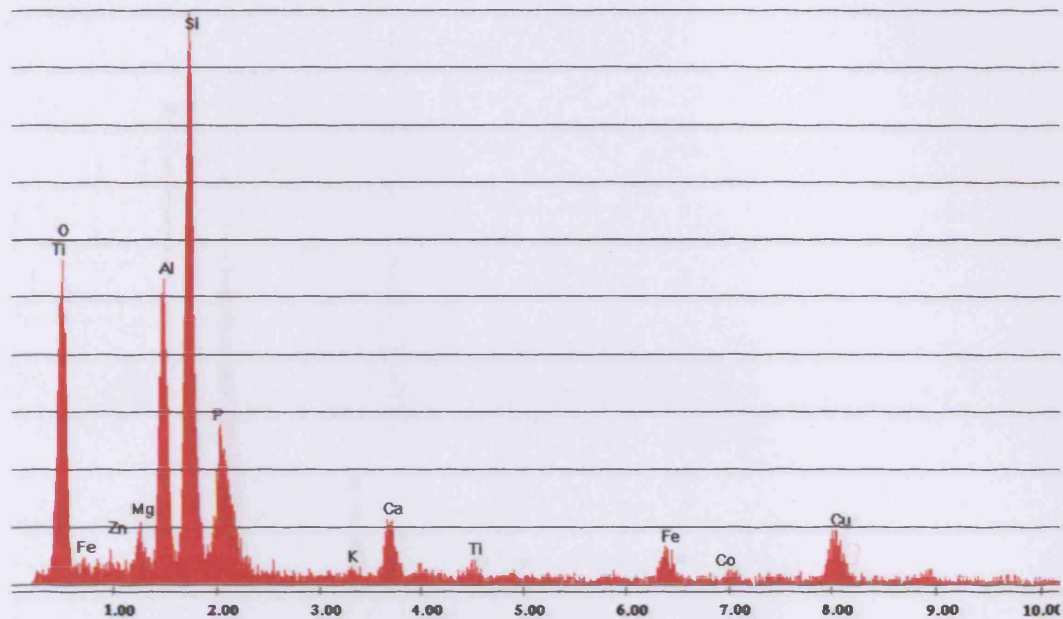
Figure 5.13 TEM particle analyses on a small FA2 particle

FA2: The analyses of the large, medium and small particles for the FA2 material are shown in Figures 5.11, 5.12 and 5.13 respectively. It can be seen that the analysis on each particle size returns similar results with the main research elements of silicon, calcium, aluminium and iron each being present. The only notable difference is the reduction in aluminium within the finer fraction of the material. It is interesting to note that although the Leco carbon analysis gave this material the highest carbon content, Section 5.3, Table 5.4; carbon was not detected on any of these analyses.
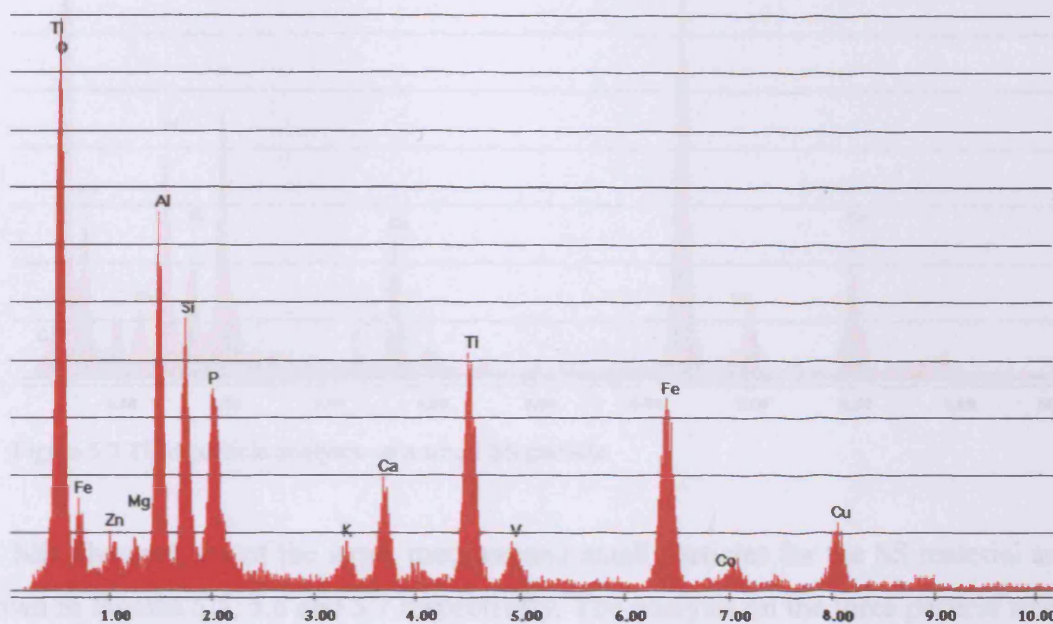
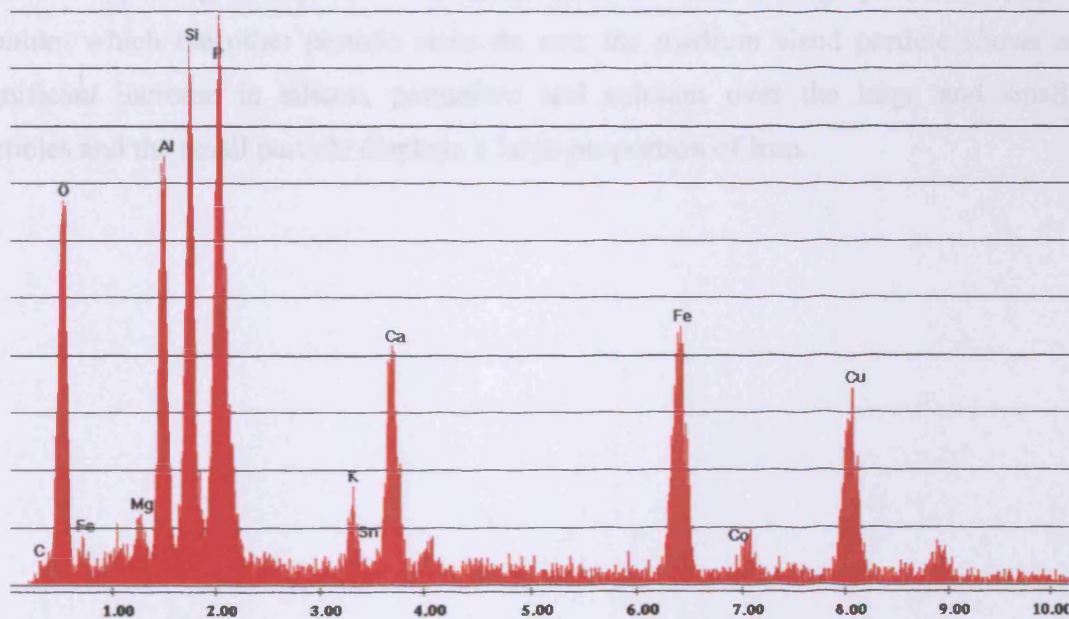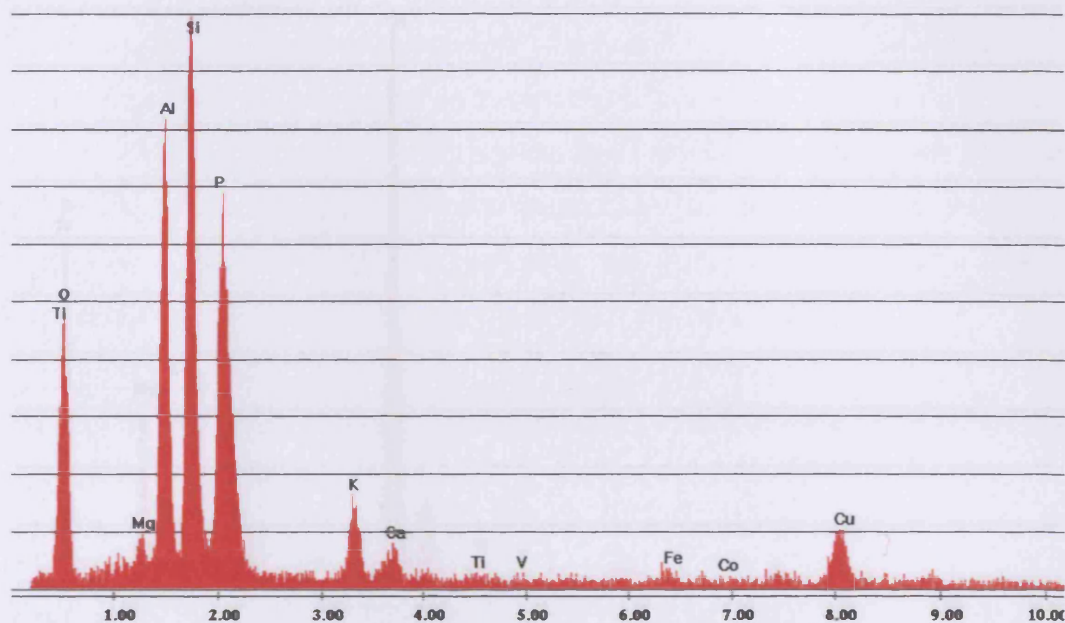Figure 5.14 TEM particle analyses on a large IM particle
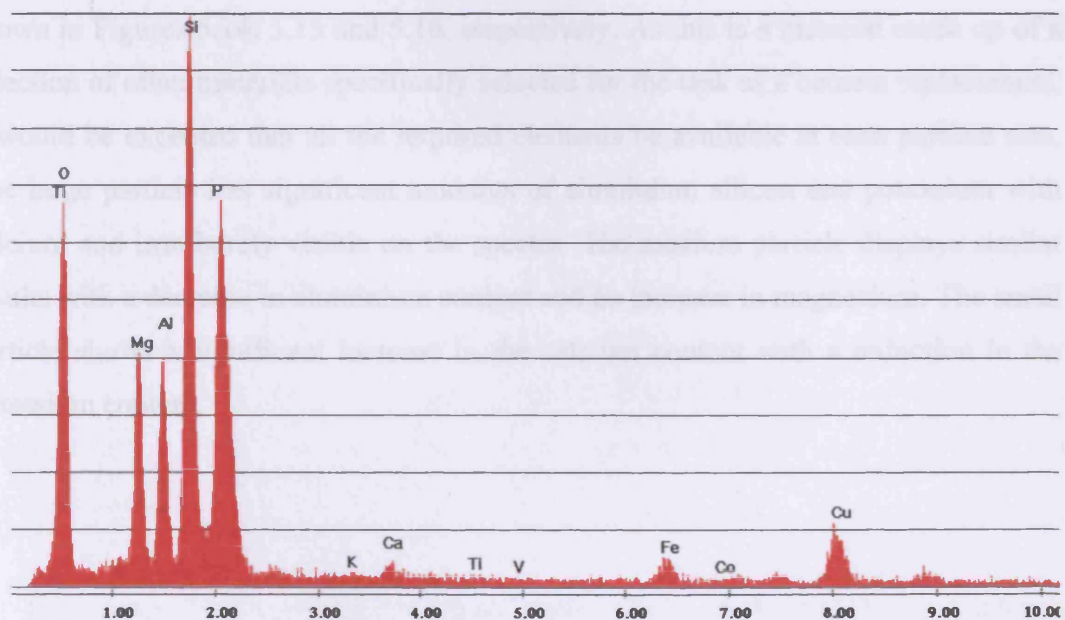
Figure 5.15 TEM particle analyses on a medium IM particle
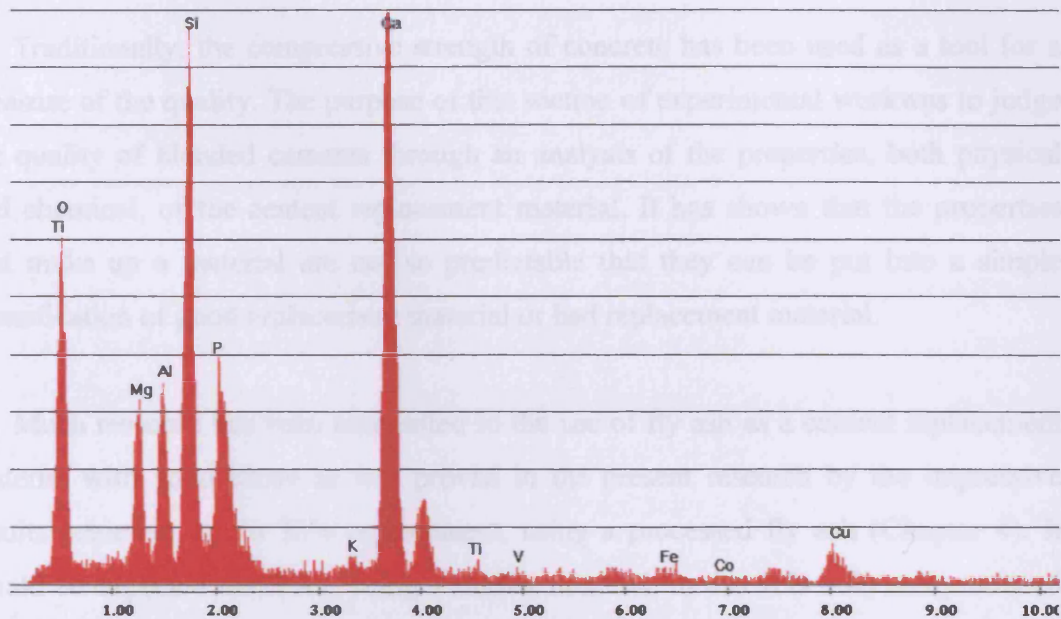
Figure 5.16 TEM particle analyses on a small IM particle

IM: The analyses of the large, medium and small particles for the IM material are shown in Figures 5.14, 5.15 and 5.16, respectively. As this is a material made up of a selection of other materials specifically selected for the task as a cement replacement, it would be expected that all the required elements be available at each particle size. The large particle has significant amounts of aluminium silicon and potassium with calcium and iron barely visible on the spectra. The medium particle displays similar results with a decrease in aluminium content and an increase in magnesium. The small particle shows a significant increase in the calcium content with a reduction in the potassium content.

5.5   Discussion

Traditionally, the compressive strength of concrete has been used as a tool for a measure of the quality. The purpose of this section of experimental work was to judge the quality of blended cements through an analysis of the properties, both physical and chemical, of the cement replacement material. It has shown that the properties that make up a material are not so predictable that they can be put into a simple classification of good replacement material or bad replacement material.

Much research has been committed to the use of fly ash as a cement replacement material with good cause as was proved in the present research by the impressive results achieved, up to 33% replacement, using a processed fly ash (Chapter 4). It would be expected that FA2, being a similar material, in that it is a fly ash produced from the burning of coal, should perform close to if not as well as the control using GGBS. However, the compressive results are disappointing when the replacement level increases above 20%. What could be done to this material to improve its worth as a cement replacement? Looking at the grading, it can be seen that FA2 is coarser than that recommended, so increasing the fineness could improve performance. IM on the other hand is a fine material which follows the assumed requirements for a material and yet its compressive strength is only competitive at 10% replacement.

The SEM images show that FA2 contains an amount of both spherical and, to a lesser extent, irregular shaped particles. If these irregular particles were removed would the resulting mix become more fluid requiring less water and the associated increase in strength? Possibly; however, the SS material has achieved similar w/b ratios as that of FA2 and the SEM images show there to be only non-spherical particles available.

The Loss on Ignition and the chemical analysis have shown that the FA2 material has a relatively low LOI at 5.69%. Dhir et al (1981) demonstrated that there is strength reduction as the LOI of fly ash increases with approximately $3N/mm^2$ being lost between 2% and 6% LOI. The MSW and IM materials follow this prediction with

the MSW having the higher LOI giving the lower strength. This is not true of the FA2 and SS materials, with the FA2 material having the higher LOI and also the higher strength. The chemical analysis of FA2 confirms that this is a siliceous fly ash as it conforms to the requirements of EN 450-1 2005, whilst the other materials conform only partly to this specification. To use this information to guess the success of a particular material as a cement replacement will require some knowledge of the reactions within cement and its relationship to the replacement material.

This research has shown the fly ash FA2 to be the best replacement material from the four samples tested, with SS, IM and MSW following in descending order of quality. This material has consistently bettered the strengths of the other samples, although it has not improved on the strength produced by the GGBS control. As discussed in Chapter 4, the properties of the material follow the recommended pattern with the fineness, particle shape and elemental make up all being within the vicinity of each of the suggested ranges. The SS material is a coarse material with 65% retained on the 45μm sieve (procedure to BS EN 196-6 Determination of fineness, sieving method) and particles illustrating a rough irregular shape. The carbon content is low and the SiO_2 content is not far short from that of siliceous fly ash. Even with the low w/b ratio, the material does not compare to the GGBS control or the FA2 material. Kiattikomol et al (2001) showed that the fineness of the fly ash, not the chemical composition, had a significant effect on the strength of mortar. This material may perform better if it were processed to remove the coarser particles.

The MSW material is also a coarse material with an angular irregular particle shape. Although the fineness improves over the SS material, the high carbon content, high w/b ratio and low SiO_2 content contribute to it being the worst performer out of the four materials. None of the elemental properties of this material compare with the idealised ranges, as shown in Table 5.6.

The IM sample has the potential to work well as a replacement material. It is a fine material, although its particles are rough and irregular, with a high SiO_2 content. This material showed positive results at low replacement levels however high w/b ratios and high LOI results prove detrimental to the compressive strengths of the concrete. The results from the analysis would have shown the potential for this

material as a cement replacement, noting the high carbon content, with further trials being recommended.

Table 5.7 presents a scoring system which scores the candidate replacement material based on how it performed relative to the idealised cement replacement through each of the analysis. The scoring system is based upon the judgement of the reviewer who must accurately assess the candidate material performance. The scoring system uses a 4 point scale:

o   A score of 4 indicates that the material fits the idealised requirement for a cement replacement material. A score of 1 indicates that the material has very little, if anything, in common with the idealised material requirement. Scores of 2 or 3 can be used for intermediate scoring.

o   A weighting is applied to the chemical analysis score as there are a number of comparisons to be made, which if are all matched exactly, will have a greater benefit to the replacement material greater than, for example, the fineness which can be manipulated through grinding.

Table 5.7
Performance ratings of the candidate materials using a scoring system as an indictor to the materials effectiveness as a cement replacement based on results from the analysis

Property	Weighting factor	Material			
		FA2	SS	IM	MSW
Fineness	1	3	1	4	3
Shape	1	4	1	1	2
LOI	1	3	4	1	1
Chemical components	2	4	3	2	1
Score		18	12	10	8
Rank		1	2	3	4

Ratings:

1 - Poor   2 - Moderate   3 - Good   4 - Excellent

Reviewing the fineness property in Table 5.7, studying the IM and FA2 materials, it can be seen in the material grading, Figure 5.2, that the grading curve of the IM material follows that of the CEM I and the processed fly ash whilst the FA2 material is coarser. Therefore, the IM material receives a score of 4, being the idealised grading, whilst FA2 receives a score of 3 being just below the idealised grading.

With respect to shape, the SEM images show that the majority of the particles in the FA2 material are spherical therefore a score of 4 is awarded as this is the ideal particle shape. The MSW achieves a score of 2 because the particles are generally angular with a few having a spherical appearance. The SS and IM materials are both angular with no spherical particles visible and hence receive the lowest score.

With regards to the LOI scores, a score of 4 would be awarded to a material with a LOI of less than 5%, a score of 3 would have a LOI of less than 7% but larger than 5%, whilst a score of 2 would have a LOI result larger than 7% but less than 9%, with a score of 1 being greater than 9%.

The chemical analysis scores are based on how closely the material analysis matches that of the idealised chemical composition as presented in Table 4.15. FA2 gets a score of 4 as this material follows the requirements of the siliceous fly ash fairly accurately with iron being the only anomaly. SS receives a score of 3 as this material is fairly close to the siliceous fly ash however the material is slightly low on the main element of silicon and the Al + Si + Fe value is also lower than required. The IM material is similar to that of the SS, however, this material gives closer resemblance to GGBS. The results show that the calcium level is significantly lower than required for GGBS and the value for (Ca + Mg)/Si is also too low therefore the IM material scores a 2. MSW compares to the GGBS through its iron content and (Ca + Mg)/Si values being higher than required and its calcium content being the minimum acceptable amount for GGBS. All other elements are low, with the major element of silicon being a fifth of the content required for GGBS. These low values necessitate the lowest score of 1 for the chemical components of MSW.

The performance ratings have been introduced in order to rate and compare candidate cement replacement materials and predict their suitability prior to any further investigation. This method has the advantage that it is fairly simple to use and researchers with some knowledge of the essential properties of a cement replacement material can make accurate judgements for the scoring.

It can be seen from Table 5.7 that the ranking of the materials reflect those of the majority of the compressive strength results as presented in Figure 5.1. For this research Table 5.7 has proved to be a suitable method for assessing the results. However, other materials may not be so clear cut and Table 5.7 may require reviewing to improve its accuracy.

5.6   Conclusions

In summary the conclusions from this chapter are:

o   An indication as to whether an unknown material will work as a cement replacement can be gained from the analysis performed within this chapter. With some knowledge of the use of cement and cement replacements, it is possible to compare the physical and chemical, properties of an unknown material to those researched here and get an indication as to the materials potential as a cement replacement prior to mixing as a concrete.

o   A performance table with a scoring system is an accurate method of scrutinising the results from the analyses to predict the candidate materials worth as a cement replacement.

o   The ideal candidate for a quality cement replacement must possess a chemical composition similar to one of those in the acceptable ranges and be of a comparable fineness to OPC.

o   Particle shape does not necessarily reduce the free water requirement.

6. Results - inter-grinding fly ash with clinker

6.1 Introduction

6.2 Grinding

6.3 Test results of the inter-ground material

6.4 Cost analysis

6.5 Conclusions

6.1 Introduction

The vast majority of cement produced throughout the world is ground in ball or rod mills. These are rotating tubes which contain steel balls or rods in a range of sizes through which the clinker passes (Moir 2003). The sizing action required to regulate the performance of ball mills is obtained by operating the mill in a closed circuit with a classifier, (Gaudin 1939). Although vast changes have been made through natural evolution and technology, the principle of closed circuit grinding has not changed for many years. A closed-circuit mill, illustrated in Figure 6.1 below, contains two separate chambers divided by a slotted diaphragm wall through which the partially ground material is allowed to pass. Each of the chambers contain steel balls, the first having a diameter range of generally 60-90mm and the second a diameter range of generally 19-38mm, Figure 6.2 shows the actual ball mill used at Aberthaw cement works. The cement is discharged through a separator which divides the particles that have been reduced to the requisite size from those that have not yet been sufficiently reduced (i.e. oversize), the fine particles being stored whilst the coarser particles are returned to the mill once again (Moir 2003). Closed-circuit grinding delivers tight control of particle size whilst open-circuit mills, which do not contain the separating stage, are less efficient especially at high cement finenesses (above $350m^2/kg$) (Moir 2003).
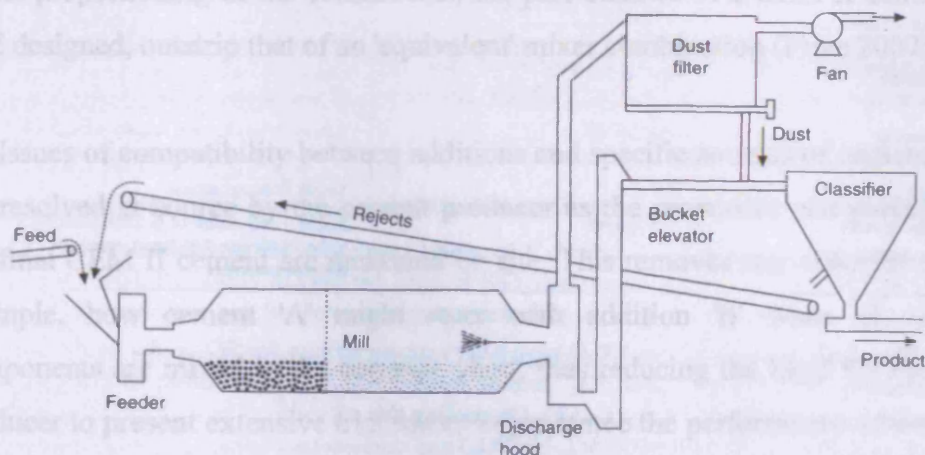
Figure 6.1 Schematic diagram of a closed-circuit grinding mill
     Source Moir 2003

| (a) | (b) |

Figure 6.2 Photographs taken at Aberthaw cement works showing (a) the ball mill grinder, (b) the
     inside of a replacement ball mill

There are a number of benefits available for the producer of CEM II cement by the on-site blending of the materials, as opposed to the blending of the materials being achieved in the batching mixer at the concrete plant. The first is that the producer will have controls, unavailable to mixer combinations, to improve the performance of the cement. These could include the optimisation of the sulphate content to regulate setting without compromising strength development and / or using additives to improve water demand or early-age strength. There is a substantial body of evidence from the UK and elsewhere that, because the cement manufacturer can optimise the properties of the Portland cement component and control the grinding regime, as well

as the proportioning of the constituents, the performance of a CEM II cement can, if well designed, outstrip that of an 'equivalent' mixer combination (Price 2007).

Issues of compatibility between additions and specific sources of cement (CEM I) are resolved at source by the cement producer as the properties and performance of the final CEM II cement are measured on site. This removes any concerns about, for example, how cement 'A' might react with addition 'B' when the individual components are mixed in the concrete plant, thus reducing the need for the concrete producer to present extensive trial mixes to guarantee the performance of the concrete produced.

Pandey et al. (2003) observed that, when inter-grinding with clinker, an increasing addition of fly ash produced an increase in the Blaine fineness of all samples. This was put down to the increase in 'grindability' of clinker as well as the crushing and disagglomeration of the fly ash particles. Tsvilis et al. (1999a) reported that materials having different grindabilities influence the particle size distribution, which in turn influence cement hydration and finally performance. However, an excessive amount of secondary material inhibits the grinding of both clinker and limestone resulting in a coarser grading of these materials.

Elkhadiri et al. (2002) found that, during the grinding stage, results showed that increasing the amount of added fly ash in the blended cement significantly reduced the grinding time. This indicated that fly ash enhances the grinding operation. So, inter-grinding clinker and fly ash promotes the grinding process and yields an increase in fineness in less time, hence less grinding energy is consumed, consequently, an energy saving is obtained. Further studies have also indicated that, for the blended cements when the fly ashes were ground together with the clinker, the time required to obtain the same Blaine fineness as the laboratory produced Portland cement was reduced (Stoltenberg-Hanson 1984, Bouzoubaa 1998). This would effectively increase output from the shorter grinding time required; as more grinding could be achieved in the same time period, leading to reduced costs as output increases, not just from the addition of fly ash, but from this reduced grinding time.

The aims of this chapter are to study whether there is a benefit to the cement works at Aberthaw to introduce the Aberthaw fly ash to the ball mill during the cement manufacture process. Each of the three states of fly ash, (raw, processed and classified) were subjected to inter-grinding with clinker and further studied to see the effect that this process had on the resulting CEM II.

6.2   Grinding
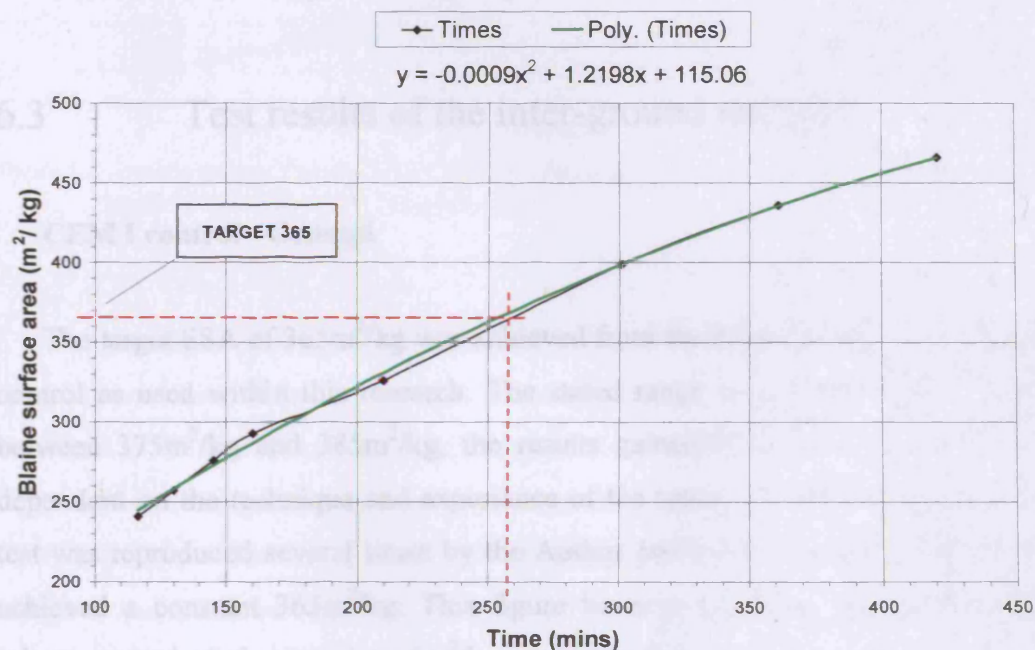
Figure 6.3 Graph plotting Time against Blaine specific surface area to establish a grinding time which achieves a material surface area of 365m²/kg

The grinding of the constituents of the cement (clinker, limestone and gypsum), together with the fly ash and grinding aid was carried out by the Author at Cardiff University, using a ball mill as described in Chapter 3. The clinker and limestone were reduced in size by crushing firstly using a jaw crusher followed by a gyratory crusher in order to reduce the grinding time. The constituents were then weighed into a container mixed and poured into the ball mill. The grinding time for the constituents was found by comparing the Blaine Specific Surface Area (SSA) of the CEM I ground in the laboratory to that as produced by Aberthaw cement works. This was achieved by measuring the SSA of the material over periods of time and plotting the

results on to a chart. The target SSA was $365m^2/kg$ and the time required to achieve this was calculated as 258 minutes (4hours 18minutes), Figure 6.3 presents the results from this. The full method can be found in Chapter 3, Experimental Methods.

The mix designs used for researching the inter-grinding of the materials were identical to the designs used throughout this research. Two replacement percentages were used that of 27% and 33%, as these gave good results in the previous work, the 33% being mixed with concrete whilst the 27% material was tested as mortar only. The cement contents used for the concrete mix designs were $140kg/m^3$, $300kg/m^3$ and $450kg/m^3$.

6.3   Test results of the inter-ground material

CEM I control - Ground

The target SSA of $365m^2/kg$ was achieved from the Blaine analysis on the CEM I control as used within this research. The stated range used at the cement works is between $375m^2/kg$ and $385m^2/kg$, the results gained from this test are, however, dependent on the technique and experience of the tester. For this reason, the Blaine test was reproduced several times by the Author and it was recorded that the results achieved a constant $365m^2/kg$. This figure became the target for fineness with a tolerance used of plus or minus $5m^2/kg$ as used within the industry. The average SSA for the ground CEM I has been reported as $360m^2/kg$ which is within the accepted range.
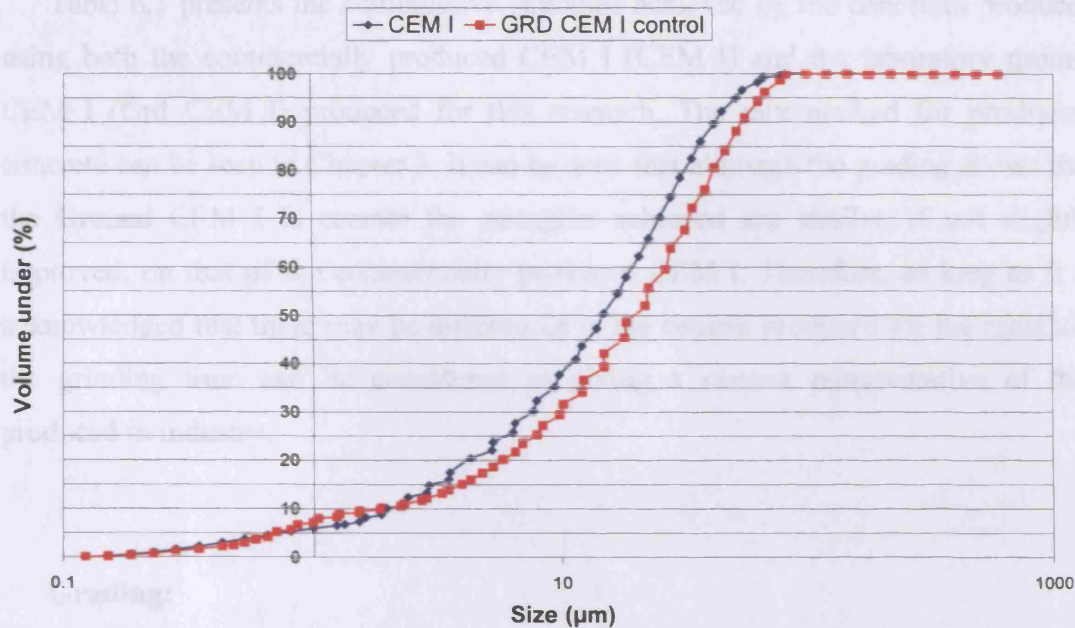
Figure 6.4 Grading comparison between CEM I produced at the cement works and the CEM I ground using the ball mill within the laboratory

The grading of the CEM I and the laboratory Ground CEM I (GRD CEM I) controls was carried out using the Mastersizer X laser sizer as per the method described in Chapter 3, and the results can be seen in Figure 6.4. It can be seen from Figure 6.4 that the grading curves do not exactly match each other and that the GRD CEM I is coarser than the CEM I. The difference between the two materials appears marginal and it can be seen that the ground CEM I is in the region of 10% coarser than the CEM I. The effect of this difference in fineness, if any, would be in the increase in free water requirement which would then affect the compressive strength of the concrete made using this material due to the increased water / binder ratio.

Table 6.1
Compressive strength of concrete comparison between the CEM I control and the laboratory ground CEM I (Grd CEM I)

Cement content (kg/m³)	Compressive strength (N/mm²)	
	CEM I	Grd CEM I
140	14	16
300	50	51
450	68	65

Table 6.1 presents the compressive strengths achieved by the concretes produced using both the commercially produced CEM I (CEM I) and the laboratory ground CEM I (Grd CEM I) produced for this research. The mix method for producing concrete can be seen in Chapter 3. It can be seen that although the grading shows that the Ground CEM I is coarser the strengths achieved are similar, if not slightly improved, on that of the commercially produced CEM I. Therefore, as long as it is acknowledged that there may be differences in the cement produced for the research, the grinding time can be considered as giving a cement representative of that produced in industry.

Grading:

On establishing the grinding time, the fly ash was mixed with the clinker, limestone and gypsum and inter-ground in the ball mill to produce a blended CEM II cement. The grinding method is detailed in Chapter 3. Figures 6.5 and 6.6 show the grading of the blended materials at both 27% replacement and 33% replacement respectively. It can be seen that in both instances the blended materials produce a finer material than that of the ground CEM I control. The outstanding feature of this is the fact that the raw fly ash, when inter-ground at 33%, produces a much finer mid range material than that of the processed fly ash and is comparable with the grading of the classified fly ash. The grading of the raw fly ash, detailed in Chapter 4, showed it to be the coarsest of all the researched materials; however, the process of inter-grinding has produced this fine material. At 27% replacement, the grading of the CEM II cements have a wider spread than those at the 33% replacement and their order tends to match that of their individual grading, i.e. classified being the finest material with the raw being the coarsest. However, both cases show an improvement on the fineness of the CEM I.
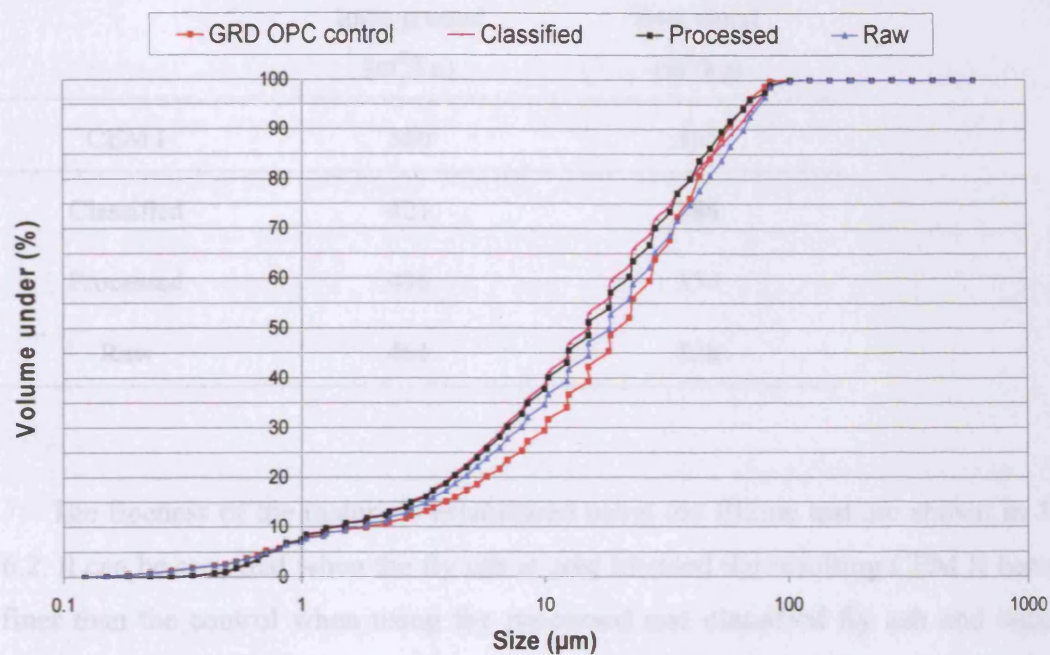
Figure 6.5 Grading of inter-ground CEM II cement at 27% fly ash replacement 73% OPCRM
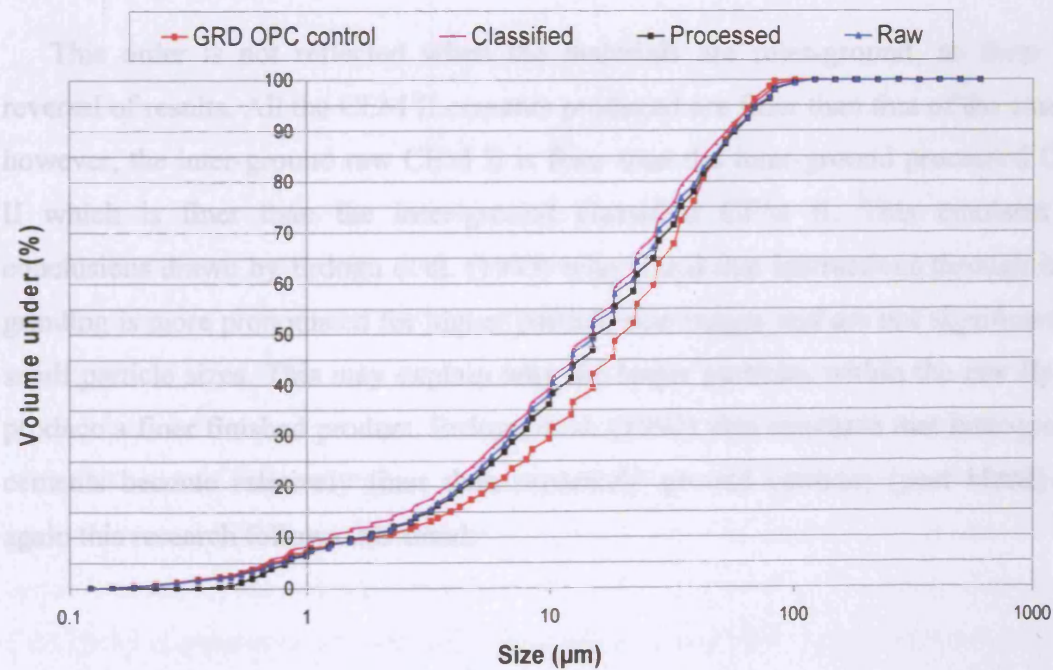
Figure 6.6 Grading of inter-ground CEM II cement at 33% fly ash replacement 67% OPCRM

Table 6.2 Fineness of the cements at 33% replacement using the Blaine test

	Inter-ground (m^2/kg)	Post blend (m^2/kg)
CEM I	360	365
Classified	421	386
Processed	436	374
Raw	461	338

The fineness of the materials established using the Blaine test are shown in Table 6.2. It can be seen that when the fly ash is post blended the resulting CEM II becomes finer than the control when using the processed and classified fly ash and becomes coarser when using the coarser grade of the raw fly ash. This reflects the particle size distribution of the individual fly ash materials, whereby the classified material is finer than the CEM I the processed fly ash is generally finer than the CEM I and the raw fly ash is coarser than the CEM I, refer to Chapter 4.

This order is not reflected when the materials are inter-ground, as there is a reversal of results. All the CEM II cements produced are finer than that of the control; however, the inter-ground raw CEM II is finer than the inter-ground processed CEM II which is finer than the inter-ground classified CEM II. This emulates the conclusions drawn by Erdogu et al. (1999) who stated that interactions through inter-grinding is more pronounced for higher particle size ranges and are not significant for small particle sizes. This may explain why the larger particles within the raw fly ash produce a finer finished product. Erdogu et al. (1999) also conclude that inter-ground cements become relatively finer than separately ground cements (post blend) and again this research follows this trend.

Compressive strength

Ultimately, any cementitious material will be required to produce concrete, so a measure of the compressive strength within concrete requires examination. The blended 33% fly ash produced through inter-grinding has been used to produce concrete using the method stated in Chapter 3. Three concrete strengths have been studied, namely 140kg/m³, 300kg/m³ and 450kg/m³, and the 28 day compressive strength results are presented in Table 6.3 below.

Table 6.3
Compressive strength comparison of concretes containing CEM I a blended GGBS 50% /50% and the inter-ground fly ash at 33% fly ash 67% CEM I

	Compressive strength (N/mm²)					
Cement content (kg/m³)	CEM I	GGBS 50% CEM I 50%	Ground CEM I	Inter-ground Classified ash 33%	Inter-ground Process ash 33%	Inter-ground Raw ash 33%
140	14	15	16	14	10	10
300	50	40	51	50	41	37.5
450	68	59	65	66	62	54

The inter-ground classified ash blend produces the best results from all the fly ash blends. The blend competes with the CEM I controls at each cement content and generally betters that of the blended GGBS control. The inter-ground processed fly ash shows a compressive strength in the region of 33% lower than the control mixes at the 140kg/m³ cement content. The higher cement contents slightly improve on that of the blended GGBS mix, but only compete with the CEM I controls at the 450kg/m³ cement content. The inter-ground raw fly ash fails to compete with the CEM I controls at any of the cement contents being in the region of 33% weaker throughout. This blend compares more favourably to the blended GGBS control and even though it fails to match the strength of the GGBS the results fall within 5N/mm² at each cement content.
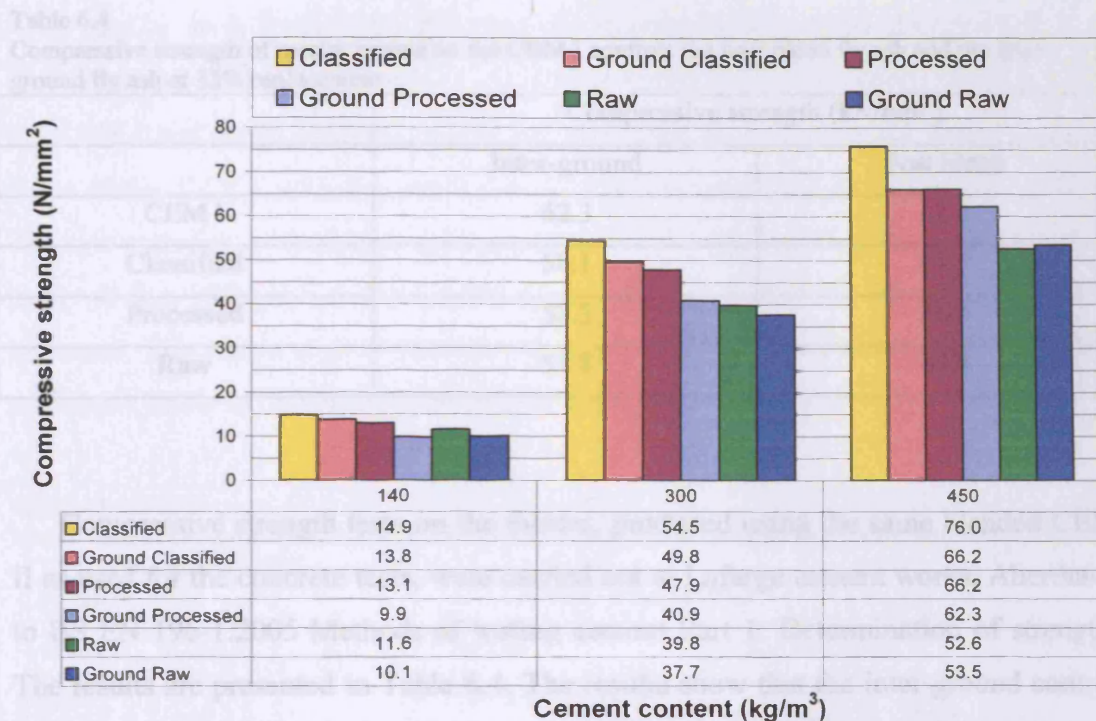
Figure 6.7 Comparison between compression strength of post blend and inter-ground (Ground) concrete at 33% fly ash replacement 67% CEM I

	140	300	450
Classified	14.9	54.5	76.0
Ground Classified	13.8	49.8	66.2
Processed	13.1	47.9	66.2
Ground Processed	9.9	40.9	62.3
Raw	11.6	39.8	52.6
Ground Raw	10.1	37.7	53.5

Figure 6.7 examines the compressive strength of the concrete produced using the inter-ground CEM II and the post blend CEM II. From Figure 6.7 it can be seen that, with the exception of the 450kg/m³ cement content containing the raw fly ash, the post blend material out performs that of the inter-ground material at each cement content and blend. Although there is generally little difference between the compressive strengths at the lower cement content, the differences are more significant as the cement contents increase, with a 10N/mm² improvement by the classified over the ground classified at 450kg/m³ cement content.

Table 6.4
Compressive strength of mortar prisms on the CEM I controls the post blend fly ash and the inter-ground fly ash at 33% replacement

	Compressive strength (kN/mm^2)	
	Inter-ground	Post blend
CEM I	62.3	62.4
Classified	58.1	47.3
Processed	58.3	46.3
Raw	51.8	43.6

Compressive strength tests on the mortar, produced using the same blended CEM II as used for the concrete tests, were carried out at Lafarge cement works, Aberthaw, to BS EN 196-1:2005 Methods of testing cement Part 1: Determination of strength. The results are presented in Table 6.4. The results show that the inter-ground control CEM I produces a similar result to that of the post blend CEM I increasing confidence in the grinding procedure employed. The inter-ground material shows improved compressive strength at each state of fly ash over their post blend comparison. This is in stark contrast to the compressive strength results of the concrete, where the post blend material gave the best performance. It is interesting to see that whilst the post blend material follows the expected pattern of the classified material giving the stronger mortar, the inter-ground does not. Both the classified and processed materials give similar results to each other, with the processed slightly improved on that of the classified, whilst the expected drop in compressive strength is recorded for the raw material.

Water / binder ratio

The water / binder ratios for the concrete produced using the inter-ground material are presented in Table 6.5 below. Examining the control CEM I and the laboratory ground CEM I it can be seen that the water requirements are similar to each other at each cement content. Again, these similar results shows that the laboratory ground CEM I produces a satisfactory cement to use a comparison.

It can be seen from Table 6.5 that the inter-ground material shows lower w/b ratios than the GGBS in all cases. The classified material shows improvement on both the CEM I and ground CEM I, whilst the processed fly ash gives identical results to those of the CEM I with the slight variation when compared to the ground CEM I. The raw material gives similar results to those of the processed fly ash being slightly lower at the 140kg/m³ cement content, but slightly higher as the cement content increases. The higher cement contents of 300kg/m³ and 450kg/m³ are all within their respective limits as required by the British Standards.

Table 6.5
Water / binder comparison between concrete mixes using CEM I controls and the inter-ground fly ash at 33% fly ash 67% CEM I

Cement content (kg/m³)	Water / binder ratio						
	CEM I	GGBS	Ground CEM I	Inter-ground (33%)			BS 8500 Limit
				Classified	Processed	Raw	
140	1.06	1.43	1.09	0.94	1.06	1.02	-
300	0.47	0.56	0.46	0.40	0.47	0.48	0.6
450	0.34	0.41	0.36	0.31	0.34	0.36	0.45

Table 6.6 presents a comparison of the w/b ratios between the inter-ground material and the post blend. It can be seen that all of the inter-ground results have lower w/b ratios than their respective post blend results. This lower water content would normally have been a major factor to the compressive strength; however, it has been shown that the compressive strength of the post blend material exceeds that of the inter-ground at all cement contents.

Table 6.6
Water / binder ratios comparison between concrete mixes using inter-ground and post blend fly ash

Cement content (kg/m3)	Inter-ground (33%)			Post blend (33%)		
	Classified	Process	Raw	Classified	Processed	Raw
140	0.94	1.06	1.02	1.23	1.30	1.31
300	0.40	0.47	0.48	0.48	0.57	0.59
450	0.31	0.34	0.36	0.37	0.40	0.47

The mortar tests were carried out to BS EN 196-1 Methods of testing cement - Part 1: Determination of strength. This standard has a requirement that the water cement ratio be fixed at 0.5.

Durability

Figures 6.8 and 6.9 show the graphical results of the permeability tests on concrete containing the three inter-ground fly ash mixes (classified, processed and raw), with the ground CEM I and the control CEM I. The results are tabulated in Table 6.7 giving a clearer indication as to the value achieved, in time, by the various samples. Table 6.6 includes the results from the previous work on the post blend fly ash for completion. This work was carried out using the procedure described in Chapter 3.
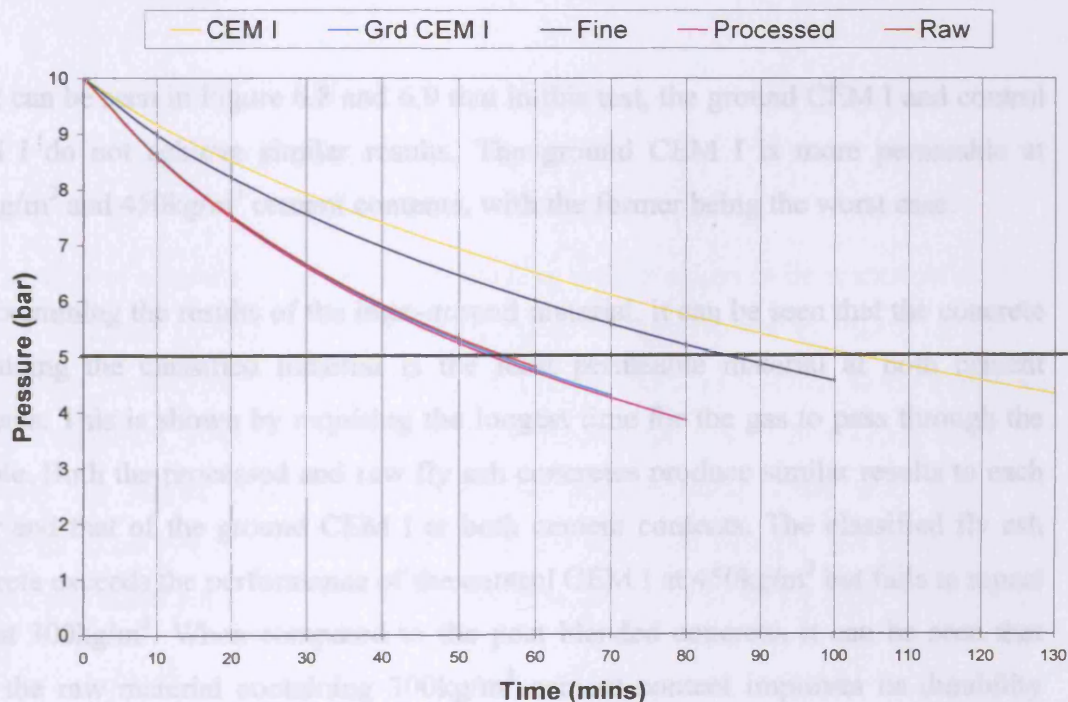
Figure 6.8 Permeability results for the CEM I as compared to the inter-ground fly ash at 300kg/m³ cement content and 33% replacement 67% CEM I
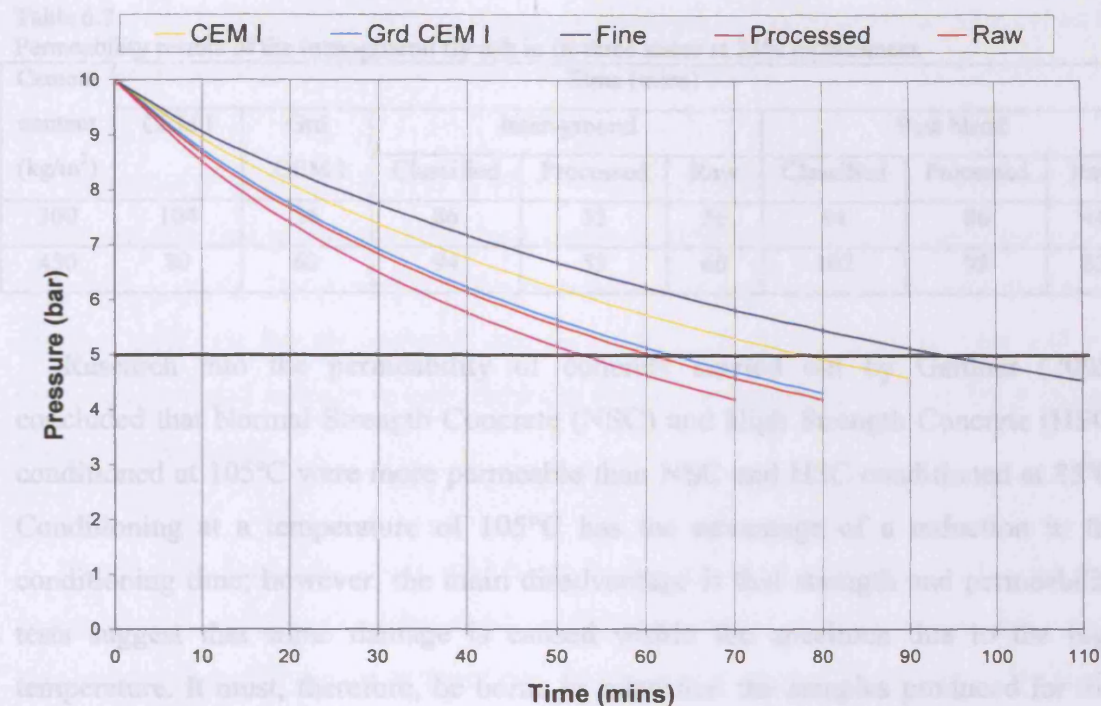
Figure 6.9 Permeability results for the CEM I as compared to the inter-ground fly ash at 450kg/m³ cement content and 33% replacement 67% CEM I

It can be seen in Figure 6.8 and 6.9 that in this test, the ground CEM I and control CEM I do not achieve similar results. The ground CEM I is more permeable at 300kg/m³ and 450kg/m³ cement contents, with the former being the worst case.

Examining the results of the inter-ground material, it can be seen that the concrete containing the classified material is the least permeable material at both cement contents. This is shown by requiring the longest time for the gas to pass through the sample. Both the processed and raw fly ash concretes produce similar results to each other and that of the ground CEM I at both cement contents. The classified fly ash concrete exceeds the performance of the control CEM I at 450kg/m³ but fails to repeat this at 300kg/m³. When compared to the post blended concrete, it can be seen that only the raw material containing 300kg/m³ cement content improves its durability over the post blend material, all other inter-ground blends at both cement contents fail to better the post blend results and are, therefore, less durable.

Table 6.7
Permeability results of the inter-ground fly ash in its three states at 33% replacement

Cement content (kg/m³)	Time (mins)							
	CEM I	Grd CEM I	Inter-ground			Post blend		
			Classified	Processed	Raw	Classified	Processed	Raw
300	104	56	86	55	56	94	86	44
450	80	62	94	53	60	102	98	82

Research into the permeability of concrete carried out by Gardner (2005) concluded that Normal Strength Concrete (NSC) and High Strength Concrete (HSC) conditioned at 105°C were more permeable than NSC and HSC conditioned at 85°C. Conditioning at a temperature of 105°C has the advantage of a reduction in the conditioning time; however, the main disadvantage is that strength and permeability tests suggest that some damage is caused within the specimen due to the high temperature. It must, therefore, be borne in mind that the samples produced for this study were all conditioned using a temperature of 105°C and may, therefore, be prone to this internal damage.

6.4   Cost analysis

The cost of a product is often the overriding consideration in its marketability and general customer satisfaction. Consequently, all costs involved in manufacturing a high quality product must be fully analysed. The total cost of manufacturing a product includes materials, plant and equipment, labour and fixed costs. The material costs are generally the largest percentage of the total manufacturing costs and should be monitored to control wastage and also to ensure value for money. The possibility of substituting materials is an important consideration in minimising costs (Kalpakjian 2001).

As with all commercially led projects, the financial implications on the company need to be explored along with the materials performance. This section reports upon cost analysis software, designed and produced by the Author, which analyses the cost of a concrete mix, by exploring its constituents, and projects cost implications based on past sales data. Through manipulation of the material quantities within a mix, and

the costs associated with each material, a decision as to whether a new material should be implemented within the mix design can be made.

The concept of the model was to allow the investigation of different cost scenarios within the mix design, and supplier cost range, to predict financial changes associated with each scenario. For example, if a new supplier, or new material, became available, the new cost rate for the material can be substituted for the existing rate and the projected potential savings in cost between the two rates analysed from the previous twelve months sales.

The Results Summary sheet, which can be viewed in Appendix 4, on the disc and as a hard copy at the back of this thesis, collates all the information and presents it on two pages as a confirmation of input and its associated output. Sheet one presents the input displayed as input for Mix 1 at the top and Mix 2 below this. This confirms the costs, the description and the replacement percent of the cement and the replacement material. The average cost, per cubic metre, of each concrete designation is displayed enabling the differences to be viewed. The total saving for each of these designations is then presented as a breakdown of concrete categories and total.

Sheet two breaks the results down further identifying the savings to be made from each individual mix design. These costs are based on past sales; therefore, showing the potential available if the material had been introduced into production twelve months earlier. The cement addition column tells you if additional cement has been added, possibly to make up the strengths if the performance of a particular cement replacement is not quite good enough. The next column shows the cost difference from the perspective of mix 2, as this would be the comparative mix. The best combination is then shown with the material producing the more cost effective mix identified in the last column. If the mix 1 material produces the more cost effective mix then the best combination column becomes zero as no benefit has been gained and the variance from mix 2 becomes a negative value as by its introduction a loss would be made from incorporating this material into these mix designs. The material column has been introduced so as to help recognise those mix designs into which the company will benefit from the introduction of the new cement replacement.

This model is by no means the completed article as the final user will no doubt have thoughts on its progression and continual improvement. At this point the model serves its purpose and achieves what is required for this research.

A copy of the model and user manual can be found in Appendices 3 on the disc accompanying this Thesis.

Table 6.8
Results summary sheet one as output from the cost analysis showing input data and collated results

Results Summary

Page 1 of 2

Mix 1						
	Cost (ton)	Material	Percentage			
			Designed	Proprietary	Designated	Standardised
Cement	63.7	Blue Circle	50	50	50	40
Replacement	53.33	GGBS	50	50	50	60
Cost (m^3)			£164.72	£65.54	£168.87	£78.46

Mix 2						
	Cost (ton)	Material	Percentage			
			Designed	Proprietary	Designated	Standardised
Cement	63.7	Blue Circle	70	70	70	70
Replacement	19	PFA	30	30	30	30
Cost (m^3)			£141.57	£56.32	£145.14	£68.65

Total saving per mix			£57,273.46	£26,749.10	£26,654.95	£3,754.12

Total concrete sales (m^3)		56240.35
Total concrete cost mix 1	£	817,410.75
Total concrete cost mix 2	£	702,979.13
Variance	£	114,431.62

	Designed	Proprietary	Designated	Standardised	Total
Variance from mix 2	£57,273.46	£26,749.10	£26,654.95	£3,754.12	£114,431.62
Best combination of mix 1 and 2	£57,273.46	£26,749.10	£26,654.95	£3,754.12	£114,431.62

Notes :

Table 6.9
Results summary sheet two as output from the cost analysis examining the cost implications of various mix designs

Results Summary

Page 2 of 2

Mix	Mix 1	Mix 2	Cement	Variance from	Best		Material
Designed	Total cost	Total cost	Addition	mix 2 only	Combination		
C8/10	£ 3,137.57	£ 2,696.55	0	£ 441.02	£ 441.02		PFA
C12/15	£ 1,328.00	£ 1,141.33	0	£ 186.67	£ 186.67		PFA
C16/20	£ 104,209.36	£ 89,561.46	0	£ 14,647.90	£ 14,647.90		PFA
C20/25	£ 20,349.47	£ 17,489.10	0	£ 2,860.37	£ 2,860.37		PFA
C25/30	£ 43,758.25	£ 37,607.49	0	£ 6,150.76	£ 6,150.76		PFA
C28/35	£ 112,557.00	£ 96,735.73	0	£ 15,821.26	£ 15,821.26		PFA
C32/40	£ 43,144.57	£ 37,080.07	0	£ 6,064.50	£ 6,064.50		PFA
C35/45	£ 733.78	£ 630.64	0	£ 103.14	£ 103.14		PFA
C25/30 P	£ 10,199.46	£ 8,765.80	0	£ 1,433.66	£ 1,433.66		PFA
C28/35 P	£ 61,674.81	£ 53,005.66	0	£ 8,669.15	£ 8,669.15		PFA
Proprietary				£ 57,273.46	£ 57,273.46		
RCM	£ 78,595.01	£ 67,547.52	0	£ 11,047.49	£ 11,047.49		PFA
GPM	£ 371.28	£ 319.09	0	£ 52.19	£ 52.19		PFA
HFM	£ 15,766.87	£ 13,550.64	0	£ 2,216.23	£ 2,216.23		PFA
LFM	£ 56,995.07	£ 48,983.72	0	£ 8,011.36	£ 8,011.36		PFA
PQM	£ 38,572.50	£ 33,150.67	0	£ 5,421.84	£ 5,421.84		PFA
Designated				£ 26,749.10	£ 26,749.10		
RC 30	£ 2,848.39	£ 2,448.02	0	£ 400.38	£ 400.38		PFA
RC 35	£ 98,307.69	£ 84,489.34	0	£ 13,818.35	£ 13,818.35		PFA
RC 40	£ 10,855.70	£ 9,329.80	0	£ 1,525.90	£ 1,525.90		PFA
RC 35 P	£ 23,270.25	£ 19,999.33	0	£ 3,270.92	£ 3,270.92		PFA
Gen 1	£ 23,179.84	£ 19,921.63	0	£ 3,258.21	£ 3,258.21		PFA
Gen 2	£ 5,665.42	£ 4,869.08	0	£ 796.34	£ 796.34		PFA
Gen 3	£ 18,688.81	£ 16,061.87	0	£ 2,626.94	£ 2,626.94		PFA
PAV 1	£ 6,215.02	£ 5,341.43	0	£ 873.60	£ 873.60		PFA
FND2	£ 105.33	£ 90.52	0	£ 14.81	£ 14.81		PFA
FND3	£ 389.12	£ 334.43	0	£ 54.70	£ 54.70		PFA
				£ 26,654.95	£ 26,654.95		
Totals =				£ 114,431.62	£ 114,431.62		

6.5 Conclusions

From the work carried out in this Chapter the conclusions are:

o   It is possible to reproduce CEM I using a ball grinder in a laboratory which reflects the properties and characteristics of a CEM I produced in industry

o   Inter-grinding fly ash with the raw materials required to make a CEM I material increases the fineness of the finished product when ground for the same period of time. To produce a similar fineness to the CEM I would necessitate a reduction in the grinding time which would provide time and cost benefits

o   Inter-grinding fly ash with the raw materials required to make a CEM I material has no benefit over a similar post blend fly ash mix with respect to compressive strength.

o   Mortar benefits from increased compressive strength when the fly ash is inter-ground

7. Conclusions and Recommendations

7.1 Conclusions

7.2 Recommendations for further study

7.1 Conclusions

The conclusions established from this thesis which looks to advance the understanding and use of waste materials as cement replacements within concrete are summarised below:

- o Applying the STi process to the fly ash is a quick and easy method of lowering the carbon content within the ash producing a material which satisfies both British and European standards. Utilising this process has produced a usable fly ash which, when blended at 33% fly ash to 67% OPC, has shown a concrete compressive strength improvement over that of the industry standard 50% GGBS blended with 50%OPC.

- o Reducing the particle size of the fly ash further through classification provides additional compressive strength benefits to the concrete containing the CEM II cement.

- o Some indication as to whether an unknown material will work as a cement replacement can be gained from the analysis performed within this thesis. Materials can be judged on their suitability to perform as cement replacement materials through the analysis of certain material properties. These properties have been established through the work on the processed fly ash. The measured properties are the chemical constituents, concentrating mainly on SiO_2, Al_2O_3, CaO and Fe_2O_3, and the acceptable

ranges of a candidate material have been presented. Loss on ignition as required by the British and European standards is to be below 7%, whilst the material fineness is required to match that of the OPC.

o It is possible to reproduce CEM I using a ball grinder in a laboratory which accurately reflects the properties and characteristics of a CEM I produced in industry. Whilst inter-grinding fly ash with the raw materials required to make a CEM I an increase in material fineness, of the final CEM II, was observed this provides economic advantages to the cement manufacture industry. However, the inter-grinding of fly ash in this way has no benefit, when mixed as concrete, over a similar post blend fly ash mix with respect to compressive strength. This was found not to be the case with the compressive strength of mortar, however, as there is benefit from increased compressive strength when the fly ash is inter-ground.

7.2 Recommendations for further study

This research is viewed as a first step into producing a workable specification for the requirements of a cement replacement material. Further work required to progress this research further is discussed below:

o It is well known in the cement and concrete industry that laboratory trials are the results of idealised circumstances and generally do not reflect exactly that which happens in industry. Therefore, full scale plant trials should be initiated using various mix designs to assess a more realistic performance of the materials being trialled.

o Fly ash and GGBS are just two materials that industry has accepted for use as a cement replacement. It has been shown that the properties of these two materials vary considerable yet both contribute to, and improve, cement properties. Other established materials, such as metakaolin and silica fume,

should be examined and their attributes documented alongside the findings of this research. This could offer a further dimension to the properties of a cement replacement or improve the requirements already highlighted. Further work needs to be done to examine the variables documented and judge them against other accepted cement replacement materials.

o The Industrial mix (IM) was included in this research as it had compared favourably with CEM I when tested as a mortar. As a concrete, the material failed to produce comparable compressive strength results to the controls and, therefore, is not suitable as a cement replacement in its present form. The analysis identified that the elemental make up of the material did not match any of the suggested forms. If this matter is addressed, the resulting blended material produced may show enhanced performance becoming a functional material.

8. References

8.1 References
8.2 World wide web references
8.3 British and European standards

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8.3 British and European standards

The major British and European standards relevant to this research are presented below.

BS EN 206-1:2000 "Concrete – Part 1: Specification, performance, production and conformity"

BS EN 8500-1:2002 "Concrete – Complimentary British Standard to BS EN 206-1 – Part 1: Method of specifying and guidance for the specifier"

BS EN 8500-2:2002 "Concrete – Complimentary British Standard to BS EN 206-1 – Part 2: Specification for constituent materials and concrete"

BS EN 197-1:2000 "Cement – Part 1: Composition, specifications and conformity for common cements"

BS EN 450-1:2005 "Fly ash for concrete – Part 1: Definition, specifications and conformity criteria"

BS EN 450-2:2005 "Fly ash for concrete – Part 2: Conformity evaluation"

BS EN 196- Methods of testing cement – Parts 1 - 3 and 5 - 9

BS EN 12620: 2002 "Aggregates for concrete"

BS EN 12390 – "Testing hardened concrete" Parts 1 - 8

BS EN 12350 – "Testing fresh concrete" Parts 1 - 7

9. Appendices

These Appendices can be viewed on the CD-ROM accompanying this thesis. The research paper can be seen as a hard copy at the rear of this thesis as can the cost analysis results sheets.

1 – Mix designs

      1.1 – Design sheets

2 – Aggregate

      2.1 – Aggregate properties

      2.2 – Aggregate properties

3 – Results from analysis

      3.1 – Chemical analysis

      3.2 – Compressive strength

      3.3 – Permeability

      3.4 – Particle grading

      3.5 – SEM

      3.6 – TEM

      3.7 – XRD

      3.8 – Collated materials

      3.9 – Tensile strength

      3.10 – Mortar results

      3.11 – Specific gravity

      3.12 – Grinding

Influence of cement replacement materials on properties of concrete products – strength, durability and environmental stability.

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Cardiff University, UK

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ABSTRACT

This paper presents the experimental results of an ongoing investigation into various properties related to the performance and durability of concretes made using existing and new cement replacements. The process of cement and concrete production is investigated focusing on product performance and environmental performance. The overriding factor for the progression of a material will be product performance however; each material selected will have many intrinsic environmental benefits.

The study combines Ordinary Portland Cement (OPC) with each cement replacement candidate using the most common replacement percentages, 10, 20, 25, 30 and 50 percent. A 35N/mm^2 concrete is then prepared and analysed in the fresh and hardened state. In addition, a chemical and physical analysis of each replacement material has been performed and results compared to the control samples containing OPC only and Ground Granulated Blast Furnace Slag (GGBS) as a replacement.

The results show that in their present form the replacements used in this research do not compare with the strengths achieved by the controls. The right balance of chemical composition and particle grading needs to be achieved to produce a realistic replacement material. The processes required to achieve this must strike a balance between monetary and environmental cost.

1. INTRODUCTION

The past ten years have shown an increasing emphasis on sustainable development within industry throughout the UK. By the ratification of the Kyoto protocol, industrialised countries have targets set to lower overall emissions of greenhouse gases. In the UK a climate change levy has been introduced which taxes the use of energy in industry, commerce and the public sector, with offsetting cuts in employers National Insurance Contributions and additional support for energy efficient schemes and renewable sources of energy. The introduction of the EC Directive on the Landfill of wastes 1999/31/EC requires the appropriate treatment of waste streams prior to landfill to reduce their hazard, volume and facilitate handling and/or enhance recovery (Davies, 2003). Industry is being encouraged to minimise its waste and is being penalised through landfill taxes for not doing so.

In the production of concrete, cement manufacture accounts for the highest cost and is the most energy intensive process from all its constituents. The production of OPC contributes significantly to CO_2 emissions. For every tonne of Portland cement produced, approximately one ton of CO_2 is released into the atmosphere (Bouzoubaa et al, 1997). This equates to 5% of global emissions originating from cement production (Hendricks et al, 2004).

As part of the Kyoto agreement, European countries have agreed to an 8% reduction in

Greenhouse Gas emissions, based on 1990 levels, by the year 2012. The cement manufacturing industry is one where quotas have been imposed by the European Union (EU) to cap hazardous emissions. Failure to meet the obligations of the agreement will result in heavy fines however; improving on these limits can provide financial benefits (Defra, 2006). Already the industry has demonstrated its ability to improve its climate change performance. Between 2001 and 2004 an improvement in energy consumption of 21.2% had been achieved and is well on its way to the 2010 target of 26.8% reduction (BCA). Short term actions are to include maximising the use of waste as fuels and replacement materials for the principal cement raw material, limestone.

The European standard BS EN 450-1 covers a range of fly ash produced by the combustion of hard coal. Co-combustion with certain materials is allowed within this standard, however fly ash produced from the burning of other materials alone is not. It has been reported that the use of hard coal produced fly ash has turned out to be beneficial with regards to the properties of the concrete, especially in relation to its resistance to aggressive species (Bertolini, 2004). This being the case, could other ashes, at present being condemned to landfill sites, also be of benefit to the properties of concrete.

On completing this initial study it will be possible to identify if a particular ash is acceptable as a safe replacement material for cement and if so the environmental benefits gained from its use.

2. MATERIALS

Three types of ash, a blend of industrial wastes and a GGBS have been selected for this study and compared with a control mix of neat OPC. The OPC has been produced to meet the specification as required by BS EN 197 while the GGBS, also used as a control due to its already proven benefits within concrete, complies with the requirements of BS 6699.

The three ashes used in the study are from a coal fired power plant (FA), a municipal solid waste incineration plant (MSW), and a sewage sludge incineration plant (SS). Only FA has been processed and prepared for supply back into industry, the remaining two are raw materials direct from the incinerator.

IM combines several industrial wastes each chosen for their chemical compositions. Each of these waste materials contain elements similar to those found in OPC and hence could be viewed as being a substitute rather than a replacement.

Coarse aggregates used are crushed lime stone quarried locally with marine sand used as fine aggregate both conforming to BS EN 12620:2002.

A Portland cement (CEM I) 52.5N was used conforming to BS EN 197.

A water reducing and plasticizing agent (Sika Plastiment 160) was mixed with potable water (Cardiff city supply) quantified at 0.4% of the cement content. The use of additives within concrete is an accepted norm within the industry and any detrimental effects from their use need to be identified.

3. EXPERIMENTAL PROGRAM

3.1 Mix designs

The object of mix design is to determine the most appropriate proportions in which to use the constituent materials to meet the needs of the work. This research has based itself around a single design for a standard concrete with a cement content of 275kg/m^3. This design is used within industry and has been fashioned through the production of trial mixes. Its selection was based on its popularity through sales and having a cement quantity large enough to highlight the differences between materials and mix proportions.

3.2 Experimental procedure

There are two main variables within this study. Firstly, the amount of replacement material blended with the cement. BS 8500-2 gives an allowable range of 6 – 55%

combination fly ash/CEM I. Mixes used in this research contain 10, 20, 25, 30 and 50% replacement, by mass, as this is most representative of actual use.

Secondly, the amount of water required to obtain a controlled workability or consistency. Workability is the ease at which the concrete can be compacted, the ease at which the concrete can flow and ability of the concrete to remain a homogenous mass without the constituents segregating. The measure of consistency for this research was the slump test to BS EN 12350-2. BS EN 206-1 gives five consistency classes, S1 to S5, each with a range of slumps measured in millimetres. For general use the industry standard is an S2 with a range 50mm to 90mm the target being 70mm. Adding water to the mix reduces yield but also reduces cohesion. The addition of a dispersing admixture causes the cement particles to distribute more uniformly, therefore increasing the fluidity of the mix at a given water content. All of the mixes used within this research achieved a slump of 70mm.

3.3 Compressive strength

Traditionally, the compressive strength of concrete has been used as a tool for a measure of the quality. Both strength and durability are controlled by the ratio of cement contained within the mix design and water used to hydrate the mix. By ensuring an adequate strength has been achieved and the water/binder (w/b) ratio remains within British Standard limits a sufficient level of durability is also ensured. Testing for compressive strength has been carried out in accordance with BS EN 12390-3 at 1, 2, 7 and 28 days using concrete cubes of 100 x100 x 100 mm, w/b ratio limits are taken from BS EN 8500-2.

3.4 Particle distribution

The particle distribution and size are of particular significance to the use of a cement replacement material. To achieve a high strength low permeability and durable concrete, it is necessary to reduce the porosity
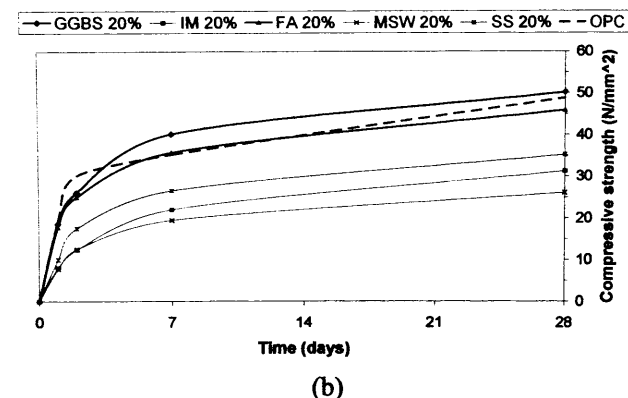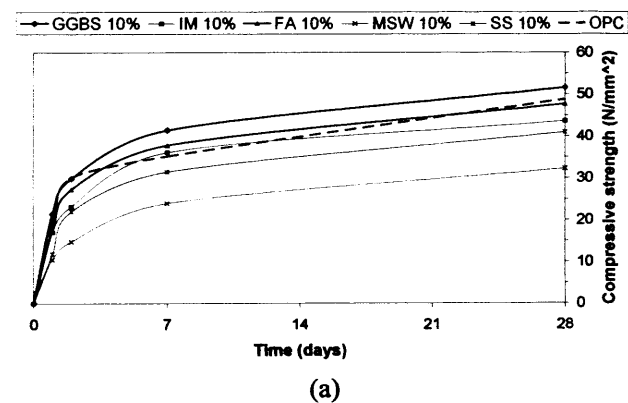
of the cement paste. It is well know that the incorporation of a pozzolanic material as a partial replacement of cement refines the porosity and pore size distribution of the paste (Chindaprsirt, 2005).

4. RESULTS AND DISCUSSION

4.1 Compressive strength

BS EN 206-1 states that the compressive strength of the concrete shall exceed the design strength by an adequate margin at 28 days. The margin given by the standard is twice the expected standard deviation and should fall between the values of 6 – $12N/mm^2$. The standard deviation used for this research is $3.5N/mm^2$, that of the company supplying the mix design. Therefore, the compressive strength at 28 days should be $42N/mm^2$ for conformity.

Figure 1 (a-e) shows the compressive strength of the concretes at 10, 20, 25, 30 and 50% replacement respectively together with the standard OPC mix. It is well recorded that concrete containing combination cements tend

(a)

(b)

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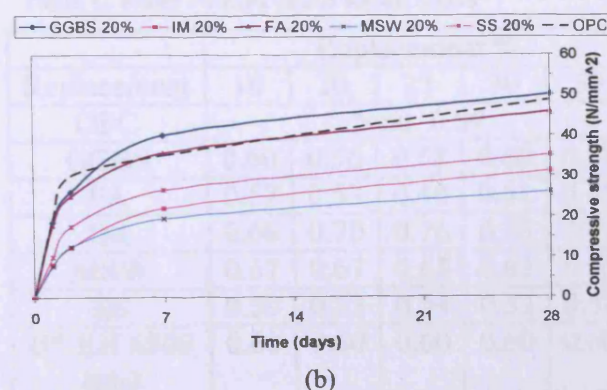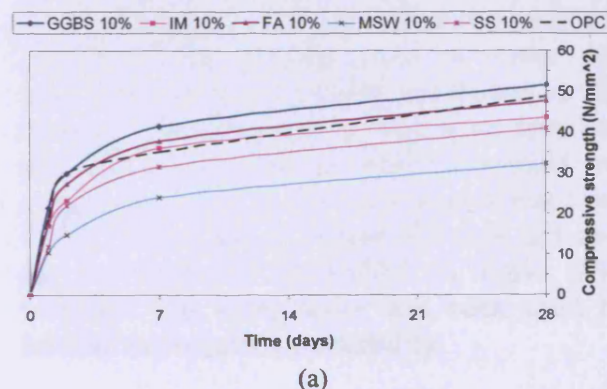
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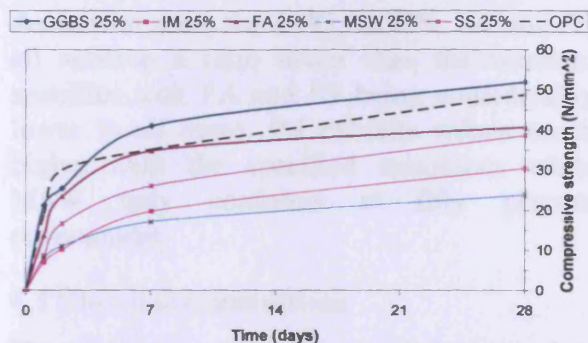
4. RESULTS AND DISCUSSION
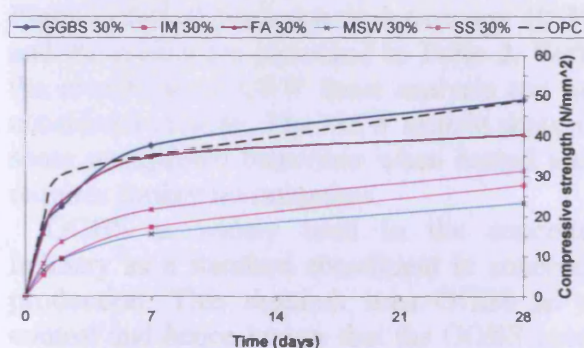
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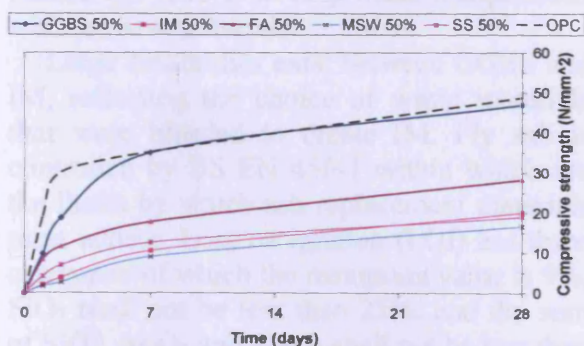

(a)

(b)

(c)

(d)

(e)

Figure1.Compression strength development for concretes with varying amounts of replacements

to gain strength slower than that of OPC alone, this is due to the pozzolanic reaction required between the SiO_2 and $Ca(OH)_2$. Kiattikomol reported on the effect of fineness of materials on setting times. It was found that mortars containing finer materials enhance early strength and achieve higher compressive strengths than mortars containing coarser materials (Kiattikomol, 2001). The results of the present study appear to follow that pattern with only the GGBS surpassing the OPC on day one. The coarser materials, SS and MSW

are both slow to start the strength gain and although progress, fail to achieve the strengths of OPC or GGBS. Remembering that the target strength is $42N/mm^2$ it can be seen that at 10% replacement MSW falls well short of the target at $32N/mm^2$ while SS is low at $41N/mm^2$ these are therefore non-conforming.

At 20% replacement the compressive strength of IM drops considerably to $31N/mm^2$. This now becomes non-conforming.

FA performs well up to 25% replacement where its compressive strength falls to $41N/mm^2$. There is very little change when the percentage of FA is increased to 30% with the strength reducing to $40N/mm^2$.

4.2 Water / binder ratio, w/b

There are two reasons for adding water to concrete, first to hydrate the cement and second to make the concrete workable. The water of hydration chemically binds in the cement hydrates while the water added for workability occupies a system of capillary pores. The more of these pores produced the weaker and less durable the final concrete will be. The w/b ratio will determine the capillary porosity of the cement paste. A lower w/b ratio will see more cement distributed in the mixing water through the aggregate particles and the larger part of space occupied by mixing water will be filled by cement reaction. Table 1 shows the w/b ratios for each mix and the limit from BS EN 8500-2. A higher ratio indicates that more water has been used to achieve the required workability.

Table 1. Water / binder ratios for all mixes

Replacement	Replacement %				
	10	20	25	30	50
OPC	Neat 0.59				
GGBS	0.60	0.56	0.58	0.60	0.58
FA	0.57	0.53	0.48	0.51	0.55
IM	0.66	0.70	0.76	0.73	0.71
MSW	0.67	0.67	0.65	0.62	0.51
SS	0.59	0.53	0.54	0.52	0.51
BS EN 8500 limit	0.60	0.60	0.60	0.60	0.60

As can be seen, the OPC, GGBS, FA and SS all achieve a ratio lower than the standard specifies with FA and SS being considerably lower in all cases. IM exhibits values much higher than the specified maximum while MSW only conforms at fifty percent replacement.

4.3 Chemical compositions

The chemical compositions of the materials were analysed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP) and the results are presented in Table 2. With the exception of MSW these analysis can be considered reliable. The MSW sample showed some unexpected behaviour when heated and requires further investigation.

GGBS is widely used in the concrete industry as a standard constituent in concrete production. This research uses GGBS as a control and hence knows that the GGBS used adheres to all specifications. The analysis carried out here is to help make comparisons with the new materials.

Large similarities exist between GGBS and IM, reflecting the choice of waste materials that were blended to create IM. Fly ash is controlled by BS EN 450-1 within which are the limits by which ash replacement materials must adhere. Loss on ignition (LOI) has three categories of which the maximum value is 9%, SiO_2 shall not be less than 25%, and the sum of $SiO2$ Al_2O_3 and Fe_2O_3 shall not be less than 70% all of these by mass.

Studying the three ashes, FA, MSW and SS, we can see that FA and MSW fall outside the LOI boundary. Further to this MSW fails to achieve the sum of 70% by mass of the three elements by a considerable amount. The FA and SS samples exceed the minimum SiO_2 content, however again MSW falls well short of the target figure.

4.4 Grading

BS EN 450-1 Section 5 identifies two categories, N and S. Category N requires that no more than 40% be retained on a 45μm sieve while category S requires no more than

Table 2. Chemical analysis of replacements

	OPC	GGBS	IM	FA	MSW	SS
SiO_2	20.3	32.8	39.6	50.1	2.5	33.5
Al_2O_3	4.2	12.8	12.2	27.3	0.8	15.8
Fe_2O_3	2.2	0.3	1.6	2.7	0.9	20.8
MgO	2.5	7.9	11.5	1.6	0.6	1.8
MnO	0.1	0.4	0.3	0.0	0.0	0.2
CaO	66.3	39.3	25.7	7.2	41.0	9.8
K_2O	0.6	0.5	0.8	0.6	3.2	1.5
Na_2O	0.2	0.3	0.7	0.2	3.9	0.9
TiO_2	0.2	0.7	0.3	1.3	0.2	0.9
BaO	0.0	0.1	0.2	0.2	0.0	0.1
LOI	4.9	1.0	2.9	10.3	9.8	5.5

12% be retained. Grading of the materials was carried out using a Mastersizer X laser sizer from Malvern Instruments; the results are shown in Figure 2. GGBS, IM and FA all fall within category S. MSW is coarser and falls into category N. However SS, retaining more than 65% on the 45μm sieve, is therefore the coarsest material and is outside the boundaries of the British standards.
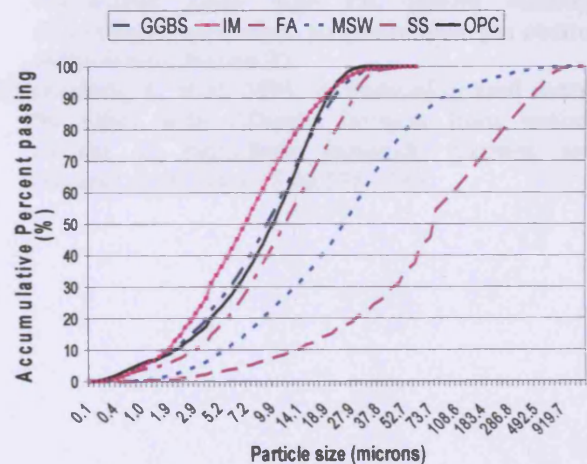

Figure 2. Particle size distribution of the replacements as received

Having identified from the particle size analysis that the MSW and SS ashes are coarse materials producing the lower compressive strengths, the available options to produce a finer ash must be considered. A finer ash would bring the materials in line with British standards, reduce the water content and w/b ratio and have an effect on the strength

gain of the concrete. Grinding the material produces an additional cost in both monetary and environmental terms and measures should be put in place to assess both the positive and negative effects gained from the use and processing of these materials (Bijen, J, 1999).

IM on the other hand is the finest of all the materials and yet does not produce compressive strengths that conform to standard requirement at replacement concentrations above 10% m/m.

5. DISCUSSION AND CONCLUSIONS

According to the experimental results, conclusions can be drawn as follows:

1. The grading of the materials are important, too coarse a material will not have any pozzolanic reaction while too fine a material might have an adverse effect on strength.
2. Reproducing the chemical makeup of OPC and grinding to achieve the same fineness does not necessarily make a new cementitious material (see conformity of IM in Table 2).
3. The measure of concrete strength is recorded at 28 days. The present study here finds that in addition to the well known blast furnace slags (GGBS), and PFA, the ash derived from sewage sludge incinerator ashes has attractive properties. The FA required upgrading from the raw material in order to achieve its performance and it is therefore likely that by using a similar process on the SS its performance might be even better.
4. Achieving the right balance of chemical composition and particle grading is the basis to producing a credible cement replacement material.

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