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Hydrothermal Performance of Pulverised Fuel Ash and the Manufacture of Autoclaved Aerated Concrete

by

Robert Alexander Carroll B.Sc. (Hons)

A Doctoral Thesis

Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University

November, 1996

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Abstract

Pulverised fuel ash (PFA) is a reactive silica source used in the manufacture of autoclaved aerated concrete (AAC). Experiments studied the hydrothermal reactions of PFA samples from two UK power stations with calcium hydroxide at 457 K, for periods up to 21 h. These conditions are comparable to those used in the manufacture of AAC.

The process is characterised by the rapid consumption of ash particles. Associated with this is the solubilisation of large amounts of silica, alumina and alkalis. The formation of a semi-crystalline calcium silicate hydrate and a hydrogarnet phase occurs during the early stages of autoclaving. The hydrogarnet phase persists under the conditions studied, but conversion of the calcium silicate hydrate into tobermorite occurs with prolonged autoclaving. Differences in the hydrothermal performance of the two PFA samples are evident, which cannot be explained by the bulk elemental composition.

Ash fractions obtained from a centrifugal air classifier have different reactivities during autoclaving and can result in specimens with different compressive strengths. Quantitative x-ray diffractometry showed that high levels of aluminosilicate glass are associated with the fine ash fractions, whereas most quartz, haematite and magnetite is associated with the coarse fractions. Significant differences exist in the mineralogical analyses of the two sets of ash fractions obtained from the bulk ash samples. The coarse ash fractions have the most varied morphology and composition.
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My appreciation is also extended to Dr. F.G. Buttler for his ideas and analysis involved in the solubilisation studies.
Formulae and lime/silica ratio

Cement chemistry notation has been used within the thesis to describe many of the inorganic phases and reactions. Established abbreviations have been used:

\[ C = \text{CaO} \quad S = \text{SiO}_2 \quad A = \text{Al}_2\text{O}_3 \quad F = \text{Fe}_2\text{O}_3 \]

\[ M = \text{MgO} \quad K = \text{K}_2\text{O} \quad \bar{S} = \text{SO}_3 \quad N = \text{Na}_2\text{O} \]

\[ T = \text{TiO}_2 \quad P = \text{P}_2\text{O}_5 \quad H = \text{H}_2\text{O} \quad \bar{C} = \text{CO}_2 \]

Conventional chemical formulae have also been used within the text. The abbreviation C/S used in the text refers to the molar lime/silica ratio (molar CaO/SiO\(_2\) ratio). In the experimental sections the lime/ash weight ratios of specimens are also quoted.
Chapter 1

Introduction

1.1 Autoclaved aerated concrete

Autoclaved aerated concrete (AAC) is a lightweight building product used in the construction of domestic dwellings and commercial buildings. It is manufactured as blocks or steel reinforced panels. The material has a fine cellular structure and a high ratio of compressive strength to density. This allows AAC to be used as a load-bearing unit where efficient thermal insulation is required.

AAC is made by reacting together finely divided calcareous and siliceous raw materials in steam, at temperatures above 373 K. The calcareous raw material is normally quicklime, or a combination of quicklime and cement. The siliceous component is often finely divided quartz. Alternatively, a raw material containing amorphous silica or aluminosilicate glass may be used. Pulverised fuel ash (PFA), the by-product of most coal burning power stations, is such a siliceous raw material.

The cellular structure of AAC is achieved either by gas evolution from a chemical process or by mechanically entrained air. Addition of fine aluminium flakes (1) to the cementitious mix is the usual means of forming a cellular structure.

The intercellular matrix of AAC is bound together by the reaction products formed during autoclaving, either calcium silicate hydrates, or a combination of calcium silicate hydrates and calcium aluminosilicate hydrates. These materials are generally more crystalline than analogous binding phases formed in normal concrete or mortar.

1.1.1 History

Experiments with autoclaved concrete were conducted in the 19th century and in 1866 the manufacture of sand-lime bricks was patented in Britain, by Van Derburgh (2). Cellular concrete has also been produced since the last century. Johan Axel Ericksson, a Swedish architect, successfully
combined these technologies and in 1924, patented the method for producing autoclaved aerated concrete (3). Full scale production of AAC began in Sweden during 1929 and it rapidly became an established building material throughout Scandinavia. After the Second World War, the manufacture of AAC started in other European countries. Germany, the Netherlands and the Soviet Union were amongst the first countries to exploit the material. AAC was introduced to the United Kingdom in the early 1950's. Global production figures for AAC are given in Table 1.1, based on data of Shen (4) and Dubral (5).

**Table 1.1**

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<tr>
<th>Region</th>
<th>AAC production (Mm$^3$ y$^{-1}$)</th>
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<tr>
<td>W. Europe †</td>
<td>8.6</td>
</tr>
<tr>
<td>Russia and E. Europe †</td>
<td>20</td>
</tr>
<tr>
<td>S. America, Australia and Africa †</td>
<td>1</td>
</tr>
<tr>
<td>Japan and S.E. Asia †</td>
<td>6</td>
</tr>
<tr>
<td>China ‡</td>
<td>4.2</td>
</tr>
<tr>
<td>Total</td>
<td>39.8</td>
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† Dubral, 1991 data
‡ Shen, 1989 data

Buildings made of AAC have considerable resistance to earthquake damage. The low density of the material means that the inertial forces on structures during tremors are moderate. Therefore, AAC is suitable for seismically active regions of the world, such as Japan, Indonesia, Iran, Turkey, Italy, Greece, Algeria and Mexico.

North America is the only industrialised region that has not manufactured AAC in significant amounts. The availability of inexpensive timber construction products in Canada and the USA may be the explanation.
However, a manufacturing plant, using ground sand as the siliceous raw material, was commissioned in Georgia during 1995. AAC production may also become an environmentally acceptable way of using PFA, rather than disposal in lagoons or other landfill sites (6).

### 1.1.2 Manufacture

A low viscosity, water based slurry, containing ground sand or PFA (62%), cement (29%), quicklime (7%) and anhydrite (2%) is produced in a mixer. Finely divided aluminium powder (0.05 to 0.1%) is the final raw material to be added to the mix. A total mixing time of 3 to 4 minutes is typical, but the aluminium powder is dispersed for only 10 to 20 s before the slurry is cast into oiled rectangular steel moulds. Contact with the alkaline mix (pH 9 to 12) leads to the reaction of the aluminium, liberating hydrogen gas:

$$2\text{Al} + \text{Ca(OH)}_2 + 2\text{H}_2\text{O} = \text{Ca(AlO)}_2 + 3\text{H}_2$$

Numerous discrete bubbles of hydrogen, typically 0.2 to 2.0 mm across, form within the slurry. The cast mix expands up to 220% of its original volume within 15 to 25 minutes to form a stable cellular structure. The cement and quicklime within the cake react exothermically with the water. Gels of calcium silicate hydrate and calcium aluminate hydrate form by the hydration of cement grains. The quicklime slakes to gelatinous calcium hydroxide:

$$\text{CaO} + \text{H}_2\text{O} = \text{Ca(OH)}_2$$

These changes increase viscosity and stiffen the "cake". The internal temperature rises, from 318 K (45°C) at casting, to between 348 and 363 K after about 120 minutes. The hydrogen rapidly diffuses out to be replaced by air. At this stage, the cellular mass has gained sufficient green strength to allow demoulding, handling and cutting into individual blocks by a series of reciprocating steel wires. Typically, a 3 to 4 m³ "cake" is cut into 300 to 400 individual blocks. Hydrothermal curing in steam autoclaves at 443 to 473 K is the critical process in AAC manufacture, involving the stages:

1. Purge - removal of air by entry of low pressure steam
2. Pressurisation - steam pressure increased at a specified rate
3. Dwell - autoclave held at constant pressure for a specified time
4. Depressurisation - steam pressure decreased at a specified rate
A steam pressure of 1100 kN m\(^{-2}\) is typically used for the manufacture of AAC, which has a temperature of 457 K, if saturated conditions are assumed. The stages of an autoclaving cycle are illustrated in Fig 1.1

![Fig. 1.1 Stages of autoclaving in AAC manufacture](image)

1.1.3 Physical properties

AAC consists of air-filled cells, a result of hydrogen evolution, and a dense intercellular matrix. The matrix forms a network of narrow bridges surrounding the cells, accounting for only 20 to 30% of the volume of AAC, but responsible for its strength and, therefore, the load-bearing characteristics of the material. The amount and nature of the reaction products within the matrix and its microporosity are important factors in determining the compressive strength of the bulk material.

The intercellular matrix forms from a slurry of high water/solid (w/s) ratio, which surrounds the hydrogen bubbles. Setting gives a cementitious mass containing significant intercellular porosity. Autoclaving results in a matrix containing reaction products, unreacted raw materials, but with considerable microporosity.
The compressive strength of AAC is the property which determines the load-bearing characteristics of structures made with the material. There is an inverse relationship between strength and macroporosity. Consequently, a direct relationship exists between strength and density, as shown in Fig. 1.2, reproduced from the original RILEM publication (7).

![Fig. 1.2 Relationship between compressive strength and density of AAC (7)](image)

The range of strengths illustrated is significant. At a given density, the compressive strength achieved depends on the choice of raw materials and the autoclaving conditions used (8). Experience of producing AAC has shown that the strength obtained for a specific autoclaving temperature and duration is affected by the siliceous raw material used. The particular PFA source chosen often determines the ultimate compressive strength which may be attained. Indeed, batch to batch variations of material obtained from a single power station may cause significant changes in the compressive strength.

The thermal conductivity of AAC, at a particular moisture content, is directly related to density, as illustrated in Fig. 1.3. As a means of energy conservation, regulatory bodies in the industrialised countries have specified improved thermal insulation for new dwellings (9). This requires building products of lower thermal conductivity. For AAC this means lower density and the trend is likely to continue. However, the relevant standards for building
materials (10), specify compressive strengths that must be achieved in order to maintain the load-bearing characteristics of structures. Selecting raw materials which maximise compressive strength at a particular density is, therefore, of considerable industrial importance. Experimental procedures which can predict the behaviour of particular PFA samples in autoclaved products are valuable for successful process development.

Fig. 1.3 Variation of thermal conductivity of AAC with density (7)

1.2 Pulverised fuel ash as a raw material for cementitious products

Pulverised fuel ash has been used as a significant raw material in many industrial processes this century.

1.2.1 Use in concrete and mortar

Helmuth (11) referred to experiments undertaken in 1914, using PFA for the partial replacement of Portland cement. Early trials were reviewed by Davis and co-workers in 1937 (12). Incorporation of PFA into large concrete pours decreases the amount of heat generated during the hydration of cement, thereby reducing the amount of thermal cracking. The building of the Hungry Horse Dam, Montana, in 1948 was the first recorded large scale use of PFA for
a civil engineering project. An estimated 100,000 t of ash was used to construct what was at the time the fourth largest dam in the world. Interest was generated throughout the United States in the use of PFA for other concrete structures, resulting in specifications for ash itself and Portland-pozzolan cements being drafted in 1954 (ASTM C350 54T and ASTM C340 54T respectively). Subsequently, national standards were drafted in Japan (1958), the Soviet Union (1963) and the United Kingdom (1965). France adopted a standard for Portland-pozzolan cements in 1959, as did Japan in 1960.

The compressive strengths achieved after 7, 14 and 28 days are important specifications for structural concrete and mortar. However, these strengths are largely determined by the physical properties of the concrete mix. The aggregate type, degree of compaction and the w/s ratio are critical parameters. This is also true for mixes which contain PFA. It is the extent to which the presence of ash modifies the rheology and water demand of fresh concrete or mortar that determines these early strengths. Taylor (13) considered the ability of PFA to decrease the water demand of concrete to be important and it was noted that this was influenced by the amount of unburnt carbon. The decrease in mix water achieved with PFA has sometimes been explained by reduced friction within the mix, brought about by the ball bearing effect of numerous spherical ash particles (14). An alternative mechanism was proposed by Dhir et al (15). The wide range of particle sizes within ashes gives a high packing efficiency and a more cohesive mix. Pietersen (16) stressed the ability of fine PFA particles to disperse cement grains within a concrete mix, thereby, reducing viscosity and allowing water reduction. This effect was attributed to deflocculation caused by the negatively charged ash particles adhering to the positively charged cement grains (calcium silicates or calcium aluminates).

The fineness of PFA has been considered a critical factor affecting strength. Thorne and Watt (17) reported a good correlation between the specific surface area of ash and mortar cube strengths up to 91 days. Interestingly, the correlation diminished with time after 91 days. Dhir et al (18)
noted a relationship between the 45 μm sieve residue and 28 day strength, whilst Ravina (19) reported a more limited relationship. However, Cabrera et al (20) obtained no correlation between the 45 μm sieve residue and 28 day strength.

Eventually, PFA in a concrete mix reacts, undergoing pozzolanic reactions. This affects the long term strength and durability of the material. Pozzolanic reactions are chemical reactions between finely divided siliceous, or siliceous-aluminous raw materials, with calcium hydroxide in the presence of water to form cementitious compounds. Raw materials, such as PFA, which undergo these reactions are termed pozzolans, but unlike hydraulic materials, these do not react with water themselves. The extent to which the chemical and mineralogical composition of PFA influences the long term strength of concrete is not, however, fully understood. Mehta (21) considered that even after prolonged curing at ordinary temperatures PFA particles coarser than 45 μm remained unreacted. The nature of the pozzolanic reactions which PFA undergoes and the significance of these in autoclaved products will be discussed in more detail in Chapter 2.

1.2.2 Use in AAC

Lindman (22) patented the use of PFA as a siliceous raw material in AAC manufacture in 1931. Generally, ground sand (finely divided quartz) is used in continental Europe and Japan, but PFA is well established in the U.K., South Africa, the former Soviet Union, and other Eastern European states. China (4) uses predominantly PFA in AAC manufacture.

The inherent variability of PFA is a factor which sometimes limits its use in AAC. Indeed, Mitsuda (23) cited this as the reason for the raw material not being used in Japan. In contrast, ground sand may be derived from a high purity source and produced to a stringent fineness specification, thereby, reducing process irregularities. Advantages associated with the use of PFA include the environmental benefits of using a waste raw material rather than a primary aggregate. A less obvious benefit is that the thermal conductivity of AAC made with PFA is marginally lower than that made with ground sand.
The behaviour of PFA within autoclaved products may be similar to the pozzolanic reactions which occur in conventional concrete. The chemical, mineralogical and microstructural properties of PFA which affect these reactions will, therefore, be discussed in some detail in Chapter 2.

### 1.2.3 PFA Classification

Classification is an industrial process by which coarse ash particles may be removed from PFA (24). Much of the unburnt carbonaceous matter exists in large particles. Thus, a "classified" PFA is finer than the original ash and normally has a lower loss on ignition. Benefits associated with classified PFA include more consistent concrete mix properties and a faster pozzolanic reaction due to a larger surface area.

Fineness and loss on ignition are the two properties of PFA which most influence initial performance of concrete. National standards (25, 26) specify a minimum fineness and a maximum loss on ignition value. "Run of station ash", obtained directly from a power station may not consistently meet these specifications. The properties of PFA are dependent upon the operating conditions of the power station. Fuel oil is often burnt with coal for several hours when a boiler is first operated from cold. Under these combustion conditions a relatively coarse ash is obtained which has a high loss on ignition. Several hours may be needed until combustion is stabilised. Power stations operating at "base load", i.e. consistently close to their maximum generating capacity, tend to produce fine ashes with small amounts of unburnt carbonaceous matter. The load factor of a power station represents the proportion of time that the plant is operating continuously. Generally, a high load factor produces a more consistent PFA.

PFA classification is likely to become more widespread in the United Kingdom as "run of station ash" becomes more variable. This is partially a result of the general reduction in coal burning, with the increased use of gas, but also because of the increased use of overseas coals. Fewer power stations will be operating at base load for extended periods, with rather more frequent start ups and power downs. Combustion conditions within boilers will,
therefore, be less consistent resulting in greater variation in the PFA produced as a by-product. A process such as PFA classification may be of increasing commercial benefit.

The advantages, if any, of using classified PFA for the manufacture of AAC have not been reported. There is little data regarding the effects that the particle size or chemistry of PFA has on the AAC produced. Several questions arise: Is there a threshold particle size for autoclaving, above which the ash particles are unreactive? What is the relationship between particle size and ash chemistry or mineralogy, and how does this affect the performance of the raw material? Are the specifications developed for dense concrete relevant for AAC manufacture?

1.2.4 Environmental considerations

About 343000 kt of PFA is produced world-wide each year (27). The developed world, as represented by the OECD states, account for 110825 kt (32%). There is increasing concern in these countries about the environmental effects of PFA disposal. Studies have been published on the effects of alkalis and heavy metals leaching from PFA into water courses (28). Storage of PFA in landfill sites, therefore, has the potential to pollute local water courses.

Within the USA in particular, landfill costs have increased over the last decade and the power utilities are actively seeking ways of using PFA. An attractive option is to sell the material for a building product such as AAC.

1.3 Relevance to Industrial Practice

Throughout the project, methods and procedures appropriate to the industrial conditions of the manufacture of AAC have been sought. This is particularly important with respect to the hydrothermal curing (autoclaving) of specimens and the ash fractionation technique chosen. Much of the data concerning the hydrothermal formation of calcium silicate hydrates applies to temperatures above 473 K and prolonged curing (i.e. several days). Stable phases form as equilibrium is approached, but such conditions are far removed from industrial practice. In the manufacture of AAC, autoclaving temperatures
of between 443 to 473 K are typical. Temperatures above 473 K are uncommon and the total autoclaving time is kept as short as possible, because of the high energy costs. In the project the autoclaving temperature was, therefore, fixed at 457 K. Generally, dwell periods up to 720 minutes (12 h) were investigated, but longer autoclaving was studied in a limited number of experiments.

Several methods of splitting PFA into fractions have been reported. Separation of particles by density have been carried out (29), but many of the dense liquids used, such as bromoform, are highly toxic which restricts the technique to small scale operations confined to a fume cupboard. Sieving is an effective means of fractionating ashes by particle size. Dry sieving is preferable to wet sieving with water, since the dissolution of salts and the hydration reactions are prevented. Dry sieving, however, becomes inefficient below about 40 μm due to blocking of the sieve. Sieving using a non-aqueous liquid, such as an alcohol, is not practical, because of the need to recover large quantities of solvent. Electrostatic extraction of the carbonaceous fractions from PFA has been attempted (30), but the commercial feasibility has not been established and, at present, this method is of limited use.

Air separation is the established industrial method for the fractionation of PFA. The technique relies on the balance between the viscous drag on ash particles in an air stream and their inertia. Most classifiers use a spinning volume of air to impart centrifugal force to the ash particles. Centrifugal classification was, therefore, the method chosen for the project.

1.4 Limitations of current knowledge

No definitive description of the hydrothermal reactions between PFA and lime has been published. The hydrothermal chemistry of the lime-silica-water system may describe the performance of ground sand (finely divided quartz), but is inadequate to explain the behaviour of PFA in autoclaved products. No correlation between either the bulk chemical analysis, or the mineralogy of PFA and hydrothermal performance has been demonstrated. The concept of pozzolanic reactions occurring at increased
rates may be a valid description, but there is little experimental evidence to support this approach. Consequently, there are no relevant tests for ashes, which are to be used within autoclaved products.

1.5 Aims and research objectives

The purpose of the project was to investigate and measure the hydrothermal reactions of pulverised fuel ash (PFA) with calcium hydroxide, under conditions which are comparable to industrial autoclaving practice. In particular, to use procedures which were relevant to the manufacture of AAC. The specific research objectives were:

(1) To develop appropriate test methods to measure the performance of PFA samples in autoclaved products.

(2) To identify the main reaction products which form during autoclaving.

(3) To correlate the fineness, chemistry and mineralogy of a PFA sample with its performance during autoclaving.

(4) To compare the reactions of two PFA samples obtained from UK power stations.

(5) To relate the physical properties of autoclaved specimens made with PFA to the microstructure and mineralogy of the reaction products.

(6) To assess the effects of air classification on the performance of PFA within autoclaved products.
1.6 References

10. BS 6073 Parts 1 and 11, 1981


23. Mitsuda, T., Private communication.


Chapter 2

Reactions between lime and siliceous raw materials

2.1 Calcium silicate hydrates

Calcium silicate hydrates are considered to be the reaction products which make the largest contribution to the development of strength within autoclaved materials.

2.1.1 General

Calcium silicate hydrates form by the reaction of calcium ions and solubilised silica "through solution", to give insoluble products that are generally poorly crystallised. Autoclaving accelerates the process and results in further crystallisation of initial CSH phases. The concentration of both calcium ions and solubilised silica within the aqueous phase determines if saturation occurs and the C/S ratio of initial CSH phases. The solubilities of both lime and silica, therefore, affects hydrothermal reactions. Temperature and pH are two important factors affecting solubility. The phases in the lime-silica-water system are given in Fig. 2.1.

Fig. 2.1 Phases in the lime-silica-water system (1)
Many of the phases in the diagram form at, or near, equilibrium. As Taylor (2) noted, the attainment of equilibrium is slow at 373 to 473 K and may require several months.

2.1.2 Dissolution of silica

The mechanism of silica dissolution under alkaline conditions was described by Iler (3) and involves the adsorption of OH\(^-\) ions to form a transitional complex. Cleavage of the silicon-oxygen bonds occurs and solvated silicate ions are removed from the surface (Fig. 2.2). Orthosilicic acid (Si(OH)\(_4\)), either in a hydrated or ionic form is produced.

![Mechanism of silica dissolution](image)

The various forms of silica have different solubilities. Greenberg (4) calculated the heat of dissolution of \(\alpha\)-quartz as 31 kJ mol\(^{-1}\), whereas, the figure for amorphous silica was 11 kJ mol\(^{-1}\). Iler used the data to determine the solubilities of both types of silica at different temperatures (Fig. 2.3).

![Solubility of crystalline and amorphous silica](image)
Silica solubility rises with temperature. It is significant that amorphous silica is more soluble than quartz at all temperatures. Iler noted that the solubility of amorphous silica reaches a maximum at about 473 K. Above this temperature, crystallisation decreases the amount of solubilised silica. In the initial stages of autoclaving, conditions are far removed from equilibrium and the rate of dissolution of silica may be a more significant factor than true solubility. Results obtained by Stober (5) illustrate the more rapid dissolution rate associated with amorphous silica (Table 2.1).

Table 2.1 Dissolution rates for various types of silica (5)

<table>
<thead>
<tr>
<th>Type of silica</th>
<th>Rate of Dissolution (10^-6 g ml^-1 day^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fused silica (amorphous)</td>
<td>39.0</td>
</tr>
<tr>
<td>Quartz</td>
<td>2.8</td>
</tr>
<tr>
<td>Cristobalite</td>
<td>6</td>
</tr>
<tr>
<td>Tridymite</td>
<td>4.5</td>
</tr>
<tr>
<td>Coesite</td>
<td>0.7</td>
</tr>
<tr>
<td>Stishovite</td>
<td>11</td>
</tr>
</tbody>
</table>

The pH of the aqueous phase affects silica solubility. The data of several authors was represented by Iler in a single plot (Fig. 2.4)
Silica solubility increases with pH, therefore, high dissolution rates are evident in strongly alkaline conditions. This is due to the reaction of orthosilicic acid (Si(OH)₄) with hydroxyl ions:

\[
\text{Si (OH)₄} + \text{OH}^- = \text{Si (OH)}^\cdot_5 \\
\text{Si (OH)}^\cdot_5 + \text{OH}^- = \text{Si (OH)}^2_6
\]

The elevated temperatures during autoclaving will also increase the solubilisation rate of silica. Results obtained by Goto (6) illustrate the combined effect of pH and temperature (Fig. 2.5).

![Fig. 2.5 Combined effect of pH and temperature on silica solubilisation (6)]

The temperature and pH expected within an autoclaved product is indicated by the arrow. Rapid dissolution of silica is likely, particularly if amorphous silica is present.

### 2.1.3 Dissolution of lime

Calcium hydroxide ionises in two stages:

\[
\text{Ca(OH)}_2 = \text{CaOH}^{+\text{(aq)}} + \text{OH}^-\text{(aq)} \quad (1)
\]

\[
\text{CaOH}^{+\text{(aq)}} = \text{Ca}^{2+} + \text{OH}^-\text{(aq)} \quad (2)
\]

Ca(OH)₂ solubility falls rapidly with temperature (7). This is illustrated in Table 2.2. At the typical commercial autoclaving temperatures between 453 to 473 K, CaO concentrations less than 0.1 g per litre within the aqueous phase would be expected.
Table 2.2 Calcium hydroxide solubility in water at various temperatures (7)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>CaO concentration (g l⁻¹)</th>
<th>Temperature (K)</th>
<th>CaO concentration (g l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>273</td>
<td>1.3</td>
<td>372</td>
<td>0.5</td>
</tr>
<tr>
<td>288</td>
<td>1.2</td>
<td>393</td>
<td>0.4</td>
</tr>
<tr>
<td>298</td>
<td>1.1</td>
<td>398</td>
<td>0.4</td>
</tr>
<tr>
<td>313</td>
<td>1</td>
<td>423</td>
<td>0.3</td>
</tr>
<tr>
<td>323</td>
<td>0.9</td>
<td>463</td>
<td>0.1</td>
</tr>
<tr>
<td>334</td>
<td>0.8</td>
<td>473</td>
<td>0.1</td>
</tr>
<tr>
<td>355</td>
<td>0.7</td>
<td>523</td>
<td>0.01</td>
</tr>
<tr>
<td>363</td>
<td>0.6</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

The presence of hydroxyl ions in alkaline conditions shifts the ionisation equilibria to the left in equation 2, suppressing calcium ion formation. Babushkin et al (7), determined the effect of pH on Ca(OH)₂ dissociation (Table 2.3).

Table 2.3 Effect of pH on Ca(OH)₂ dissociation (7)

<table>
<thead>
<tr>
<th>Form of lime</th>
<th>Percentage at various pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH 6</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>0</td>
</tr>
<tr>
<td>Ca(OH)⁺⁺</td>
<td>0</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>100</td>
</tr>
</tbody>
</table>

Calcium ion concentration falls between pH 10 and 11. At pH 12 calcium ion formation is inhibited and the lime is largely in the form of undissociated calcium hydroxide. Conditions for the initial stages of calcium silicate hydrate formation may be finely balanced in alkaline autoclaved products. Elevated temperatures and high pH maximise silica dissolution, but under these conditions calcium ion concentration may be suppressed.
2.1.4 Thermodynamics

The thermodynamics of the formation of the major crystalline calcium silicate hydrates were studied by Babushkin et al. Nine minerals were considered (Table 2.4).

Table 2.4 Common calcium silicates hydrates (7)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Crystallochemical formula</th>
<th>Stoichiometric formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hillebrandite</td>
<td>Ca_{12}<a href="OH">Si_{6}O_{17}</a><em>{4}·12Ca(OH)$</em>{2}$</td>
<td>2CaO·SiO$<em>{2}$·1.17H$</em>{2}$O</td>
</tr>
<tr>
<td>Afwillite</td>
<td>Ca$<em>{3}$2H$</em>{2}$O[SiO$<em>{3}$(OH)$</em>{2}$]</td>
<td>3CaO·2SiO$<em>{2}$·3H$</em>{2}$O</td>
</tr>
<tr>
<td>Foshagite</td>
<td>Ca$<em>{4}$<a href="OH">Si$<em>{6}$O$</em>{17}$</a>$</em>{6}$</td>
<td>4CaO·3SiO$<em>{2}$·1.5H$</em>{2}$O</td>
</tr>
<tr>
<td>Xonotlite</td>
<td>Ca$<em>{6}$<a href="OH">SiO$_{17}$</a>$</em>{2}$</td>
<td>6CaO·6SiO$<em>{2}$·H$</em>{2}$O</td>
</tr>
<tr>
<td>Riversideite</td>
<td>2{Ca$<em>{10}$<a href="OH">Si$<em>{12}$O$</em>{31}$</a>$</em>{6}$·3H$_{2}$O}</td>
<td>5CaO·6SiO$<em>{2}$·3H$</em>{2}$O</td>
</tr>
<tr>
<td>Tobermorite</td>
<td>Ca$<em>{10}$<a href="OH">Si$<em>{12}$O$</em>{31}$</a>$</em>{6}$·8H$_{2}$O</td>
<td>5CaO·6SiO$<em>{2}$·5.5H$</em>{2}$O</td>
</tr>
<tr>
<td>Plombierite</td>
<td>Ca$<em>{10}$<a href="OH">Si$<em>{12}$O$</em>{31}$</a>$</em>{6}$·18H$_{2}$O</td>
<td>5CaO·6SiO$<em>{2}$·10.5H$</em>{2}$O</td>
</tr>
<tr>
<td>Gyrolite</td>
<td>Ca$<em>{4}$<a href="OH">Si$<em>{6}$O$</em>{17}$</a>$</em>{2}$·4H$_{2}$O</td>
<td>2CaO·3SiO$<em>{2}$·2.5H$</em>{2}$O</td>
</tr>
<tr>
<td>Okeneite</td>
<td>3{Ca$<em>{3}$[Si$</em>{6}$O$<em>{13}$] 2H$</em>{2}$O·4H$_{2}$O}</td>
<td>CaO·2SiO$<em>{2}$·2H$</em>{2}$O</td>
</tr>
<tr>
<td>Truscottite</td>
<td>4{Ca$<em>{3}$[Si$</em>{6}$O$<em>{13}$]·2H$</em>{2}$O}</td>
<td>CaO·2SiO$<em>{2}$·0.67H$</em>{2}$O</td>
</tr>
<tr>
<td>Nekoite</td>
<td>Ca$<em>{3}$[Si$</em>{6}$O$<em>{13}$]·2H$</em>{2}$O·4H$_{2}$O</td>
<td>CaO·2SiO$<em>{2}$·2H$</em>{2}$O</td>
</tr>
</tbody>
</table>

The Gibbs free energy ($\Delta G^\circ$) of formation of each calcium silicate hydrate was calculated from mean bond energies. The Si-O bond energy was calculated from the heat of formation of $\beta$-quartz, the Ca-O bond energy from the heat of formation of wollastonite ($\beta$-CaSiO$_{3}$) and O-H bond energy from the heat of formation of water. The bond energies of the Ca-OH group were determined from the heat of formation of calcium hydroxide. Entropy terms were assigned to each bond type, for example, the entropy of a single Si-O bond was obtained by dividing the entropy associated with $\beta$-quartz (SiO$_{2}$) by four, the valency of silicon. The reactants were assumed to be pure $\beta$-quartz and calcium hydroxide. The $\Delta G^\circ$ values at several C/S ratios and at different temperatures for each calcium silicate hydrate were calculated. The calcium silicate hydrates displayed maximum stabilities between the C/S ratio range of 0.83 to 1.33 (Fig. 2.6).
At a particular C/S ratio the most stable phase which formed was dependent on temperature. For example, at 298 K and a C/S ratio of 1.0, tobermorite was calculated to be the most stable calcium silicate hydrate, whereas at 448 K, xonotlite was predicted to be the stable product.

For a C/S ratio of unity, tobermorite and gyrolite are the stable phases at low temperatures, but above temperatures of 473 to 493 K xonotlite (C₆S₆H) becomes stable. In lime-rich mixtures, however, hillebrandite is the stable phase. This contrasts with silica-rich mixtures, in which gyrolite (C₂S₃H) becomes the stable calcium silicate hydrate. In a study of the lime-silica-water system, cured at 453 K for 6 months, Peppler (8), confirmed that xonotlite and hillebrandite were the end products and concluded that these phases were the thermodynamically stable calcium silicate hydrates.

Djuric et al (9) calculated the Gibbs free energy of formation (ΔG°) of the initial CSH phase formed during autoclaving, for C/S values ranging from 0.83 to 1.2, at temperatures of 298, 448 and 463 K. Calculations of ΔG° used Gibbs free energies for the ions Ca²⁺, H₂SiO₄⁻, and OH⁻. Entropies of formation and heat capacity functions for calcium silicate hydrates were also obtained (7), as were solubility product data (10).

Fig. 2.6  ΔG° of formation for 9 CSH phases as a function of C/S ratio at 298 and 448 K (7)
The plot of Gibbs free energy of formation of the C-S-H phase versus C/S ratio obtained by the authors is reproduced below (Fig. 2.7). Gibbs free energy has an inverse linear relationship with the C/S ratio. Higher C/S ratios give more negative $\Delta G^\circ$ values. High-lime calcium silicate hydrates are, therefore, thermodynamically more stable than silica-rich phases. The most significant feature of Fig. 2.7 is that the hydothermal reaction at 463 K (190°C), rather than at 448 K (175°C), gives very little difference in the Gibbs free energy of formation. Thus, it is the C/S ratio of the reactants, rather than the autoclaving temperature which largely determines the stability of the reaction product.

![Graph showing relationship between Gibbs free energy and C/S ratio](image)

**Fig. 2.7** Relationship between Gibbs free energy and C/S ratio (9)

### 2.1.5 Phases detected in autoclaved products

Kalousek (11) used XRD analysis to investigate 24 commercially produced autoclaved products. Within 22 of the samples the major phase detected was tobermorite, which was considered to be the binding phase, but different degrees of crystallinity were noted. In the remaining two examples the binders were reported as poorly crystalline tobermorite and a phase of
composition $\hat{C}_{2o}S_0H$. The phase C-S-H(I) was not observed in any of the commercial products.

Fifty-five UK commercial calcium silicate brick samples manufactured between 1958 - 1966 were tested by Purton (12). Free lime was detected in sixteen of the samples. The type of calcium silicate hydrate present was determined, and a composition range consistent with C-S-H(II) and C-S-H(I) noted. DTA results also agreed with the presence of C-S-H(I). Limited XRD analysis showed broad, weak diffuse lines due to C-S-H(I) and a small amount of $\alpha$-C$_2$S hydrate was observed. Purton estimated the C-S-H(I) content to be of the order 10 to 22%.

Ludwig and Pohlmann (13) discussed the phases formed within commercial calcium silicate bricks and AAC. High compressive strength was associated with low density phases which possessed high specific volumes. Of the phases most commonly detected in commercial products, gyrolite and C-S-H(I) would be expected to have the highest strength. Tobermorite was also claimed to be a high strength material. In contrast, xonotlite and $\alpha$-C$_2$S hydrate were considered to have low binding properties, because of their poor "space filling" ability.

Mitsuda and Chan (14) examined three commercial samples of Japanese AAC produced at 453 K. Chemical analysis, XRD, electron microscopy and DTA/TGA methods were used to investigate the materials. Each sample of AAC had been produced from lime, ordinary Portland cement, ground sand, water and used aluminium powder to generate the cellular structure. Tobermorite was the main binding phase detected in all samples and was considered to be of the "anomalous type", resulting from the substitution of aluminium ions into the crystal lattice.

Lach and Knazeva (15) investigated samples of Czech and Russian AAC. The binding phases detected were C-S-H(I), tobermorite and $\alpha$-C$_2$S hydrate. The amount of each phase which formed was dependent on the starting minerals and the processing technology.
Sun et al (16) studied 28 samples of AAC manufactured during the period from 1980 to 1982. The major reaction products determined by XRD were either a CSH gel or tobermorite, but a hydrogarnet phase was also detected. Within sixteen of the samples investigated CSH gel was the dominant phase and tobermorite was the major phase in the remaining 12 samples.

Mitton (17) analysed AAC produced in the UK during 1967, using XRD and DTA methods. The crystalline phases detected were tobermorite, quartz and mullite. The presence of hydrogarnet was also suspected. No free lime was detected and tobermorite was assumed to be the main binding material within the specimens. DTA studies indicated that C-S-H(I) was also present and the broad nature of a 1243 K peak was attributed to Al-substitution within the tobermorite.

2.2 Hydrothermal reactions

The hydrothermal reactions of cementitious materials takes place above 373 K within a steam environment.

2.2.1 Lime-silica systems

The diagram given in section 2.1 provides no information on the curing conditions and is, therefore, of limited industrial use. A more relevant representation of the hydrothermal synthesis of calcium silicate hydrates is Fig. 2.8, which was also derived by Taylor. The curing conditions of commercial autoclaved products may be considered and predictions made regarding the likely calcium silicate hydrates formed. Phases above the 473 K boundary are unlikely to form. Phases placed near the lower limit for hydrothermal cure of 373 K, form in the early stages of curing, for example, C-S-H(I) and C-S-H(II). Compounds placed below, but close to 473 K are likely to form in the latter stages of the autoclaving process.
Fig. 2.8  Approximate conditions of formation of CSH phases (1)

Phases which may be expected within commercial autoclaved products are therefore:

1) Z-phase (CS$_2$H$_2$)
2) 1.1nm tobermorite (C$_2$S$_6$H$_3$)
3) 1.4nm tobermorite (C$_2$S$_6$H$_6$)
4) xonotlite (C$_6$S$_6$H)
5) afwillite (C$_3$S$_2$H$_4$)
6) α-C$_2$S hydrate
7) gyrolite (C$_2$S$_3$H$_2$)
8) hillebrandite (C$_2$SH)
9) C-S-H(I)
10) C-S-H(II)

Note: 1.1 nm tobermorite is simply termed tobermorite in subsequent text.

Phases 1) to 8) form over a narrow C/S ratio range, but C-S-H(I) and C-S-H(II) form over a wide composition range. Under such "commercial conditions" Taylor noted the likely products are the semi-crystalline phases i.e. C-S-H(I) and C-S-H(II), accompanied by crystalline phases, such as tobermorite and α-C$_2$S hydrate. At higher temperatures, or with prolonged curing, xonotlite and gyrolite may be expected to form.
The influence of the C/S ratio is stressed by many authors. Indeed, this is apparent from the composition ranges given in Fig. 2.8. Many investigations have used pure homogeneous raw materials, finely interground and hydrothermally cured for long periods. Under these conditions the C/S ratio of starting materials and the reaction products will converge. Within a product based on a heterogeneous by-product, such as PFA, cured for a relatively short time, the C/S ratio is difficult to assess. Whilst the CaO level can be estimated from solubility data, the degree of the solubilisation of silica at any stage in the reaction is uncertain.

Kalousek (18) studied the reactions of lime with both amorphous silica and quartz at temperatures ranging from 398 to 448 K and bulk C/S ratios between 0.8 and 4.0. Autoclaving periods up to several days were studied. At 398 K a slow reaction was evident, requiring up to 3 weeks to reach completion. Conversely, autoclaving at 448 K produced crystals within 6 to 14 hours. A common reaction pathway was proposed for quartz and amorphous silica, but there were differences in the rates of formation of each phase, and their stabilities as autoclaving proceeded. A significant feature was a fall in the C/S ratio of the reaction products, as illustrated for a mixture of amorphous silica and lime with a bulk C/S ratio of 0.8 (Table 2.5).

Table 2.5 Reaction of amorphous silica and lime at 448 K (18)

<table>
<thead>
<tr>
<th>Autoclaving time (h)</th>
<th>C/S ratio of reaction product</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>1.1</td>
</tr>
<tr>
<td>5.0</td>
<td>1.0</td>
</tr>
<tr>
<td>7.0</td>
<td>1.0</td>
</tr>
<tr>
<td>9.0</td>
<td>0.9</td>
</tr>
<tr>
<td>12.0</td>
<td>0.8</td>
</tr>
<tr>
<td>17.0</td>
<td>0.8</td>
</tr>
<tr>
<td>19.0</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Amorphous silica consumed calcium hydroxide within 40 minutes at 448 K (confirmed by monitoring DTA peak at 773 K). This contrasted with several hours for the mix containing quartz. A sequence of reactions was proposed in
terms of compounds of well defined stoichiometry. Kalousek recognised the alternative interpretation of related phases showing a gradual change in C/S ratio and increasing crystallinity. The first stage involved the combination of lime with the liberated silica from the quartz, or amorphous silica, to form an initial lime-rich phase:

\[ 7C + 4S +aq \rightarrow C_2S_nH_n \]  

Consumption of lime was rapid with amorphous silica, whereas, this stage required several hours with quartz. The initial phase was structurally related to hillebrandite (C₂SH) and once all the lime had been consumed a series of reactions occurred in which the calcium silicate hydrates combined with the solubilised silica.

\[
5C_7S_4H_n + 8S = 7C_3S_nH_n \quad (2)
\]

\[
C_5S_4H_n + S = 5CSH_n \quad (3)
\]

\[
4CSH_n + S = C_4S_5H_n \quad (4)
\]

Equation (4) represents the final step in the consumption of silica. SEM microscopy revealed that phases C₅S₄Hₙ, CSHₙ and C₄S₅Hₙ all had fibrous morphologies and were poorly crystallised. Conversion of the poorly crystallised fibrous C₄S₅Hₙ phase of equation (4) into well crystallised tobermorite completed the reaction sequence. The reaction profile obtained was determined by the nature of the silica source (Fig. 2.9).

![Fig. 2.9 Reaction of quartz and amorphous silica with Ca(OH)₂ at 448 K](image_url)
The reaction of lime and amorphous silica was characterised by the rapid formation of the CSH\textsubscript{n} phase within 2-3 h and its persistence for up to 10 h. Also noteworthy, was the slow transformation of the poorly crystalline fibrous phase into plate-like crystals of tobermorite. The rapid formation of CSH\textsubscript{n} was considered to be due to the high rate of silica solubilisation. Kalousek considered the low rate of formation of tobermorite surprising, but noted that in commercial products containing aluminium the transformation of the fibrous phases into tobermorite would be accelerated.

The hydrothermal reactions of amorphous silica and lime were studied by Assarson and Ryberg (19) at temperatures between 393 and 493 K for 2 to 48 h. XRD characterised the reaction products and a diol/alcohol extraction was used to measure unreacted calcium hydroxide and, thereby, monitor lime consumption. Mixes with bulk C/S ratios of 0.67 and 1.0 showed complete consumption of lime within 4 h at temperatures of 433 K or above. At 393 K, however, small amounts of lime were detected, even after 24 h. Mixes with C/S ratios of 1.5 and 2.0 also showed some unreacted lime even after prolonged curing at 493 K. An initial low temperature phase comparable to C-S-H(I) formed with a C/S ratio of 1.0 to 1.2, which subsequently converted to a high temperature phase. Hillebrandite, xonotlite, gyrolite and tobermorite phases were detected. The transition boundary from the low to high temperature phases was governed by the temperature and the duration of autoclaving (Fig. 2.10).

![Fig. 2.10 Temperature/time relationship for formation of CSH phases (19)](image-url)
The particular high temperature phase formed was governed by the initial bulk C/S ratio of the mix (Fig. 2.11).

<table>
<thead>
<tr>
<th>Molar ratio</th>
<th>Low-temperature phases</th>
<th>High-temperature phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1</td>
<td>1.5 CaO:SiO₂·nH₂O</td>
<td>Hillebrandite and b-2CaO·SiO₂·H₂O</td>
</tr>
<tr>
<td>1.5:1</td>
<td></td>
<td>Hillebrandite and Xonotlite and 3CaO·3SiO₂·H₂O</td>
</tr>
<tr>
<td>1:1</td>
<td></td>
<td>Xonotlite and Gypsum and 2CaO·3SiO₂·2H₂O</td>
</tr>
<tr>
<td>0.67:1</td>
<td>CaO·SiO₂·nH₂O</td>
<td>Xonotlite and Gypsum and +Tobermorite and CaO·SiO₂·H₂O</td>
</tr>
</tbody>
</table>

Fig. 2.11 Influence of bulk C/S on formation of high temperature phase (19)

Assarson (20) further investigated the reactions of lime and amorphous silica mixes at curing temperatures of 433 to 493 K and proposed a modified reaction scheme involving three stages:

Stage (1) - Rapid formation of a poorly crystalline phase similar to C-S-H(1) of variable composition. The actual composition of the phase was determined by the initial bulk C/S ratio of the raw materials and was unaffected by the curing temperature.

Stage (2) - Conversion of the initial phase to a metastable compound, either phase Z or tobermorite. The nature of the metastable phase was determined by the composition of the initial CSH phase and, therefore, the bulk C/S ratio of the raw materials. There was considerable overlap in the composition ranges of tobermorite and phase Z.
Stage (3) - Crystallisation of the metastable phases into products related to gyrolite, xonotlite or hillebrandite (Fig. 2.12).

Conversion of the transition phases into the stable products needed autoclaving times beyond 24 h. Within commercial autoclaved products, therefore, the major phases are likely to be C-S-H(1) and tobermorite or phase Z.

Garashin and Sizov (21) investigated the reactions which took place during autoclaving of AAC with finely divided quartz as the silica source. After curing for 8 h at 448 K, C-S-H(1) with a C/S ratio of 1.25 formed. A fibrous morphology was noted using SEM microscopy. Curing at 465 K for a similar time produced "partial solidification of crystals". The transformation of fibrous C-S-H(1) crystals into crystals of tobermorite was evident from the SEM micrographs. Associated with this was a drop in the C/S ratio from 1.25 to 0.8. Prolonged autoclaving resulted in a maximum compressive strength, followed by a fall in strength which correlated with the conversion of a large quantity of C-S-H(I) into tobermorite. It was noted that C-S-H(I) formed by
the direct reaction of calcium hydroxide and silica, with no evidence for intermediate lime-rich phases, such as $\alpha$-C$_2$S hydrate.

Ludwig and Pohlmann (13) considered the reactions which occurred during the manufacture of calcium silicate bricks and AAC. Normal commercial practice was considered to involve hydrothermal curing at 423 to 493 K for 3 to 10 h. Lime-rich phases, such as $\alpha$-C$_2$S hydrate and C-S-H(II) were assumed to be the initial products formed. Later semi-crystalline phases, such as C-S-H(I) formed. The minerals xonotlite, tobermorite of gyrolite were considered the final crystalline phases to be synthesised.

Kondo (22) conducted an interesting study of the reaction of lime with silica, in the form of quartz or silica glass. Pastes with a bulk C/S ratio of 1:1 were prepared, cast into cylinders and autoclaved at 353, 425, 454 and 489 K for periods of 0.5, 2, 6, 12 and 24 h. Compressive strength and oven dry density of the autoclaved specimens were measured. Free lime (diol/alcohol extraction), unreacted silica (HCl/Na$_2$CO$_3$ extraction) and combined water were also measured, as was the C/S ratio of the reaction products. XRD was used to identify reaction products. A correlation between compressive strength and a property termed the reaction conversion ($\alpha$) was reported (Fig. 2.13):

$$\alpha = \frac{\text{combined CaO + combined SiO}_2}{\text{total (CaO + SiO}_2)}$$

![Graph](image-url)

**Fig. 2.13** Reaction conversion ($\alpha$) versus compressive strength (22)
Specimens made with quartz showed a steady decrease in both free lime and free silica at temperatures of 353, 425 and 454 K with no abrupt change of slope. There was an overall fall in the C/S ratio of the reaction products. At 489 K, however, a sharp drop in C/S ratio was observed for up to 2 h, followed by a rise.

Specimens made with silica glass gave sharp reductions in both free lime and free silica in the first hour of autoclaving at 353, 425 and 454 K. The free silica curves were subsequently nearly horizontal, indicating little solubilisation of the silica. Steady falls in the free lime contents showed continued lime consumption. Consequently, the C/S ratio of the reaction product increased as autoclaving proceeded (Fig. 2.14). This is contrary to the experience of many authors. At 489 K, however, the normal case of a continuous decline of the C/S ratio was noted.

![C/S ratios of reaction products for silica glass and quartz](image)

**Fig. 2.14** C/S ratios of reaction products for silica glass and quartz (22)

The depth of the reaction layer was calculated and plotted against autoclaving time and showed different mechanisms operated for silica glass and quartz (Fig. 2.15). Specimens made with quartz showed a continuous growth
of the reaction layer. Increased rates were evident at higher temperatures. Silica glass reacted at 353, 425 and 454 K within 1 h to give a 1 μm thick layer, but further growth was not observed.

![Diagram showing thickness of reaction layer versus autoclaving time](image)

**Fig. 2.15** Thickness of reaction layer versus autoclaving time (22)

Kondo proposed that silica glass was solubilised more rapidly than quartz in the early stages of autoclaving, to form a thin impervious layer of calcium silicate hydrate on the particle surfaces. This initial product had low permeability to silica, thereby, inhibiting further solubilisation. The CSH phase formed at 489 K was considered to be more porous and, therefore, allowed silica transfer to take place.

The results show that rapid initial solubilisation of silica from siliceous surfaces does not in itself maximise calcium silicate hydrate formation; rather reactions can be inhibited by a thin impervious layer of CSH phase formed in the early stages of autoclaving.
2.2.2 Lime/PFA systems

The hydrothermal reaction of lime and various non-quartz siliceous materials including a PFA sample were studied by Midgley and Chopra (23). Mixes containing quartz were also produced for comparative purposes. Lime/PFA blends of weight ratios 10:90, 20:80, 30:70, and 40:60 were autoclaved at 457 to 462 K. The elemental composition of the PFA used is given in Table 2.6. Carbon, mullite, quartz and amorphous glass were the phases detected by XRD.

Table 2.6 Elemental composition of PFA (23)

<table>
<thead>
<tr>
<th>Oxide</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>42.9</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>26.7</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>7.9</td>
</tr>
<tr>
<td>CaO</td>
<td>4.1</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.2</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.2</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.9</td>
</tr>
<tr>
<td>LOI</td>
<td>10.1</td>
</tr>
</tbody>
</table>

The low-lime mixes studied by Midgley and Chopra are of particular relevance since they approximate to the proportions of raw materials within AAC. Curing periods of 2, 6, 16, and 48 h were investigated. Lime was consumed within 2 h in mixes with lime/PFA weight ratios of 10:90 and 20:80. By contrast, free lime was still evident up to 16 h in the more lime-rich mixes. Tobermorite was the major reaction product detected by XRD and the degree of crystallinity inferred from the intensity of the 1.1 nm peak. This varied from totally absent in some lime-deficient mixes, to strong in the lime-rich mixes.

Lime/PFA mixes with weight ratios 30:70 and 40:60 tended to yield poorly crystallised "tobermorite" gel after short curing periods. Prolonged autoclaving gave crystalline tobermorite, but a hydrogarnet phase was also detected.
Hope (24) compared the performance of three North American fly ashes as partial cement replacements in concrete hydrothermally cured at 450 K for 8 h. Mixes with silica flour were also produced as controls. Analyses of the samples are given below (Table 2.7).

**Table 2.7** Elemental analyses of North American PFA samples (24)

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Chicago PFA</th>
<th>Forestburg PFA</th>
<th>Lakeview PFA</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>38.50</td>
<td>50.40</td>
<td>42.60</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>20.10</td>
<td>24.30</td>
<td>24.80</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>7.40</td>
<td>5.20</td>
<td>17.20</td>
</tr>
<tr>
<td>CaO</td>
<td>17.40</td>
<td>12.10</td>
<td>4.60</td>
</tr>
<tr>
<td>MgO</td>
<td>1.90</td>
<td>1.90</td>
<td>1.00</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.60</td>
<td>3.60</td>
<td>0.60</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.90</td>
<td>0.60</td>
<td>1.30</td>
</tr>
<tr>
<td>SO₃</td>
<td>4.60</td>
<td>0.30</td>
<td>1.20</td>
</tr>
<tr>
<td>LOI</td>
<td>1.00</td>
<td>0.30</td>
<td>1.20</td>
</tr>
</tbody>
</table>

Mixes containing PFA/cement blends with bulk C/S ratios of 0.84 to 1.23 were investigated (CaO/SiO₂ mole ratio). It was assumed that the aggregate and sand did not contribute silica. For each PFA sample an optimum C/S ratio was noted, at which the compressive strength was maximised (Table 2.8).

**Table 2.8** Maximum strength and C/S ratios of reaction products (24)

<table>
<thead>
<tr>
<th>PFA</th>
<th>Maximum strength (MPa)</th>
<th>C/S ratio of product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chicago</td>
<td>58.00</td>
<td>1.40</td>
</tr>
<tr>
<td>Forestburg</td>
<td>42.00</td>
<td>1.10</td>
</tr>
<tr>
<td>Lakeview</td>
<td>44.00</td>
<td>1.10</td>
</tr>
<tr>
<td>Silica flour</td>
<td>35.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>
The results show that the silica content (SiO$_2$) alone cannot explain the observed compressive strength. The fact that the optimum C/S ratio is dependent on the PFA, suggests that other factors determine the performance of ashes during hydrothermal curing. Thus, though Chicago PFA contained the least SiO$_2$, it was apparently more "reactive" than the other two fly ashes or the silica flour. The Chicago PFA had a relatively high lime content, which may have influenced hydrothermal reactions.

Substitution of PFA for ground sand (finely divided quartz) within AAC cured at 488 K, was studied by Mortel (25). Replacement levels of 33, 67 and 100 % were investigated. Compared to UK samples, the fly ashes used were low in SiO$_2$ and Na$_2$O, but similar in respect to the other main oxides. The reaction products identified by XRD were tobermorite, a semi-crystalline calcium silicate hydrate and hydrogarnet. The relative amount of each phase formed was reported to be dependent on the proportions of the raw materials. A high bulk C/S ratio favoured the formation of a hydrogarnet, whilst a low ratio gave increased amounts of the semi-crystalline calcium silicate hydrate and tobermorite. The CSH phases were considered to be the binding material, whereas, the hydrogarnet had poor binding characteristics.

The compressive strength was at a minimum in specimens with a composition of 67 % PFA and 33 % quartz, which coincided with the maximum amount of hydrogarnet (C$_3$ASH$_n$). PFA particles engulfed in a reaction product rich in calcium, aluminium and silicon were revealed in SEM micrographs and this material was assumed to be hydrogarnet. Iron-rich particles were observed in which a thin siliceous layer had reacted with the pore solution to expose an underlying structure of magnetite or haematite crystals, which appeared to be inert to further reaction. Mortel stressed the poor binding properties of hydrogarnets and also noted that due to their stability, reduced amounts of silica were available for the formation of calcium silicate hydrates. These effects were given as reasons for the weakness of many autoclaved lime-rich specimens rather than the presence of low strength CSH phases such as $\alpha$-C$_2$S hydrate.
Sauman (26) studied the hydrothermal reactions between a single Czech PFA sample and lime. The analysis of the fly ash used is given in Table 2.9. XRD analysis showed that the crystalline phases present within the ash were quartz, mullite ($3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$) and small amounts of magnetite and rutile. The amorphous glass was estimated as 50-60% of the PFA sample.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>49.7</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>28.5</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>10.4</td>
</tr>
<tr>
<td>CaO</td>
<td>4.3</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>1.8</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>1.4</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.5</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>0.4</td>
</tr>
<tr>
<td>LOI</td>
<td>1.2</td>
</tr>
</tbody>
</table>

The PFA was ground to a specific surface of 2900 cm$^2$ g$^{-1}$ and mixed in the ratio of 3:1 ash to lime. The mixes were autoclaved at 448 K for periods from 2 h to 7 days. Reaction products were identified as C-S-H(I) and tobermorite. A reduction in the C/S ratio of the CSH phases was observed as autoclaving proceeded (Fig. 2.16).

![Fig. 2.16](image-url)  
Fig. 2.16 Effect of autoclaving time on C/S ratio of reaction product (26)
A sharp drop in the C/S ratio of the products from 1.73 to 1.02 was evident between 2 to 8 h of hydrothermal cure. A decline to 0.97 after 7 days was subsequently noted. C-S-H(I) was detected by XRD after 2 h and tobermorite was observed after 4 h. Lime had been consumed within 4 h of autoclaving. Tobermorite formation was maximised between 4 and 16 h of autoclaving and, subsequently, formed at a lower rate.

In a second series of experiments, mixes with C/S ratios of 1:10 to 10:1 were prepared and autoclaved at 448 K for 16 h. Total calcium silicate hydrate formation was maximised at a lime/ash ratio of 1:2. However, the largest amount of tobermorite occurred with a ratio of 1:3. The phase $\alpha$-C$_2$S hydrate was observed in mixes with lime/ash ratios of 1:1 and 1:2, but not 1:3. A hydrogarnet phase was also evident in several of the mixes.

Sauman clearly identified the formation of C-S-H(I) and its conversion to tobermorite in a PFA based system. Hydrogarnet was also identified as an additional phase. A similar reaction profile, therefore, might be expected within commercial AAC made with PFA.

2.2.3 Influence of aluminium ions

Discussion has so far considered the ternary system CaO-SiO$_2$-H$_2$O and the formation of calcium silicate hydrates. The rates of formation, stabilities and crystallinity of these phases are factors which determine the structure and binding within an autoclaved matrix. In any product containing PFA, however, significant numbers of aluminium ions are available during hydrothermal curing. Tidy (27), in a study of UK ashes, noted that dissolution of Al$^{3+}$ ions was apparent from the surface layer of PFA on contact with water. Therefore, the quaternary system Al$_2$O$_3$-CaO-SiO$_2$-H$_2$O is the simplest model of the process to be considered.

2.2.3.1 Effects on the dissolution of silica

Polyvalent ions, such as Al$^{3+}$, have a marked effect on the dissolution of silica. Low concentrations of aluminium ions can reduce both the rate of dissolution of silica and equilibrium solubility by adsorption onto silicate surfaces. Jephcott and Johnston (28) measured the solubility of finely divided
silica to be 0.017 % at 310 K. A small addition of Al₂O₃, however, reduced the solubility to 0.003 %. Boehm and Schneider (29) noted a reduction of silica solubility from 123 to 6 ppm due to the presence of aluminium ions.

Experiments conducted at pH 8.5 and 310 K by Iler (30), demonstrated that relatively small amounts adsorbed Al₂O₃ reduced the solubility of amorphous silica. Both the initial rate of dissolution of silica and the equilibrium solubility were affected. Iler calculated that the amount of Al₂O₃ adsorbed did not represent monolayer coverage of the amorphous silica surface and yet gave a marked reduction in solubilised silica. An explanation given was that there existed sufficient negatively charged sites containing adsorbed aluminium atoms to repel hydroxyl ions approaching the surface, thereby, inhibiting dissolution of silica.

2.2.3.2 Effects on CSH phases

In alkaline conditions, Al³⁺ and Si⁴⁺ ions have tetrahedral co-ordination and ionic radii of 0.050 and 0.041 nm respectively. These factors make the two species structurally similar. Therefore, Al³⁺ can substitute for Si⁴⁺ within the crystal lattice of calcium silicate hydrates. Eventually a limit is reached beyond which the lattice is distorted by the larger Al³⁺ ions.

Kalousek (31) noted that up to 5 % Al₂O₃ could be accommodated within a tobermorite lattice without any apparent change in its x-ray diffraction pattern. Further addition changed peak intensities and shifted the d-spacings because of the formation of a hydrogarnet phase with the formula C₃ASH₄. A second hydrogarnet, C₃AS₂H₂, was observed with still higher levels of Al₂O₃. To maintain charge neutrality, it was envisaged that some substitution of calcium ions occurred:

\[2\text{Al}^{3+} \text{ exchanged for } \text{Ca}^{2+} \text{ and Si}^{4+}\]

Mitsuda and Chan (32) reported that aluminium-substituted tobermorite was present within three samples of Japanese AAC made with ground sand as the silica source. Cement used in production was the source of the aluminium ions.
Mitsuda and Taylor (33), and later El-Hemaly et al (34), assessed the influence of Al\(^{3+}\) ions on the hydrothermal performance of siliceous raw materials. A common reaction route was observed with several silica sources. A CSH gel formed initially which crystallised into tobermorite on prolonged autoclaving. Colloidal silica and lime required the addition of alumina (Al\(_2\)O\(_3\)) in order to form tobermorite and crystallinity increased at higher Al\(_2\)O\(_3\) levels. Aluminosilicate gels reacted more rapidly than colloidal silica. A zeolite reacted more rapidly than either colloidal silica or aluminosilicate gels and the CSH phase crystallised readily. The stoichiometry of the reaction products was determined by the ratio of the reagents, irrespective of the period of autoclaving.

### 2.2.3.3 Formation of hydrogarnets

The formation of hydrogarnets within aluminium-rich autoclaved materials is of considerable significance for commercial products. Hydrogarnets may be regarded as the hydration products of calcium alumino silicates and have the generalised formula given by Carlson (35):

\[
3\text{CaO} \text{Al}_2\text{O}_3 \cdot m\text{SiO}_2 (6-m) \text{H}_2\text{O}
\]

\[
[m = 0 \text{ to } 3]
\]

Hydrogarnets have cubic symmetry and form solid solution series with the two end members being grossularite (C\(_3\)AS\(_3\)) and tricalcium aluminate hexahydrate (C\(_3\)AH\(_6\)). Hydrogarnets formed at moderate temperatures (below 873 K) do not generally have fixed stoichiometries, but show a graduation in composition. There is a well defined correlation between composition and unit cell dimension, ranging from 1.18 nm for C\(_3\)AS\(_3\) to 1.26 nm for C\(_3\)AH\(_6\).

Carlson noted that the hydrothermal reactions of calcium alumino silicate glasses produced hydrogarnets, but their stoichiometries was independent of glass composition. Autoclaving temperature was the prime factor in determining the nature of the hydrogarnet. Roy and Roy (36) noted that at temperatures below 573 K, a stable series of hydrogarnets formed with compositions ranging from C\(_3\)ASH\(_6\) to C\(_3\)AS\(_2\)H\(_2\). Mixes richer in silica resulted in the formation of a CSH phase and anorthite (CAS\(_3\)), in addition to hydrogarnet.
Hydrogarnet crystals are octahedral and dense, with low specific volumes. The crystals may be considered to have poor "space filling" ability; forming few points of contact and contributing little to the strength of the matrix. Strength data on individual hydrogarnets has not been reported, but Jambor (37) noted that autoclaved materials containing hydrogarnet had a relatively coarse microporosity and low strength. Multivalent ions such as Fe$^{3+}$ can substitute for aluminium ions within hydrogarnets. Again, solid solution series exist and there is a graduation in stoichiometry evident by changes in unit cell dimensions. Replacement of Al$^{3+}$ ions by Fe$^{3+}$ ions increases the unit cell dimension. Zur-Strassen (38) noted that the presence of iron oxide favoured the formation of hydrogarnet.

Sauman et al (39) observed that autoclaving mixes which contain PFA result in the formation of hydrogarnet of the general formula $\text{Ca}_3\text{Al}_2\text{Fe}_x\text{Si}_x\text{O}_{6+2x}$. Mullite reacted with lime during autoclaving at 448 K for 16 h to produce a hydrogarnet. It was also shown that sulphate ions could substitute into the phase, up to an equivalent of 4 % $\text{SO}_3$. Higher levels of sulphate ions led to the synthesis of the mineral hydroxyllestadite ($\text{Ca}_{10}$(SiO$_4$)$_3$(SO$_4$)$_3$(OH)$_2$).

2.2.4 Influence of sulphate ions

Approximately 1 to 3 % of anhydrous calcium sulphate added to AAC mixes results in higher compressive strength. Addition levels beyond this amount generally gives no further increase in strength. Bach (40) suggested that small crystals of ettringite ([Ca$_3$Al(OH)$_6$.12H$_2$O].2(SO$_4$)$_2$.2H$_2$O) act as nucleation sites for tobermorite formation. However, ettringite is unstable at typical autoclaving temperatures and, therefore, the mechanism does not seem relevant to AAC and related products.

Sauman et al (39) stated that "sulphate ions speed up considerably the kinetics of the hydothermal reactions between lime and quartz and power station ash". Takemato and Kato (41) studied the effects of sulphate ions on the compressive strength of pastes made from quartz, cement and gypsum autoclaved at 425 K for 5 h. The reaction products were CSH gel, C-S-H(1) and tobermorite. Compressive and tensile strengths were maximised at 2 %
SO$_4^{2-}$ addition in those mixes with bulk C/S ratios from 0.5 to 1.0. Increased levels of sulphate ions gave a sharp reduction in compressive strength. XRD peaks due to the mineral hydroxylellestadite ($\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_2(\text{OH})_2$) appeared. Mixes with bulk C/S ratios below 0.5 were less affected by sulphate ion concentration. Hydroxylellestadite has poor binding characteristics and its presence is considered to be undesirable.

Sauman and Vavrin (42) observed columnar crystals of hydroxylellestadite formed within quartz/lime pastes with a 10% gypsum addition. The formation of the mineral was maximised if the quartz grains were between 60 to 90 $\mu$m. Further experiments with pastes containing cement showed that sulphate content affected tobermorite formation. Up to 5% gypsum significantly increased the amount of tobermorite detected by XRD, whereas, 5 to 15% gave a marginal reduction. A sharp decline in tobermorite was evident with 16 to 20 % gypsum and this coincided with the appearance of hydroxylellestadite peaks.

Sulphate ions are reported to inhibit the synthesis of hydrogarnet during autoclaving and this could be an important mechanism in products which contain PFA.

2.2.5 Influence of alkalis

The effects of alkalis on the hydothermal reactions of quartz and lime at 433 to 453 K were studied by Shikami (43). The amounts of NaOH or KOH added to a paste with a bulk C/S ratio of 0.6 influenced the composition of the reaction product. A minimum in the C/S ratio of reaction product was achieved with 0.2% of Na$_2$O or K$_2$O. Addition of 1% of either alkali gave a product with a C/S ratio of 2.0, consistent with the stoichiometry of a dicalcium silicate hydrate. This reaction product had the lowest strength and was maximised at an addition of 0.2 to 0.4% Na$_2$O or K$_2$O. The "higher reactivity" of quartz with alkalis may be largely due to an increased silica solubilisation. Formation of alkali-calcium silicate hydrates may also remove calcium ions from the aqueous phase, thereby, reducing the C/S ratio of the
reaction product. At high alkali levels, the reduced calcium ion concentrations may inhibit calcium silicate hydrate formation (Table 2.3, page 20)

Sauman (44) demonstrated that synthetic glass, autoclaved with lime at 443 K for 16 h, did not produce tobermorite unless potassium ions were available. The tobermorite content was maximised at 3.0 % K₂O addition, but higher alkali levels reduced the amount of the phase observed.

2.3 Pulverised fuel ash

Pulverised fuel ash is the fine inorganic residue produced from the combustion of coal in power stations. It is obtained from electrostatic precipitators which prevent fine particulates being emitted into the atmosphere with the flue gases.

2.3.1 Description

Most PFA particles are spherical and nominally composed of silica (SiO₂), alumina (Al₂O₃), lime (CaO), iron oxide (Fe₂O₃), minor oxides and unburnt carbonaceous matter. The main crystalline phases are quartz, mullite, magnetite and haematite, but amorphous aluminosilicate glass is normally the major constituent. Surface deposits of alkalis and sulphates are also generally observed.

PFA is a complex heterogeneous material, the composition of which depends on coal source, grinding efficiency and combustion conditions within the boiler. Diamond (45) contrasted the formation of PFA particles to that of slag particles. In the latter case, all particles are derived from a single molten mass, in which diffusion and convection effects tend to give homogeneity. It is possible to refer to a "mean composition". With PFA, however, each particle has been derived from a discrete coal fragment, which itself may differ in mineralogy from adjacent fragments and has been subjected to particular combustion conditions. There is little exchange of material between particles. Therefore, a large number of particle types form, which vary in size, porosity, mineralogy and fine structure. Particles of relatively uniform composition may exist, but numerous types of composite particles have been reported. The
"mean composition" of a particular PFA sample represents a statistical average of the compositions of the numerous individual particle types.

To gain an understanding of the types of particles which occur in PFA, it is important to discuss the combustion of coal fragments within the burning zone of power station boilers.

2.3.2 Formation

Within most modern power stations, coal is pulverised to be finer than 300 μm. Typically, 80% of the coal particles are finer than 75 μm. Helmuth (46) quoted a median diameter of 50 μm to be typical. The pulverised coal is blown into the combustion zone at high velocity with the primary air. Secondary air is also admitted to the boiler. The retention time in the burning zone is brief, but temperatures up to 1873 K may be achieved.

Coal consists of organic material and inorganic components. The organic material is made up of a complex mix of aromatic compounds which contain linked benzene rings (napthalene, anthracene etc.) and hetercyclic rings (i.e. containing oxygen, nitrogen or sulphur). It is the organic material which burns rapidly in the oxidising conditions, generating heat. The inorganic component is derived from the minerals associated with the original coal deposit. It is the mineral fraction within the coal which transforms within the combustion zone to form PFA particles. The range of minerals which occur in coal ashes can be diverse. A list given by Diamond (47) is reproduced in Table 2.10
Flagan (48) proposed a mechanism for the formation of ash particles:
Coal fragments enter the combustion zone of the boiler and burnout of the organic matter begins. Volatilization of alkali metal salts takes place. At higher temperatures, compounds of heavy metals may boil or sublime. A char structure forms containing mineral inclusions. These inclusions melt and fuse into larger beads, whilst the char structure continues to burnout and weakens. Eventually, the char structure collapses liberating the molten droplets. Surface tension ensures that these molten droplets become spherical. Outside the combustion zone droplets of molten material cool rapidly. A temperature fall from 1773 to 473 K in 4 s has been quoted (49). Under such conditions, formation of amorphous glasses is encouraged. The volatilised alkalis condense as fine particles, often adhering to the larger ash particles.

Hydrous minerals within the coal fragments will rapidly dehydrate, liberating water vapour. Also, minerals such as calcite (CaCO₃) may generate carbon dioxide within the combustion zone. Both mechanisms will cause semi-molten droplets to bloat and form hollow particles.

British power stations burn bituminous coal or anthracite. The ashes derived from these fuels are low in lime (CaO) and high in glass. Quartz (SiO₂), mullite (3Al₂O₃·2SiO₂), haematite (Fe₂O₃), and magnetite (Fe₃O₄) are the dominant crystalline minerals present. Other phases may be present as minor constituents (less than 1 %), but cannot normally be detected by XRD.

Subbituminous coal and lignite generally have more minerals present than bituminous coal or anthracite. This explains the more complex mineralogy of the ashes derived from these fuels. Gypsum is often present in significant amounts. Dehydration and conversion to calcium oxide with the liberation of sulphur trioxide occurs during combustion:

\[
\text{CaSO}_4\cdot2\text{H}_2\text{O} = \text{CaSO}_4 + 2\text{H}_2\text{O} \\
\text{CaSO}_4 = \text{CaO} + \text{SO}_3
\]

Therefore, PFA derived from subbituminous coal or lignite has a high level of calcium oxide (quicklime) and a relatively low glass content. If such a raw material is used in cementitious mixes, contact with water leads to rapid
slaking of the quicklime and a significant viscosity increase. Ashes derived from subbituminous coals or lignite have been found to be unsuitable for AAC manufacture in experiments undertaken by the author.

2.3.3 Composition

Diamond (47) stressed the complexity of the combustion of coal fragments within power station boilers. Some of the molten droplets derived from coal minerals may cool relatively slowly, allowing partial crystallisation (devitrification) to occur. This gives composite particles with intricate microstructures. Conversely, other molten droplets are rapidly quenched, allowing vitrification to take place, forming particles composed of amorphous aluminosilicate glass. It was observed that crystalline material rarely occurs as individual particles.

The complex microstructure of ash particles was discussed by Pietersen (50). Crystalline inclusions of quartz, mullite or sulphates can exist within a glassy sphere, which itself has zones of aluminosilicate glass of different compositions. These zones of glass within a single PFA particle have been observed by other researchers (51, 52). There is no agreement about the origin of the zones. Formation of a crystalline core, followed by condensation of a mechanism was proposed by Lauf (53). Hulett et al (54) considered that molten aluminosilicate glass becomes enriched with heavy metals near the surface prior to solidification. A core of "interior glass", containing mullite and quartz crystals, surrounded by an outer layer of "reactive glass" is the structure envisaged by Warren and Dudas (51). The surfaces of particles have a layer of alkali salts which were deposited during cooling.

Hemmings and Berry (52) considered the major elements within the glass of PFA, to be either network formers (Si, Al and Fe), or network modifiers (Na, K, Ca and Mg). Network formers have a co-ordination number of 3 or 4 and are capable of replacing silicon in the polymeric network of oxygen tetrahedra, thereby, maintaining a high degree of polymerisation. Network modifiers have higher co-ordination numbers and tend to cause depolymerisation, making the glass more disordered. The occurrence of
network modifiers (reported as oxides) during coal combustion, may have a profound influence on the glass properties, affecting melting temperature, glass viscosity, the extent of phase separation and the quantity of mullite or iron oxide which forms.

Phase separation is possible during the cooling of molten droplets. Pietersen (50) noted that in the SiO₂-Al₂O₃ system, phase separation is possible over the range 10 - 50 mole % Al₂O₃. Rapid cooling tends not to give phase separation, but rather encourages the formation of aluminosilicate glass. Slower cooling, however, is more likely to give phase separation and the formation of mullite and quartz crystals within the glass. Hemmings and Berry (52) noted that PFA samples with only small amounts of the network modifiers will display extensive phase separation, due to crystallization which occurs on cooling. In contrast, PFA samples with large amounts of network modifiers show much less phase separation and aluminosilicate glass predominates.

The amounts of network modifiers (CaO, Na₂O, K₂O and MgO) within the coal minerals have a significant effect on the viscosity of the aluminosilicate glass during the formation of the PFA particles. If only small amounts of the network modifiers are present there will be a relatively high viscosity. If gas generation occurs, due to moisture loss or liberation of carbon dioxide from carbonates, the glass will be viscous enough to retain the gases generated until the droplet cools. This will result in hollow spheres. However, in molten droplets with high levels of glass modifiers, a low viscosity will exist and it is unlikely that gas can be retained. Therefore, whilst the cooled particle might have gas vesicules it will be essentially a solid sphere. This results in the crystallisation of mullite and quartz from the melt and PFA particles with composite structures.

The micro-heterogeneity may be expected to give ash particles of different pozzolanic reactivities. However, Pietersen (50) observed that little is known about relative glass reactivities and experimental evidence suggests that external factors, such as pH and temperature, determine the reaction rates of the glass within PFA. Hemmings and Berry (52) stressed that PFA should be assessed on three levels of complexity. Macrostructure considers differences in
the particle size, shape and composition between particles. Microstructure deals with differences within particles, such as inclusions. Nanostructure deals with variation in the glass at the molecular level, for example, phase separation. It is the interplay of these levels of complexity which determine the properties of a particular PFA sample.

2.3.4 Pozzolanic reactions

Pozzolanic reactions are chemical reactions between finely divided siliceous, or siliceous-aluminous raw materials with calcium hydroxide in the presence of water, which form cementitious compounds. Such raw materials are termed pozzolans, but unlike hydraulic materials, such as portland cement, do not react with water themselves.

Pozzolans may be natural, such as certain volcanic deposits, or artificial, as is the case with PFA. Pozzolans are mainly composed of an amorphous glassy component. The common structural feature of which is a highly disordered silicate, or aluminosilicate network which is metastable and, therefore, reactive.

The simplest pozzolanic reactions involve reactive siliceous pozzolans and calcium hydroxide:

\[ x \text{CH} + y\text{S} + z\text{H} \rightarrow C_xS_yH_{x+z} \]

The reaction products are calcium silicate hydrates, with C-S-H (I) often cited as the stable phase. However, intermediate reaction products occur with C/S ratios ranging from 0 to 2. If the pozzolan is an aluminosilicate, additional reactions may take place. Calcined kaolinite (Al_2O_3 \cdot 2SiO_2) may be used as an example of an artificial pozzolan:

\[ \text{AS}_2 + 3\text{CH} + z\text{H} \rightarrow \text{CSH}_{z-5} + \text{C}_2\text{ASH}_8 \]

Gehlenite hydrate (C_2ASH_8) is the additional reaction product formed. In practice, other phases from the garnet-hydrogarnet solid solution series may form (C_3AS_3 - C_3AH_6). Crystalline siliceous raw materials such as quartz, are not normally judged to be pozzolans, because of low solubility below 373 K. Under hydrothermal conditions, however, finely divided quartz may undergo pozzolanic reactions.
There are conflicting opinions regarding the usefulness of bulk elemental analysis for predicting the pozzolanic reactions of PFA. Watt and Thorne (55) noted that after 365 and 730 days there was a correlation between the crushing strength of mortar cubes and either the \( \text{"SiO}_2\text{"} \) or \( \text{"SiO}_2 + \text{Al}_2\text{O}_3\text{"} \) content of the PFA used. No correlations at early ages were noted. Helmuth (46) considered any relationship between pozzolanic behaviour and bulk analysis surprising. The effect was attributed to either the quartz and mullite particles reacting with the lime, or acting as fine aggregates. According to Hubbard et al (56), bulk elemental analysis does not provide any direct information on the pozzolanic reactivity of the PFA in mortar or concrete. For bulk analysis to be useful, complete consumption of most ash particles is necessary. This assumes some consumption of the quartz and mullite phases.

Watt and Thorne (55) considered that the pozzolanic nature of PFA was primarily the result of the reaction of aluminosilicate glass with lime. The crystalline phases quartz, mullite, magnetite and haematite took little part in the reactions. This has generally been held to be the case for concrete and mortar and many test methods attempt to measure the amorphous glass phase directly or indirectly. Helmuth (46) quoted work by Entin et al (57), which indicated that the most reactive PFA particles were not entirely glassy, but contained inclusions of mullite and quartz. Results obtained by Rodgers and Groves (58) are particularly interesting. Analytical TEM has shown one year old pastes of C\(_3\)S and PFA to contain a CSH phase formed by the partial reaction of quartz grains within ash particles.

### 2.3.4.1 Methods for assessing the pozzolanic reactions of PFA

Chemical tests have been devised to predict the pozzolanic reactivity of PFA. No specific tests for the evaluation of PFA in hydothermal conditions have been found in the literature.

Dissolution methods attempt to measure the "reactive silica" within PFA. The chemical test in DIN 1164 aims to differentiate between the total amount of silica present in a PFA sample and the "soluble silica" which is considered to take part in pozzolanic reactions. A two stage dissolution
process is used. Firstly, an acidic extraction with hydrochloric acid, followed by an alkaline treatment using sodium carbonate solution. Based on results obtained from the DIN 1164 test, Richartz (59) categorised PFA sources as:

- low reactivity = less than 10% soluble silica
- average reactivity = 10 to 18 % soluble silica
- high reactivity = greater than 18 % soluble silica

A method developed by Raask and Bhaskar (60) has been proposed as a rapid means to determine PFA reactivity. The technique relies on the dissolution of silica in dilute hydrofluoric acid and monitoring changes in conductivity of the solution. Hydrofluoric acid has a low dissociation constant and in solution remains largely as HF molecules, which carry no charge.

Hydrofluoric acid reacts rapidly with the siliceous surfaces to form fluorosilicate ions which can carry charge:

\[ 6\text{HF} + \text{SiO}_2 = 2\text{H}^+ + \text{SiF}_6^{2-} + 2\text{H}_2\text{O} \]

Therefore, silica dissolution may be assessed by monitoring the rise in conductivity of the HF solution. The method developed by Raask and Bhaskar used 0.1 molar HF solution. Calibration using highly reactive silica fume was necessary. The "pozzolanic index" (Pz) was defined as:

\[ \text{Pz} = 1000a \]

\[ a = \text{rate constant of dissolution (s}^{-1}\text{)} \]

An approximately linear relationship between Pz and pozzolanic reactivity of PFA samples was claimed. The use of "exotic chemical systems" such as HF solutions to assess the reactivity of PFA was criticised by Hubbard et al (56). Iler (3) noted that the solvent action of fluoride ions and hydroxyl ions differ.

Microscopic examination can give an indication of the distribution of particle types within a PFA sample. If assumptions are made about the reactivities of each particle type, an estimation of the reactivity of the bulk PFA
can be attempted. Watt and Thorne (61) published such a scheme. Fischer et al (62) proposed an alternative scheme, which allows the severity of exposure to heat within the furnace to be inferred. Compositions of particles are inferred from both opacity and morphology. Dark particles contain unburnt coal, or have an outer layer rich in iron oxide. In either case these are assumed to be of low reactivity. The shape of particles is related to the degree of exposure within the combustion zone of the boiler. Irregular, angular particles have been exposed to a moderate temperature, or for a brief period at a higher temperature. In contrast, spherical particles have been in the combustion zone longer or subjected to higher temperatures.

There are significant difficulties associated with any microscopic method for assessing PFA reactivity. Such a technique assumes that particles of similar appearance and size are of similar composition and reactivity. The intrinsic heterogeneity of many PFA particles means that a complex structure may lie beneath a smooth spherical exterior. Such composite structures may indeed be widespread, rather than exceptional. It may be uncommon for a PFA particle to have a glassy structure of uniform composition throughout.

2.4 Strength of hydrothermally cured products

Calcium silicate hydrates are likely to be the major binding phases within autoclaved products. The strength of these phases will have a direct effect on the load-bearing properties of the material.

2.4.1 Calcium silicate hydrates

Bach (40) stated that high strength within AAC was due to the presence of C-S-H (1), but tobermorite was also considered to confer strength. Beaudoin and Feldman (63) regarded a mixture of tobermorite and poorly crystallised C-S-H(1) as responsible for maximum strength within autoclaved products. The authors noted that concrete cured under high pressure steam, but without a finely divided silica, formed a weak porous body with $\alpha$-C$_2$S hydrate as the chief product. High strength was considered by Ludwig and Pohlmann (13) to be associated with low density phases with high
specific volumes. Of the phases most commonly detected in commercial products, gyrolite and C-S-H(I) would be expected to have the highest strength. However, it was noted that C-S-H(I) was the strongest phase. Tobermorite was claimed to provide considerable strength. In contrast, xonotlite and α-C₃S hydrate were regarded as poor binding phases due to their low "space filling" ability. Physical properties of industrially important calcium silicate were determined by Butt et al (64) and the results for six phases are summarised in Table 2.10.

<table>
<thead>
<tr>
<th>Calcium silicate hydrate</th>
<th>Bulk density (g cm⁻³)</th>
<th>Compressive strength (kg cm⁻²)</th>
<th>Tensile strength (kg cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>initial</td>
<td>after 6.5 months</td>
<td>initial</td>
</tr>
<tr>
<td>C-S-H(I)</td>
<td>1.13</td>
<td>1.43</td>
<td>230</td>
</tr>
<tr>
<td>tobermorite</td>
<td>1.12</td>
<td>1.12</td>
<td>70</td>
</tr>
<tr>
<td>xonotlite</td>
<td>1.00</td>
<td>1.22</td>
<td>120</td>
</tr>
<tr>
<td>C₂SH(A)</td>
<td>0.87</td>
<td>0.91</td>
<td>2.5</td>
</tr>
<tr>
<td>C₂SH(C)</td>
<td>0.98</td>
<td>1.11</td>
<td>15</td>
</tr>
<tr>
<td>C₃SH₂ (TSH)</td>
<td>1.45</td>
<td>1.52</td>
<td>140</td>
</tr>
</tbody>
</table>

Gyrolite was not synthesised and was considered to be metastable under the autoclaving conditions used (up to 573 K for 31 days). The results obtained by Butt and co-workers demonstrated marked differences in the mechanical strengths of calcium silicate hydrates. The high compressive strength of C-S-H(I) is particularly noteworthy. Xonotlite and C₃SH₂ also have high strengths. Interestingly, tobermorite has a relatively modest compressive strength, approximately 30% of that measured for C-S-H(I). Both the forms of dicalcium silicate hydrates have low strength.

The microstructure of the calcium silicate hydrates, as revealed by petrography and electron microscopy, correlates with the strength results. Hence, C-S-H(I), xonotlite and C₃SH₂ have fine crystalline morphologies resulting in a high degree of cross linking and many bonding sites. Tobermorite
has more plate-like crystals and, therefore, less cross linking. However, the dicalcium silicate hydrates are composed of large plate-like crystals which give matrices with few points of contact and, therefore, a limited number of bonding sites. There is an anomaly between the reported low "space filling" ability of the dicalcium silicate hydrates and their specific gravities, as reported by Butt and co-workers (Table 2.10). The figures for C₂SH(A) and C₂SH(C) are 0.87 and 0.98 g/cm³ respectively, which suggests higher specific volumes than other calcium silicate hydrates. Purton (65), however, quoted a density of 2.80 g/cm³ for the dicalcium phase α-C₂S hydrate.

The crystallinity of calcium silicate hydrates formed within AAC made with ground sand was defined quantitatively by Alexanderson (66) and related to compressive strength. Reaction products were identified as C-S-H(1) and tobermorite. Chemical analysis showed that the C/S ratios of the reaction products to be between 0.8 and 1.0. The expression derived was:

\[
\text{crystallinity} = \frac{\text{tobermorite} \times 100}{\text{total calcium silicate hydrate}}
\]

If C-S-H(1) and tobermorite are the only calcium silicate hydrates formed, then:

\[
\text{crystallinity} = \frac{\text{tobermorite} \times 100}{[\text{C-S-H(1) and tobermorite}]}
\]

Crystallinity influenced the compressive strength of AAC and multiple regression analysis derived an empirical relationship. A correlation coefficient of 0.9 was obtained with material of 500 kg/m³ density.

\[
t = 0.386T + 0.831C -0.00087 C^2 +0.39
\]

where \( t \) = compressive strength
\( T \) = total amount of CSH
\( C \) = crystallinity

Sun et al (16) related the mineralogy of Chinese AAC to both compressive strength and drying shrinkage. Tobermorite, "CSH gel" and
hydrogarnet were the reaction products detected using XRD and DTA /TGA. The term " CSH gel" is assumed to mean C-S-H (1), a mixture of C-S-H (1) and C-S-H (2). A linear relationship between compressive strength, corrected to a density of 500 kg m$^{-3}$, and the abundance of calcium silicate hydrates was observed:

$$R = a + b_1 x_1 + b_2 x_2$$

where, $x_1$ = % tobermorite

$x_2$ = %"CSH gel"

A correlation coefficient of 0.74 was claimed and regression analysis gave numerical values of $a = 17.5$, $b_1 = 0.7$, $b_2 = 1.34$. Since $b_2/b_1$ approximates to 2, the "CSH gel" contributes twice as much to compressive strength as does tobermorite. This compares with the results of Butt et al reproduced in Table 2.10, showing tobermorite to possess 30% of the strength of C-S-H(1). The role of hydrogarnet in strength development was not considered by Sun et al.

2.4.2 Significance of phase volumes

Voluminous, low density calcium silicate hydrates have been considered to be desirable for high strengths. The high volume and fine crystal structure of these phases creates numerous points of contact within the cured matrix which constitute bonding sites. Conversely, dense, low volume phases, with few points of contact, are assumed to possess low strength. The bonding achieved within autoclaved calcium silicate hydrates, may be discussed in terms of the relative volumes of the various phases compared to reactants. Changes in strength observed during autoclaving can be explained by volume changes associated to phase transformation. Purton (65) assumed the stoichiometric reaction of calcium hydroxide and silica in order to calculate volume changes associated with calcium silicate hydrate formation (Table 2.11).
Table 2.11 Volume changes during formation of common CSH phases (65)

<table>
<thead>
<tr>
<th>CSH phase</th>
<th>Volume of phase formed from 1 cm³ calcium hydroxide (cm³)</th>
<th>Volume change compared to reactants (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-C₂SH</td>
<td>1.0</td>
<td>-23.4</td>
</tr>
<tr>
<td>C-S-H(I)</td>
<td>1.6</td>
<td>12.9</td>
</tr>
<tr>
<td>C-S-H(II)</td>
<td>1.9</td>
<td>14.7</td>
</tr>
<tr>
<td>tobermorite</td>
<td>1.8</td>
<td>1.1</td>
</tr>
<tr>
<td>gyrolite</td>
<td>2.1</td>
<td>2.0</td>
</tr>
<tr>
<td>xonotlite</td>
<td>1.3</td>
<td>-20.8</td>
</tr>
</tbody>
</table>

The phase α-C₂SH forms from solution by the reaction of lime and silica, but the phase has a significantly lower volume compared to the reactants. Reaction of α-C₂SH with silica forms, in turn, C-S-H(II) and C-S-H(I), with increases in the volumes of reaction products. This explains the "space filling" ability noted for these two phases. Further autoclaving results in the crystallisation of C-S-H(I) into tobermorite, with a 14% reduction in volume and parallels a reduction in strength.

2.4.3 Porosity investigation

Satava (67) assessed the role of porosity on the strength of autoclaved prisms made from quartz and lime pastes, or silica gel and lime pastes. Specimens had a bulk C/S ratio of 0.8 and had been autoclaved at 448 K for up to 9 h. A calcium silicate hydrate with the composition of C_{1.72}SH_n formed within 2 h. Longer autoclaving produced a phase similar to tobermorite. A strength/density relationship conforming to the Schiller (68) equation was established. Mercury porosimetry differentiated between the microstructure of the two types of specimens. The different behaviour of quartz and silica gel was striking. Specimens made from silica gel possessed larger voids than those which were produced from quartz. A single linear plot was obtained, relating the tensile strength to the pore size with the highest frequency (r). There were two populations of points. One set occurred at the high strength region for
specimens made with quartz. The other set was at the lower strength region and represented specimens produced from silica gel. Satava concluded that the dominant factor in determining strength of autoclaved products was its pore size distribution rather than the nature of the reaction products. However, no explanation for the two pore types was given.

Mindess (69) investigated the strength/density relationships of cores made from quartz and calcium hydroxide, autoclaved at temperatures of 408 to 491 K, with bulk C/S ratios between 0.1 to 3.5. Tobermorite and poorly crystallised CSH gel were the reaction products identified. Three pore types were revealed by pore size distribution and a relationship with compressive strength was reported. Higher strength was associated with smaller pores (Table 2.12).

Table 2.12 Porosity of autoclaved specimens (69)

<table>
<thead>
<tr>
<th>Description of porosity</th>
<th>Pore size range (nm)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>gel pores</td>
<td>1 to 5</td>
<td>high strength</td>
</tr>
<tr>
<td>coarse pores</td>
<td>5 to 50</td>
<td>intermediate strength</td>
</tr>
<tr>
<td>macro pores</td>
<td>plus 50</td>
<td>low strength</td>
</tr>
</tbody>
</table>

The Bal'shin (70) expression gave the highest correlation between strength and porosity.

\[ S = S_0D^m \]

- \( S \) = strength
- \( S_0 \) = strength at zero porosity
- \( D = 1 - \) porosity
- \( m \) = an empirical constant

Most specimens gave compressive strength results which fitted the linear relationship described. Porosity alone, therefore, determined compressive strength. However, two sets of points from samples of low
porosity were anomalous. Specimens with high compressive strength were revealed by XRD and SEM to contain large amounts of C-S-H(I), with fine crystalline morphology and a high surface area. Other specimens had unusually low compressive strength, but contained either α-C_2S hydrate, or β-C_2S hydrate with coarse crystal morphologies and few points of contact. Both the mineralogy and the morphologies of the reaction products, therefore, influenced the compressive strength of the autoclaved material.

An interesting relationship between mineral composition and the pore structure of cementitious pastes was obtained by Jambor (37). Pastes made from various lime sources and siliceous raw materials were investigated. The pozzolans, PFA, activated kaolinite and dacite tuff were assessed, as was finely divided quartz. Specimens were autoclaved at 448 K for 24 h, or cured at 293 to 353 K for periods up to 180 days. Compressive strength and bulk density was measured. Five distinct reaction types were observed (Table 2.13)

Table 2.13 Composition of hydrate types (37)

<table>
<thead>
<tr>
<th>Hydrate type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>tobermorite plus C-S-H(I)</td>
</tr>
<tr>
<td>II</td>
<td>C-S-H(I) plus C-S-H(II)</td>
</tr>
<tr>
<td>III</td>
<td>70-80% gehlenite hydrate (C_2ASH_n) plus 20-30% C-S-H(I)</td>
</tr>
<tr>
<td>IV</td>
<td>70-80% hydrogarnet phase (C_3ASH_n) plus 20-30% C-S-H(I)</td>
</tr>
<tr>
<td>V</td>
<td>mostly tricalcium aluminate hexahydrate (C_3AH_6)</td>
</tr>
</tbody>
</table>

SEM observations showed that each hydrate type had a distinctive crystalline morphology. Pastes which contained hydrate types I or II had dense interwoven networks of either plate-like tobermorite or fine CSH fibres. Many points of contact and bonding sites were evident. Pastes with hydrate types III
contained clusters of imperfect plate-like crystals. Hydrate types IV and V had the most irregular structure, composed of globular crystals of hydrogarnets or $C_3AH_8$, with only a limited number of points of contact. The specific area, as measured by argon adsorption, decreased in the sequence I, II, III, IV, V.

A correlation between compressive strength and hydrate type was noted by Jambor. The major factors in determining the compressive strength were the hydrate type and its relative volume within a specimen.

An expression for the compressive strength ($S$), was derived for each hydrate type:

$$S = a\theta^3 + b\theta^2 + c\theta$$

where $\theta$ = volume of phase

$a, b$ and $c$ = constants depending on phase

A relationship between the mean pore size of pastes and compressive strength existed, which could be explained in terms of mineralogy (hydrate type) and crystalline morphology (Fig. 2.18).

\[Fig. 2.18\] Relationship between compressive strength and pore size (37)
2.5 Overview

Numerous calcium silicate hydrates have been synthesised hydrothermally, but six are most commonly detected in commercial products, which have been autoclaved for relatively short times. These are:- C-S-H(I), C-S-H(II), α-C₂SH, tobermorite, xonotlite and gyrolite. In the early stages of autoclaving less crystalline CSH phases may also be detected. Hydrogarnets are also likely to exist within autoclaved products made with PFA.

Most experimental results support a reaction mechanism in which a reduction in the C/S ratio occurs with an associated increase in crystallinity. However, apparently anomalous behaviour may occur if the silica source exists as a glass. This can be attributed to the initial formation of a thin impervious CSH layer.

The microporosity will influence the strength of autoclaved products, but the nature of the reaction products and crystal morphology may also be significant factors.

The evaluation methods developed for PFA used in conventional concretes and mortars are inadequate for autoclaved products. There have been few studies to correlate the chemistry or mineralogy of PFA to hydrothermal performance. This project was, therefore, undertaken to improve the knowledge and understanding of the hydrothermal reactions of PFA and lime.
2.6 References


2. ibid.


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Methods to assess the hydrothermal performance of PFA

3.1 PFA samples

Experimental work required PFA samples which were comparable to the raw material available for the manufacture of AAC within Britain. Definition of a “typical ash” is difficult, given the variability in properties of the raw material. It was decided to obtain raw material from two British power stations known to supply PFA of acceptable quality for the manufacture of AAC. The power stations selected were Ratcliffe-on-Soar and Drakelow B (to be referred to as Ratcliffe and Drakelow in subsequent text). Basic information on each power station is summarised in Table 3.1.

Table 3.1 Details of Ratcliffe-on-Soar and Drakelow C Power Stations

<table>
<thead>
<tr>
<th></th>
<th>Ratcliffe-on-Soar</th>
<th>Drakelow C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Generating capacity</td>
<td>502 (unit 1)</td>
<td>325 (unit 1)</td>
</tr>
<tr>
<td></td>
<td>502 (unit 2)</td>
<td>325 (unit 2)</td>
</tr>
<tr>
<td></td>
<td>502 (unit 3)</td>
<td>240 (unit 3)</td>
</tr>
<tr>
<td></td>
<td>502 (unit 4)</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>2008</td>
<td>890</td>
</tr>
<tr>
<td>station</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal source</td>
<td>UK bituminous coal</td>
<td>UK bituminous coal</td>
</tr>
<tr>
<td>Type of boiler</td>
<td>Pulverised fuel fired with horizontal burners</td>
<td>Pulverised fuel fired with horizontal burners</td>
</tr>
<tr>
<td>Environmental</td>
<td>Flue gas desulphurisation</td>
<td></td>
</tr>
<tr>
<td>engineering</td>
<td>installed. Low NOx</td>
<td></td>
</tr>
<tr>
<td></td>
<td>burners fitted on unit 2</td>
<td></td>
</tr>
</tbody>
</table>
3.2 Evaluation of PFA samples

The PFA samples, and ash fractions derived from these, were characterised by physical, chemical and mineralogical analyses.

3.2.1 Particle size distribution

Particle size distributions of the raw ashes, and fractions derived from these, were determined using a Malvern 3600E laser particle sizer, fitted with a 63 mm focal length lens. The "powder in liquid" algorithm provided with the device was used to calculate particle size distributions.

Method

PFA, or ash fraction (5 g), was dispersed in distilled water (5 cm³). An aliquot (5 cm³) of 4 % penta-sodium triphosphate solution was added as a dispersion aid. After vigorous mixing for 15 ± 1 s, the suspension was poured into the receiving bath of the Malvern particle sizer and subjected to ultrasonic agitation for 15 ± 1 s. A particle size distribution was obtained using the procedures given in the operating instructions.

3.2.2 Specific gravity

The method given in ASTM C188-84 (1) was used to determine the specific gravity of PFA samples and ash fractions.

Method

A 250 cm³ capacity Le Chatelier flask, graduated between 0 to 1 cm³ and 18 to 24 cm³, was used as the pycnometer. An accuracy of ± 0.05 cm³ was claimed by the manufacturer (ELE Limited). Equipment and reagents were allowed to reach a temperature of 293 K before measurements were taken. A sample of PFA, or ash fraction (approximately 100 ± 0.001 g), was weighed into a vessel. The pycnometer was filled with analytical grade propan-2-ol, to between the 0 and 1 cm³ graduation, stoppered and allowed to stand for 10 minutes. The liquid level within the flask was recorded and powder was added to the pycnometer using a 5 mm wide spatula. Care was taken to prevent build-up of material in the neck of the flask. Sufficient powder was added to
raise the liquid column to between the 23 to 24 cm$^3$ graduations. The pycnometer was stoppered, gently rocked and rotated for 5 minutes to remove entrained air. The flask was placed on a level surface and left undisturbed for 15 minutes. The new level of the displaced propan-2-ol was recorded. The powder remaining in the beaker was weighed (± 0.001 g) and the amount added to the pycnometer calculated by difference from the original weight. The volume of propan-2-ol displaced was determined and the specific gravity (g cm$^{-3}$) of each sample calculated using the formula:-

$$\text{specific gravity} = \frac{\text{mass of powder}}{\text{volume of propan-2-ol displaced}}$$

Duplicate measurements were taken for each sample and the mean calculated.

3.2.3 Elemental analysis

Elemental analysis of PFA samples and ash fractions, was carried out at the Geology Department, University of Leicester. A combination of X-ray fluorescence (XRF) (2), and carbon/sulphur analysis by a LECOTM CS-125 apparatus was used (Appendix 1). Results are given as mass percentages of nominal oxides (e.g. silicon as SiO$_2$ %), except for carbon, which is reported as the element.

3.3 Research autoclaves

Five research autoclaves are available for the hydrothermal curing of test specimens (Figs. 3.1 and 3.2). Each vessel has a nominal internal volume of 0.05 m$^3$. A steam manifold supplies steam from two coal-fired boilers, each capable of delivering 1.8 kg s$^{-1}$ of steam. The research autoclaves are located within 15 m of the boilers, ensuring a minimal pressure drop. Entry and exit of the steam into each vessel is by means of electrically operated valves, which are controlled by dedicated microprocessors. Controlled pressurisation of each research autoclave is achieved. All stages of the autoclaving cycle may be programmed, controlled and monitored. Thermocouples fitted within the vessels allow the temperatures of specimens to be directly measured during

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autoclaving. An illuminated viewport in a single research autoclave allows specimens to be inspected throughout the hydrothermal curing process.

Fig. 3.2 Unloading a 250 mm AAC cube from a research autoclave
3.4 Small scale AAC specimens

Production of small scale AAC specimens (250 mm cubes) has proved to be an effective means of evaluating and comparing different raw materials. Differences in compressive strength due to raw materials have been demonstrated (3). It is possible to rank PFA sources, or cements, by their influence on the compressive strength attained in AAC specimens.

Small scale AAC specimens are of limited use for the analysis and monitoring of hydrothermal reactions. The compositions of mixes are complex, consisting of PFA, cement, quicklime and anhydrite. There is no simple chemical parameter to use as an indicator of hydrothermal reactions. Measuring the consumption of lime is not possible, because cement liberates calcium hydroxide at an unknown rate. It is not easy to follow the reactions by XRF, since the spectra are complex and not readily interpreted. The anhydrous calcium silicates and calcium aluminates present in cement can give significant peak overlap in the region of 25 to 35° 2θ. For example, unreacted alite will produce a strong diffraction peak around 32.2° 2θ, which is the position where a major peak due to hydogarnet may be expected.

3.5 Ash/lime pastes

The simplest test procedure which can be envisaged, yet still be of relevance to AAC manufacture, is a mixture containing PFA, calcium hydroxide and water. An important factor in the procedure is selection of a suitable calcium hydroxide. Experiments with pastes (Chapter 4), used analytical grade calcium hydroxide. Tests with other types of ash/lime specimens used a grade of fine calcium hydroxide supplied by Rhone Poulenc (Chapter 6).

By using calcium hydroxide as a starting material, it is possible to follow the hydrothermal reactions of PFA, or ash fractions, by monitoring the consumption of free lime, either chemically, or by observing changes in the x-ray diffraction peaks. Interference from XRD peaks of cement constituents does not occur.

The XRD spectra of ash/lime pastes are much simpler to interpret than those of AAC specimens. The main peaks for calcium hydroxide (portlandite) correspond to 0.490, 0.263 and 0.193 nm. The bulk of any PFA sample is
amorphous aluminosilicate glass, which has no diffraction peaks, but rather a broad hump. However, a few peaks due to the crystalline phases quartz, mullite, magnetite and haematite are normally detected. Autoclaving of specimens gives rise to new peaks, notably from the formation of CSH phases or hydrogarnet, occurring at d-spacings between 0.50 to 0.25 nm. If CuKα radiation is used, this corresponds to 2θ angles between 18 and 36°.

3.5.1 Preparation of ash/lime pastes
Method
Calcium hydroxide (1.000 g) was blended with PFA (2.066 g) in a 50 cm³ capacity polymethylpentene beaker. Care was taken to ensure an intimate mix of the powders. Distilled water (2.5 cm³) was added from a graduated pipette. The mix was stirred vigorously with a polypropylene rod to obtain a homogeneous paste. The beaker was covered with polyethylene film to reduce the risk of atmospheric carbonation. Beakers containing the moist pastes were uncovered and placed on the shelf of a research autoclave. Each beaker was covered with a loose fitting watch glass. The autoclave door was closed and the vessel sealed prior to entry of steam.

Pastes were subjected to autoclave cycles consisting of 10 minutes steam purge (373 K), 10 minutes linear pressurisation to 1100 kN m⁻² (457K), a dwell period at 1100 kN m⁻² ranging from 15 to 720 minutes, followed by a 10 minute linear depressurisation to atmospheric pressure. Measurements from thermocouples placed in selected pastes confirmed that the required temperature was achieved. After autoclaving, pastes were air dried for 10 minutes, sealed in polyethylene bags and stored in air-tight polypropylene vessels containing Carbosorb™ to minimise CO₂ contamination.

3.5.2 Analysis of autoclaved ash/lime pastes.
Procedures developed to analyse autoclaved ash/lime pastes were:
(1) measurement of free lime
(2) solubilization studies
(3) qualitative XRD
Infrared spectroscopy (IR) of oven-dried fragments of pastes was also investigated. A 10:1 by weight dilution with potassium bromide was used and spectra were run on a Nicolet DKZ FTIR spectrometer. Results were generally unsatisfactory. Absorbance bands due to changes in vibrational energy were noted, but these could not be readily assigned to specific functional groups. This was attributed to the complex mixtures of silicates, aluminosilicates and hydrates, each of variable stoichiometry, present in the specimens.

3.5.2.1 Free lime measurement

One satisfactory measure of the hydrothermal reactions of a PFA sample, or ash fraction, is the rate at which lime is consumed during autoclaving. Therefore, chemical methods for measuring the free lime (CaO and Ca(OH)₂) were investigated. The basis of the work were methods developed for testing mortars and concrete.

Specific reagents may be used, which selectively dissolve free lime from concrete and mortars. Once dissolved as complexed calcium ions, the free lime may be titrated with dilute acid of known molarity, thereby, allowing the calcium content to be determined. Precautions are required to prevent carbonation of the solution, otherwise insoluble bicarbonates or carbonates may form, reducing the apparent level of "free lime". Common reagents capable of selectively dissolving "free lime" are ethyl acetoacetate dissolved in butan-2-ol (Franke method), sucrose solution and 1, 2 ethane diol (4, 5, 6).

The Franke method was chosen as the most appropriate method of measuring free lime in autoclaved specimens. Benefits of the procedure include the protection of extracting solution from atmospheric CO₂, intimate contact with the sample during refluxing and a distinct end point during titrations.

Experiments were undertaken to determine a suitable extraction period for the Franke method. A sample of autoclaved ash/calcium hydroxide paste was extracted for periods ranging from 15 to 480 minutes and the free lime measured. With an extraction time of 240 minutes (4 h) a near constant value was reached. This represented the stage at which all free lime (CaO and Ca(OH)₂) had been removed from the paste. Any further apparent increase in the amount of calcium hydroxide reacted would be due to the removal of lime.
from CSH phases. However, after 120 minutes extraction time, the majority of the free lime had been removed and this period was adopted as a feasible standard extraction time. It was considered important to use as short an extraction time as possible, since this would minimise the amount of lime removed from the semi-crystalline CSH phases.

Method

Finely ground dry material (0.5 ± 0.05 g) was placed in a 250 cm$^3$ capacity dry Erlenmeyer flask with a mixture of ethyl acetoacetate (12 cm$^3$) and butan-2-ol (80 cm$^3$). A water-cooled spiral reflux condenser, fitted with a drying tube containing soda lime, was attached to the flask. The flask was heated under reflux for 2 h. The contents of the flask were filtered before cooling, through a Buchner funnel using a Whatman No 40 filter paper. The flask and the filtration equipment were washed three times with warm propan-2-ol. The filtrate was transferred to a 250 cm$^3$ capacity conical flask and a few drops of bromophenol blue dissolved in ethanol was added. The filtrate was titrated against 0.1M hydrochloric acid (Convol$^\text{TM}$). An end point was achieved with a colour change from blue to yellow.

3.5.2.2 Solubilisation studies

PFA has limited solubility in dilute hydrochloric acid, but calcium hydroxide is readily soluble. Most products of hydrothermal reactions between PFA and lime are also likely to be readily acid soluble. This difference may be exploited to compare the reactivities of different ashes. Consider a dry mixture of PFA and calcium hydroxide treated with dilute acid. Total dissolution of calcium hydroxide will occur, but the aluminosilicate glass and crystalline phases will be generally unreactive. A mixture which has undergone hydrothermal reaction behaves differently. Such autoclaved specimens may be assumed to consist of three components, unreacted calcium hydroxide, reaction products and unreacted PFA particles. The calcium hydroxide is readily acid soluble. The reaction products, such as CSH phases, are generally soluble in dilute acid. Unreacted PFA particles consist of glassy fragments or regions composed of crystalline phases, such as quartz,
mullite, haematite and magnetite, and have low solubility in dilute acid.

The amount of insoluble residue is a measure of unreacted PFA. As autoclaving proceeds the PFA is effectively solubilised. This offers one means of monitoring hydrothermal behaviour. For each autoclaved paste, the fraction of insoluble residue \((r)\) may be measured, the fraction of PFA \((a)\) in the original composition is also known. Therefore, the amount of PFA reacted during autoclaving may be estimated:

\[
\% \text{ PFA reacted} = \frac{r \times 100}{a}
\]

The acidic filtrate contains calcium from the calcium hydroxide, but of more relevance, also solubilised silicon, aluminium, sodium and potassium. These elements, which are initially held in the glassy aluminosilicate matrix of the PFA samples, become incorporated into the reaction products during autoclaving and, therefore, are solubilised. Analysing the acidic filtrate is a means of monitoring the solubilisation of silicon, aluminium and alkalis from PFA particles during hydrothermal reactions. A method of measuring solubilised material from PFA particles was suggested by Dr. F.G. Buttler. Samples of ash/lime pastes, autoclaved at 457 K for dwell times from 15 to 720 minutes were submitted for analysis. Details of the method used by Buttler are given in Appendix 2.

3.5.2.3 Qualitative XRD

XRD was used to monitor the formation of reaction products as autoclaving proceeded. Fragments of pastes were oven-dried at 378 K for 60 minutes and allowed to cool for 5 minutes. Approximately 5 g of material was crushed using a mortar and pestle to pass a 90 μm sieve.

Specimens for XRD were prepared by gently compacting each powdered sample to a depth of 2 mm in an aluminium sample holder. A glass microscope slide was used to obtain an even surface. Each sample was scanned at 1° min\(^{-1}\), from 5 - 60° 2θ, using CuK\(_{\alpha}\) radiation.
3.6 Overview of ash/lime pastes

Preparation and analysis of autoclaved ash/lime pastes is a means of understanding the basic hydrothermal reactions which occur between PFA and lime. Differences in the rates of lime consumption, the appearance of reaction products, and the solubilisation of particular elements, may be observed. The water/solids (w/s) ratio of the pastes is comparable to that of production mixes of AAC. This means that reactions are not limited by the availability of water as a reactant. Transport of reacting species, in particular calcium and silicate ions is facilitated. The concentration of ions which builds up in the aqueous phase should be similar to that which exists in production AAC mixes. A significant drawback of autoclaved ash/lime pastes is that they are unsuitable specimens from which to obtain strength or density measurements.

3.6.1 Criteria for ash/lime specimens

The strength which AAC achieves as a result of autoclaving is of fundamental importance since it determines the load-bearing characteristics of any structure. Specimens used to characterise the hydrothermal performance of PFA samples, or ash fractions, should satisfy the criteria given below:

1. Have a w/s ratio similar to that of AAC production mixes.

2. Achieve sufficient green strength to survive handling before autoclaving. In particular, to be strong enough to allow removal from moulds.

3. Be capable of surviving the thermal stresses of autoclaving without damage such as crazing, spalling or cracking.

4. Have a regular geometry to enable compressive strength and bulk density to be readily measured.

5. Give a failure load within the calibrated range of a compression testing machine.
3.6.2 Choice of ash/lime specimens

Three types of ash/lime specimens were made and evaluated in experiments using the raw ashes obtained from Ratcliffe and Drakelow. Each method was judged against the criteria given in section 3.6.1.

3.6.2.1 Ash/lime discs

Discs made from PFA, calcium hydroxide and water were pressed and autoclaved. Strength was determined using the "Brazilian test", an indirect method of measuring tensile strength, developed independently by Carneiro and Barcellus (7) and Akazawa (8). The method was also used by Price (9) to measure the green strength of unfired clays and ceramic bodies. Advantages cited for the method are its simplicity, suitability for small samples and the fact that it is less influenced by surface conditions than other measurements of strength. Load is applied diametrically across a cylindrical specimen. Pads of compressible material, usually cardboard, are placed between the specimens and the platens of the test machine. This reduces the effect of point loading along the axis of the cylinder caused by irregularities.

Each disc had a nominal diameter of 38 mm and a thickness ranging from 11 to 13 mm. W/s values between 0.09 and 0.25 were investigated. Autoclaving experiments were undertaken with purge times of 30 or 60 minutes and pressurisation times between 30 to 120 minutes. Damage to specimens during autoclaving was severe with the majority of discs. Cracking, bloating and delamination of the discs were typical failures which occurred. Whilst the autoclaving cycle had some influence, the major effect was due to the moisture content of the discs. High water contents made the discs more susceptible to thermal damage during autoclaving. A w/s value of 0.1 gave minimum damage, but still retained sufficient plasticity to allow pressing into discs. A possible explanation for this is that insufficient green strength exists during the early stages of autoclaving (Figs. 3.3 and 3.4).
Fig. 3.3  A satisfactory ash/lime disc (w/s = 0.1)

Fig. 3.4  An ash/lime disc showing severe damage as a result of autoclaving
Method

PFA (206.6 g) was blended with calcium hydroxide (100.0 g) by vigorous shaking in a polyethylene bag for 120 to 180 s. The dry components were further mixed within a planetary mixer for 30 ±1 s and distilled water (31 cm³) was slowly added. Mixing continued for 120 ±1 s to form a moist paste. The paste was removed from the planetary mixer and sealed within a polyethylene bag to minimise carbonation. Sub-samples of paste (24.8 to 25.2 g) were added to an oiled 38 mm diameter die fitted to a laboratory press. A load of 1.56 kN was applied and maintained for 15 ± 1 s, when the load was gently released using a bleed valve. The pressed disc was removed and stored in a polyethylene bag prior to autoclaving. For each set, 14 individual discs were made and tested.

Discs were cured with an autoclave cycle consisting of 60 minutes steam purge (373 K), 60 minutes linear pressurisation to 1100 kN m⁻² (457 K), a dwell period at 1101 kN m⁻² up to 1080 minutes, followed by a 60 minute linear depressurisation to atmospheric pressure. Once cured, the discs were allowed to cool for approximately 15 minutes and sealed in polyethylene bags in order to minimise carbonation.

Discs were placed in freshly boiled distilled water and soaked for 4 days at 293 ± 2 K. After soaking, specimens were removed from the water and wiped with paper tissue to remove excess water. The diameter and thickness of each disc was measured to an accuracy of ±0.05 mm using a digital caliper. At least four readings of each dimension were obtained and a mean value calculated. Discs were placed between the platens of a compression cage fitted to a Monsanto tensometer. Cardboard pads were placed between the circumference of the disc and the platen in order to minimise the effect of irregularity within the specimens. Load was steadily applied until failure of the disc. The load at failure was noted and the diametral compressive strength (S) calculated by:

\[ S = \frac{2p}{\pi ld} \]

- \( p \) = applied load
- \( l \) = length of cylinder
- \( d \) = diameter of cylinder
3.6.2.2 Ash/lime cylinders

To make ash/lime discs which survive autoclaving requires low water contents (w/s = 0.1). Thus, criterion [1] given in section 3.6.1 is not satisfied, since specimens will have significantly less water than typical AAC mixes. Such high water contents make it necessary to cast ash/lime mixtures as viscous slurries into moulds and allow some green strength to develop. This requires a period of precure at elevated temperatures (338 to 348 K). Initial experiments used 30 mm diameter cylinders, tested in axial compression. These specimens were produced in cylindrical steel moulds 1 mm thick by 50 mm high, but split along the axis to allow release. Saturated compressive strengths for the cylindrical specimens were determined.

Method

PFA (413.2 g) was blended with calcium hydroxide (200.0 g) by vigorous shaking in a polyethylene bag for 120 to 180 s. The dry components were further mixed within a planetary mixer for 30 ± 1 s and distilled water (245 cm³) slowly added. Mixing continued for 120 ± 1 s to form a viscous slurry. The slurry was removed from the planetary mixer and placed in a 1000 cm³ capacity beaker which was covered in polyethylene film to minimise atmospheric carbonation.

Sub-samples of slurry (45.0 to 55.0 g) were poured into oiled steel moulds. Each mould was sealed with polyethylene film and placed in an oven at 448 ± 2 K. After 5 h, the cylinders were stripped from the moulds and placed into a warm research autoclave. Cylinders were cured with an autoclave cycle consisting of 30 minutes steam purge at 373 K, 60 minutes linear pressurisation to 1100 kN m⁻² (457K), a dwell period at 1100 kN m⁻² of 15 to 720 minutes, followed by a 60 minute linear depressurisation to atmospheric pressure. Once cured, the cylinders were allowed to cool for approximately 15 minutes and sealed in polyethylene bags. The cylinders were cut to a length between 20 to 25 mm using a fine diamond saw and saturated in freshly boiled distilled water and soaked for 4 days at 293 ± 2 K. After saturation, lengths and diameter were measured to an accuracy of ± 0.05 mm using a digital caliper. The cylinders were placed on the platens of the side-arm of an Avery-
Denison 7227CB compression test machine and load applied along the axes. Cardboard packing was used between the specimens and the flanges. The specimen were loaded at a rate of 10 kN/min until failure. Compressive strength (MPa) was calculated by dividing the failure load (N) by the mean cross-sectional area of the cylinder (mm²), (Figs. 3.5 and 3.6).

Fig. 3.5 An autoclaved ash/lime cylinder

Fig. 3.6 The Avery-Denison compression test machine
3.6.2.3 Ash/lime cubes

A procedure for preparing 50 mm mortar cubes given in ASTM C109-92 (10) was modified to produce ash/lime specimens which could be autoclaved, analysed by various methods and tested for compressive strength. An ash/lime slurry was cast into a "three gang" mould, with three separate cube compartments (Fig. 3.7). Two cubes from each set were used to determine saturated compressive strength, and one cube was retained for analysis.

Fig. 3.7 "Three gang" mould and autoclaved ash/lime cube

Cubes were made with w/s = 0.45 for both ashes. Slurries made with the ash fractions had different viscosities, coarser material required less water to produce a mix for casting. Thermal damage during autoclaving was largely affected by the water content of the cubes. Therefore, for each particular ash fraction a w/s value was found empirically which gave an acceptable consistency for casting, but minimised the thermal damage during autoclaving. The w/s values used for each ash fraction are summarised in Table 3.2. The five ash fractions derived from Ratcliffe PFA are designated 1 to 5 from the most fine, RC[A], to the most coarse RC[E]. Similarly, ash fractions derived from Drakelow PFA are designated DK[A] to DK[E] (sections 5.1.1 and 5.2.1).

The green strength achieved in all the specimens was modest. This was due to the slow pozzolanic reaction between the lime and the ash. However, it was evident that the green strength which was achieved was influenced by the
water content and curing before autoclaving. The procedure for producing 50 mm cubes was successful in achieving an ash/lime specimen with w/s = 0.38 to 0.46 which survived autoclaving. Thus, the water content of specimens was similar to that encountered in AAC mixes.

Table 3.2 Relationship between fineness of ashes and w/s for 50mm cubes

<table>
<thead>
<tr>
<th>Ratcliffe ash fractions</th>
<th>Drakelow ash fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference d50 (μm)</td>
<td>w/s</td>
</tr>
<tr>
<td>raw ash</td>
<td>14.2</td>
</tr>
<tr>
<td>RC[A]</td>
<td>4.6</td>
</tr>
<tr>
<td>RC[B]</td>
<td>10</td>
</tr>
<tr>
<td>RC[C]</td>
<td>24.4</td>
</tr>
<tr>
<td>RC[D]</td>
<td>41.2</td>
</tr>
<tr>
<td>RC[E]</td>
<td>51.7</td>
</tr>
</tbody>
</table>

During the manufacture of AAC, the period from casting to demoulding is typically 2 to 3h, in which time the internal cake temperature may rise from 318 to 358 K. After demoulding the cakes are cut into individual blocks and typically left 1 to 2 h prior to loading into the production autoclaves. Therefore, the temperature used to precure both the cylindrical specimens and the 50 mm cubes is comparable to that encountered by a production cake.

To assess the variability of the method for producing and testing autoclaved ash/lime cubes, 6 sets were cast using Ratcliffe PFA and autoclaved for a dwell time of 360 minutes. All three cubes within each set were saturated and tested for compressive strength (a single result from a cracked cube was discarded). The results are given in Table 3.3.

ASTM method C 109 - 92 gives the coefficient of variance expected within a single laboratory for the compressive strength of 50 mm mortar cubes produced with various cements. The values quoted for 7 day strength range from 3.6 %, for cubes containing portland cements made at a constant water-cement ratio, to 7.9 % for specimens containing masonry cement made
to a constant consistency. Therefore, the 5.7% coefficient of variance recorded in Table 3.3 appears to be acceptable.

Table 3.3 Variability of saturated compressive strength measured for 50 mm autoclaved ash/lime cubes

<table>
<thead>
<tr>
<th>reference</th>
<th>number of cubes tested from each set</th>
<th>mean saturated compressive strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>set 1</td>
<td>3</td>
<td>10.94</td>
</tr>
<tr>
<td>set 2</td>
<td>3</td>
<td>10.03</td>
</tr>
<tr>
<td>set 3</td>
<td>3</td>
<td>10.52</td>
</tr>
<tr>
<td>set 4</td>
<td>3</td>
<td>10.76</td>
</tr>
<tr>
<td>set 5</td>
<td>2</td>
<td>10.66</td>
</tr>
<tr>
<td>set 6</td>
<td>3</td>
<td>10.54</td>
</tr>
<tr>
<td>Total</td>
<td>17</td>
<td>10.57</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>overall mean</th>
<th>10.57</th>
</tr>
</thead>
<tbody>
<tr>
<td>standard deviation</td>
<td>0.61</td>
<td></td>
</tr>
<tr>
<td>coefficient of variance (%)</td>
<td>5.7</td>
<td></td>
</tr>
<tr>
<td>2 x standard deviation</td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td>3 x standard deviation</td>
<td>1.83</td>
<td></td>
</tr>
</tbody>
</table>

Method

PFA, or ash fraction (300 g), was blended with calcium hydroxide (145.2 g) by vigorous shaking in a polyethylene bag for 120 to 180 s. The dry components were further mixed within a planetary mixer for 30 ± 1 s and distilled water (170 to 205 cm³) slowly added. Mixing continued for 120 ±1 s to form a viscous slurry. The slurry was stored in a polyethylene bag, sealed to exclude air, prior to casting. A "three gang" steel mould was assembled (Fig. 3.7) and heated within an oven to 348 ± 2 K. The mould was firmly clamped to a vibratory table and its interior surfaces brushed with a release oil. Once vibration started, the ash/lime slurry was carefully added to the mould. The sections were filled sequentially to a depth of about 5 mm, with each pass.
The sections were filled to within 2 mm of the top. Vibration continued for 120 ± 2 s to remove entrained air. The mould was unclamped, covered with a sheet of polyethylene film and placed in the oven at 348 ± 2 K. After 5 h the cubes were carefully stripped from the moulds and allowed to remain in the oven for 1 h, to increase green strength prior to autoclaving. The cubes were placed in an autoclave preheated to 373 K and subjected to 60 minutes steam purge, 60 minutes linear pressurisation to 1100 kN m⁻² (457 K), a dwell time at 1100 kN m⁻² up to 1080 minutes, followed by a 60 minute linear depressurisation to atmospheric pressure.

The autoclaved cubes were allowed to cool for approximately 15 minutes. A single cube from each set was shrink wrapped within a double layer of polyethylene film and stored in a container with Carbosorb®. The remaining two cubes had the uneven top surfaces trimmed by 2 to 5 mm using a diamond studded cut-off saw lubricated with water. Two cubes from each set were saturated in freshly boiled distilled water for 4 days at 293 ± 2 K. After saturation, the dimensions of the cubes were measured to an accuracy of ± 0.05 mm using a digital caliper. The cubes were placed between the platens of the side-arm of an Avery-Denison 7227CB compression test machine. Thin cardboard packing was used between the specimens and the platen. The specimens were loaded perpendicular to the original casting direction, at a rate of 10 kN min⁻¹ until failure. Compressive strength (MPa) was calculated by dividing the failure load (N) by the mean cross-sectional area of each cube (mm²).

3.7 X-Ray Diffractometry (XRD)

XRD has been used to analyse autoclaved ash/lime pastes and cubes.

3.7.1 Role of XRD

Specific uses for the technique include:

(1) to identify reaction products within autoclaved specimens
(2) to monitor the consumption of reactants during autoclaving
(3) to identify the crystalline phases within PFA samples, or ash fractions, derived from PFA.
PFA samples, the ash fractions derived from these, and the hydrothermal reaction products with lime, are all complex mixtures of inorganic compounds. XRD discriminated between phases and the made it possible to observe differences in the behaviour of the ash fractions during autoclaving.

Qualitative and quantitative procedures have been used in the project. In particular, a quantitative method has been devised to assess the mineralogy of ash fractions obtained after classification using the Minisplit™. In conjunction with XRF results and loss on ignition data, it has allowed the bulk composition of the glass in each ash fraction to be calculated.

If a finely divided powder containing crystalline material is irradiated with x-rays, diffraction patterns may be observed. Each crystalline phase produces a "fingerprint", which may be used for identification. As McCarthy (11) noted, "every crystalline phase has a characteristic pattern, a set of peaks having characteristic angles and intensities, as a result of its internal structure and x-ray diffracting power of its particular atoms". X-ray diffraction patterns of standard materials, published by the Joint Committee on Powder Diffraction Standards (JCPDS files), may be consulted in order to identify the phases within a specimen of unknown composition. The two most important properties listed on a JCPDS file are the interplanar spacings (d-spacings) and the relative peak intensities.

For a phase to be detected by XRD it must have some crystallinity, that is, its atomic structure must be ordered to some extent. Amorphous, highly disordered structures such as glasses, do not give a strong diffraction pattern. Diffuse scattering occurs and the XRD trace has a broad hump spreading over several degrees $2\theta$. The reaction products in ambiently cured cementitious materials, such as concrete, typically exhibit a range of crystallinity. The initial calcium silicate hydrates (CSH phases), often have gel-like structures with only limited crystallinity. As these materials age the crystallinity of the CSH phases tends to increase. Consequently, XRD traces of concrete products usually show peaks for reaction products of low to moderate crystallinity. Within autoclaved products such as AAC, because of the high curing temperatures, conditions favour the formation of crystalline reaction products. XRD analysis is, therefore, a particularly useful technique for autoclaved products, since the
sharper, more distinct diffraction peaks of semi-crystalline and crystalline phases are observed.

3.7.2 Principles of XRD

The theory of XRD analysis is discussed and a quantitative method detailed.

3.7.2.1 Angular separation of diffracted peaks

Crystalline phases may be regarded as regular arrays of atoms. It can be imagined that numerous planes pass through each crystal. These lattice planes, may act as semi-transparent mirrors. Some x-rays will be reflected with an angle of reflectance equal to the angle of incidence. Other x-rays may be reflected from planes below. At most angles, diffraction will not occur, because the x-rays emerging from the specimen are out of phase and, therefore, interfere destructively. However, at certain angles, the x-rays emerging are in phase, constructive interference occurs and diffraction is observed. Diffraction is evident by a peak in x-ray intensity at the particular angular position. The relationship which must exist between the wavelength of x-rays (\( \lambda \)), the interplanar distances (d-spacings) and the diffraction angle (\( \theta \)), is given by the Bragg equation:

\[
n\lambda = 2d \sin \theta
\]

If these conditions are satisfied the emerging x-rays are in phase, i.e. they overlap by a whole number of wavelengths (n\( \lambda \)), and constructive interference occurs. The Bragg equation imposes quite rigorous conditions on diffraction. If the incident angle is incorrect by a fraction of a degree, diffraction will not occur.

If the wavelength (\( \lambda \)) is fixed and angular positions scanned, it is possible to calculate the interplanar spacings, which are characteristic of a particular phase. An x-ray diffractometer accurately measures 2\( \theta \) angles (twice the diffraction angle) and the intensities of the diffracted x-rays. Bombardment of a heavy metal anode with high energy electrons within an evacuated
enclosure may be used to generate x-rays of a characteristic wavelength. If the anode is pure copper, and the electrons are accelerated through a voltage of about 30 kV, ionisation of the 1s electrons (K shell) may occur. An electron in a higher orbital (2p or 3p) drops down to occupy a vacant 1s orbital and energy is liberated as x-ray photons. Transitions from 2p to 1s occur most frequently and give an x-ray photon with a wavelength of 0.15418 nm (CuKα radiation). Transitions from 3p to 1s correspond to a wavelength of 0.13922 nm (CuKβ radiation), but occur less frequently and, therefore, have a lower intensity. The CuKα radiation is actually split into a doublet, since the electrons may adopt one of two spin states of distinct energies and different characteristic wavelengths. The two components are CuKα1 (λ = 0.15405 nm) and CuKα2 (λ = 0.15443 nm), with an intensity weighted average for CuKα of λ = 0.15418 nm.

3.7.2.2 Intensities of diffraction peaks

The intensities of diffraction peaks are important for phase identification, since relative intensities are quoted in JCPDS files. Quantitative XRD also relies on a relationship between the weight fraction of the phase in a powder sample and the intensity of particular diffraction peaks. Unfortunately, the factors which influence intensity are complex. There is no analogous relationship to the Bragg equation which exists for angular separation.

The intensities of the diffraction peaks of a phase are dependent on the types of atoms, arrangement in the crystal and orientation of the particles within the powder sample. Scattering of x-rays from atoms within crystals determines the intensities of the diffraction peaks. A parameter, the scattering factor, or form factor (f), is used to show the influence of atomic number and diffraction angle. The scattering of x-rays is proportional to the atomic number of an atom, which means that phases with heavy elements tend to produce intense peaks. The Thomson equation, shows the influence of diffraction angle (2θ) on the scattered intensity (Ip):-

\[ Ip = (1 + \cos^2 2\theta) \]
Most intense peaks occur at low 2θ angles and few strong lines are evident at higher angles (plus 60°). It is more difficult to calculate diffraction peak intensities from first principles than d-spacings. More commonly, relative peak intensities are obtained from a well defined standard sample of a phase. Aluminium and silicon have similar atomic numbers and, therefore, scatter x-rays to a similar extent. Phases, such as aluminosilicates, which contain both types of atoms, have a large number of relatively intense diffraction peaks. The patterns of these types of phases are generally complex.

During analysis for the particular phase within a powder sample, allowances must be made for changes of diffraction peak intensities due to factors, such as instrumental differences, sample preparation, substitution of impurity atoms into the crystal lattice and the presence of compounds which produce diffraction peaks of comparable intensities and at a similar angular position.

In the project an internal standard method has been used to analyse autoclaved ash/calcium hydroxide specimens. This provides information on the relative amounts of reaction products. However, the "ratio of slopes" method has been utilised to provide estimates of the amount of mineral phases present in PFA samples and ash fractions derived from PFA.

3.7.2.3 Fineness of samples for XRD analysis

Random orientation of powder sample

A requirement for XRD analysis is that the irradiated sample is composed of numerous small crystallites, randomly oriented with respect to the incident x-ray beam. This ensures that the lattice planes are present in all possible orientations and a significant number will satisfy the Bragg conditions, producing diffraction peaks. Repacking the sample and rescanning produces the same set of peak intensities. A sample composed of relatively coarse particles may not possess sufficient correctly oriented crystallites. By chance, some orientations will be few, whilst others will be more numerous, resulting in lower and higher intensities respectively. If the sample is repacked and rescanned a different set of intensities will be observed.
Alexander and Klug (12) assessed the effects of the particle size of samples on the reproducibilities of diffraction peak intensities. Ten replicate analyses were carried out on a quartz sample of four particle size ranges. The mean percentage deviation in intensity reduced from 18.2 % for particles between 15 to 20 µm, to 1.2 % for particles less than 5 µm.

**Preferred orientation**

Preferred orientation is minimised with very fine powders. This effect is the tendency for the crystallites to align themselves in one direction. Preferred orientation is a particular problem for minerals with a layer structure, such as clays. If the crystallite length is large compared to its thickness, packing of the sample tends to cause alignment parallel to the plane of the sample holder. Since certain orientations of crystallites are encouraged, this significantly enhances the intensities of particular diffraction peaks. However, if the crystallites are ground finely enough, so that the crystallite lengths and thicknesses are comparable, the effect of preferred orientation is minimised.

**Extinction**

Extinction can reduce the overall intensities of diffraction peaks if crystallites are relatively large and contain many lattice planes. Diffraction and rediffraction may occur from several lattice planes within a crystallite and each stage will produce a phase shift of $\lambda/2$. Therefore, x-rays may emerge from the same crystallite out of phase and destructive interference will occur, thereby, reducing the intensities of the diffraction peaks. If the crystallites are smaller, with significantly fewer lattice planes, the chance of x-rays being out of phase, and destructively interfering, is much reduced and extinction effects are minimised.

**Microabsorption**

Microabsorption can occur in relatively coarse powders containing two or more separate phases, each possessing different mass absorption coefficients. The effect is to reduce the intensities of the diffraction peaks of the highly
absorbing constituent. If quantitative analysis is being carried out this results in an underestimate of the amount of the highly absorbing phase.

Absorption coefficients are dependent on the wavelength of the incident x-rays. If CuK\textsubscript{a} radiation is used to analyse iron-rich materials, microabsorption may be significant. Bish and Reynolds (13) noted that quantitative analysis can not be accomplished if microabsorption is significant. It was also observed that microabsorption effects lessen, as the size of the crystallites are reduced. A critical size exists, determined by the phase with the highest absorption coefficient, below which microabsorption does not influence the analysis.

Since the PFA samples and ash fractions analysed contain relatively large quantities of iron (haematite/magnetite), microabsorption is possible and efforts were made to minimise its affects in the project. Bish and Reynolds consider that accurate x-ray diffraction methods require crystallites of 10 \textmu m, preferably smaller. If microabsorption is a potential problem, smaller particle sizes are necessary. The grinding method used to prepare XRD specimens was chosen to obtain the small particles. A McCrone micronising mill was considered to be the most appropriate apparatus, since it was developed specifically for XRD and XRF analyses. Grinding under cyclohexane produces a narrow size distribution and localised heating due to friction between particles would be minimised, thereby, reducing surface changes. Particle size distributions were carried out using a Malvern particle sizer on ground samples used in the quantitative XRD experiments. These confirmed that the specimens were of a sufficient fineness.

3.7.2.4 Quantitative analysis by XRD

Quantitative XRD, which measures the amount of a particular phase within a specimen, was first recorded by Navia in 1925 (14). The concentration of mullite (3Al\textsubscript{2}O\textsubscript{3}.2SiO\textsubscript{2}), in fired ceramics was determined. Clark and Reynolds (15) in 1936 published a procedure which used an internal standard method for the analysis of mine dust. It was noted by Snyder and Bish (16), as recently as 1989, that "examples of quantitative phase analysis by XRD are not numerous in the literature".
Considerable effort is needed to ensure careful calibration of the instrument by using prepared standards. According to Snyder and Bish, the most widely used quantitative XRD method relies on an internal standard. The method will be outlined, and later the “ratio of slopes” procedure derived from the simple internal standard method will be discussed.

The intensity \( I_\alpha \) of an x-ray beam diffracted from a phase \( \alpha \), within a specimen is given by the equation:

\[
I_\alpha = \frac{K_\alpha \cdot x_\alpha}{\rho_\alpha(\mu)}
\]  

(1)

where,
- \( x_\alpha \) = weight fraction of phase \( \alpha \)
- \( \rho_\alpha \) = density of phase \( \alpha \)
- \( \mu \) = mass absorption coefficient of specimen
- \( K_\alpha \) = a constant for a given crystal structure, diffraction line and instrument conditions.

The mass absorption coefficient \( (\mu) \), is normally unknown, but the expression may be eliminated by using an internal standard. If a known weight of a standard material is mixed homogeneously with the specimen of unknown phase composition, the intensity is given by an analogous expression to equation (1), i.e.:

\[
I_s = \frac{K_s \cdot x_s}{\rho_s(\mu)}
\]  

(2)

where,
- \( x_s \) = weight fraction of standard \( s \)
- \( \rho_s \) = density of standard \( s \)
- \( \mu \) = mass absorption coefficient of standard \( s \)
Dividing equation (1) by equation (2) eliminates the mass absorption coefficient:

$$\frac{I_{\alpha}}{I_s} = \frac{K_{\alpha} \cdot x_{\alpha}}{\rho_{x} \cdot K_{s} \cdot x_{s}}$$ (3)

Equation (3) may be rearranged, combining the constants:

$$\frac{I_{\alpha}}{I_s} = K' \frac{x_{\alpha}}{x_s}$$ (4)

A calibration curve may be produced by plotting relative peak intensity $I_{\alpha}/I_s$ against weight ratio $x_{\alpha}/x_s$. A straight line is obtained with a slope of $K'$. However, $x_{\alpha}$ is the weight fraction of phase $\alpha$ in the mixture of the original specimen after it has been diluted by the addition of the internal standard. The weight fraction of phase $\alpha$ in the original specimen before dilution, $x_{\alpha}'$, is given by the equation:

$$x_{\alpha}' = \frac{x_{\alpha}}{(1-x_s)}$$ (5)

Normally, the weight fraction of the internal standard, $x_s$, is fixed. Therefore, $x_s$ and $(1-x_s)$ become constants and equation (4) may be simplified to:

$$\frac{I_{\alpha}}{I_s} = K'' x_{\alpha}$$ (6)

From a calibration curve with a slope of $K''$, the weight fraction of phase $\alpha$ in the original specimen may be determined.

3.7.2.5 The "ratio of slopes" method

The drawbacks to the internal standard method described above should be considered. The fixed ratio of the weights of specimens to internal standard must be accurately produced and mixed, otherwise the calibration curve
becomes invalid. A diluent is normally used in the construction of a calibration graph to allow a fixed ratio of the sample to internal standard to be maintained.

Monshi and Messer (17) proposed an alternative internal standard method, which overcame the disadvantages listed above. Two calibration curves are required. Data for a single "analysis line" is obtained by scanning a set of mixtures of the specimen and different amounts of the internal standard. For each phase being analysed, a "reference line" must also be produced. Data for the "reference line" is obtained by scanning a set of mixtures of a reference material, containing a known amount of the phase under investigation and different amounts of internal standard. The "analysis line" and "reference lines" are made by plotting relative intensities of characteristic peaks against the respective weight fractions. By calculating the gradient of each line and determining the ratio of the slopes of the "analysis line" to particular "reference lines", the weight fraction of each phase within the specimen may be estimated.

A single point on either the "analysis line" or "reference line" requires the preparation and scanning of an XRD sample. A sample for the "analysis line" is made by weighing, with high precision, the specimen ($W_A$ g) and the internal standard ($W_s$ g). The materials must be intimately mixed and of sufficient fineness for XRD analysis (see section 3.7.2.3). Likewise a sample for the "reference line" is made by accurately weighing and mixing together a pure phase ($W_R$ g) and the internal standard ($W_s$ g). For the "ratio of slopes" method, an analogous expression to equation (1) may be written for a particular phase $\alpha$ within the specimen being analysed. The expression relates peak intensity due to phase $\alpha$ within the specimen, its weight ($W_\alpha$ g) and the mass absorption coefficient ($\mu$).

$$I_\alpha = \frac{K_\alpha}{\rho_\alpha} \left( \frac{W_\alpha}{W_A + W_S} \right) \frac{1}{\mu} \quad (7)$$

Similarly, for the intensity due to the internal standard:

$$I_S = \frac{K_S}{\rho_S} \left( \frac{W_S}{W_A + W_S} \right) \frac{1}{\mu} \quad (8)$$
Dividing equation (7) by (8) eliminates the mass absorption coefficient:

\[
\frac{I_\alpha}{I_s} = \frac{K_\alpha \cdot \rho_s \cdot W_\alpha}{\rho_\alpha \cdot K_S \cdot W_S}
\]  

(9)

The weight of phase \( \alpha \) within any specimen is given by:

\[W_\alpha = W_A + \chi_\alpha \text{analysis} \]

(10)

Therefore, equation (9) may be rewritten, taking into account equation (10):

\[
\left( \frac{I_\alpha}{I_s} \right)_{\text{analysis}} = \frac{K_\alpha \cdot \rho_s \cdot W_A \cdot \chi_\alpha \text{analysis}}{\rho_\alpha \cdot K_S \cdot W_S}
\]

(11)

or,

\[
\left( \frac{I_\alpha}{I_s} \right)_{\text{analysis}} = \frac{K_\alpha \cdot \rho_s \cdot W_A \cdot \chi_{\alpha, \text{analysis}}}{\rho_\alpha \cdot K_S \cdot W_S}
\]

(12)

The analysis line may be produced by plotting the relative peak intensity \((I_\alpha/I_s)\) against the weight ratio \((W_\alpha/W_S)\). The slope \(((M))\) analysis, is therefore:

\[
\frac{K_\alpha \cdot \rho_s}{\rho_\alpha \cdot K_S} \cdot \chi_{\alpha, \text{analysis}}
\]

(13)

An expression, analagous to equation (12) may be produced for the reference line:

\[
\left( \frac{I_\alpha}{I_s} \right)_{\text{reference},} = \frac{K_\alpha \cdot \rho_s \cdot W_R}{\rho_\alpha \cdot K_S \cdot W_S} \cdot \chi_{\alpha, \text{reference}}
\]

(14)

Similarly, the reference line is obtained by plotting the relative peak intensity \((I_\alpha/I_s)\) against the weight ratio \((W_R/W_S)\). The slope \(((M))\) reference, is therefore:

\[
\frac{K_\alpha \cdot \rho_s}{\rho_\alpha \cdot K_S} \cdot \chi_{\alpha, \text{reference}}
\]

(15)
Dividing equation (13) by equation (15) gives the ratio of the slopes and the expression:

\[
\frac{(M)_{\text{analysis}}}{(M)_{\text{reference}}} = \frac{x_{\alpha,\text{analysis}}}{x_{\alpha,\text{reference}}} \quad (16)
\]

Rearranging gives:

\[
x_{\alpha,\text{analysis}} = \frac{(M)_{\text{analysis}}}{(M)_{\text{reference}}} \cdot x_{\alpha,\text{reference}} \quad (17)
\]

Thus, the weight fraction of the phase \( \alpha \) in the specimen may be determined. Equation (17) is the general expression for the "ratio of slopes" and requires that the purity of the reference sample is known (i.e. weight fraction \( x_{\alpha,\text{reference}} \)). If, however, a pure phase is used, \( x_{\alpha,\text{reference}} \) becomes unity and a simpler expression is obtained:

\[
x_{\alpha} = \left( \frac{(M)_{\text{analysis}}}{(M)_{\text{reference}}} \right) \quad (18)
\]

3.7.3 Method to assess the mineralogy of PFA samples and ash fractions

A method was developed to analyse for the main crystalline phases present in PFA, or ash fractions.

3.7.3.1 Phase composition

The phases of interest were quartz (SiO\(_2\)), mullite (3Al\(_2\)O\(_3\).2SiO\(_2\)), magnetite (Fe\(_3\)O\(_4\)) and haematite (Fe\(_2\)O\(_3\)). A "ratio of slopes" procedure, outlined in section 3.7.2.5 was developed to analyse for these phases. Rutile (TiO\(_2\)) was selected as the most appropriate internal standard for quantitative XRD analysis of ashes. Its major d-spacings of 0.325, 0.249 and 0.169 nm, which if CuK\(_{\alpha}\) radiation is used, corresponds to 2\( \theta \) angles of 27.4, 36.1 and 54.3\(^{\circ}\) respectively. These peaks do not overlap significantly with any of the main mineral phases within PFA. A 1 kg sample of rutile, grade Kronos...
3025™, was obtained from NL Chemicals Inc., and used throughout the project (Appendix 3).

Scanning from 20 to 35° 2θ provides a compact region of the x-ray spectrum, which is useful for analytical purposes. The major diffraction peaks of quartz, mullite, haematite and magnetite occur here. The internal standard (rutile) also has its main diffraction peak in this region. Slow scanning of specimens is possible. A scan rate of 0.5° min⁻¹ allows a trace to be obtained in about 30 minutes. This is important in the "ratio of slopes" method, which requires at least two specimens to be scanned in order to obtain the "analysis line" for the sample. Scanning a wide range of 2θ angles would be time consuming.

**Preparation of "analysis lines"**

The PFA sample, or ash fraction, (approx. 1 g) was blended with rutile (from 0.05 to 1.02 g) and interground in cyclohexane (10 cm³) in a McCrone mill for 24 minutes. The cyclohexane was removed by drying the slurry on a petri dish at 278 K for 10-15 minutes. A range of powdered specimens were made, with ash/rutile ratios ranging from 7.5 to 20.7.

An aluminium sample holder, with a 20 mm square and 2 mm deep recess, was filled with a powder specimen which was compressed gently with a glass microscope slide to ensure an even surface. Care was taken to prevent excessive compaction or shearing, which could cause preferred orientation of the crystallites within the specimens. Each powder specimen was mounted at the centre of the goniometer of a Siemens Type F diffractometer and scanned from 20 to 35° degrees 2θ using CuKα radiation (λ = 1.5406 nm) and X-ray spectra were recorded on a conventional chart recorder. The operating conditions used were:

- Tube voltage = 35 kV
- Tube current = 20 mA
- Scan rate = 0.5° min⁻¹
- Time constant = 4 s
For each powder specimen, relative peak intensities compared to rutile were calculated for the following peaks:

<table>
<thead>
<tr>
<th>2θ angle</th>
<th>phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.3</td>
<td>mullite</td>
</tr>
<tr>
<td>26.6</td>
<td>quartz</td>
</tr>
<tr>
<td>33.2</td>
<td>haematite</td>
</tr>
<tr>
<td>30.1</td>
<td>magnetite</td>
</tr>
</tbody>
</table>

Areas under each peak were calculated by a "cut and weigh" procedure. Peak intensities, compared to rutile, were plotted against weight ratios for each peak arising from a particular phase. A best fit straight line graph was drawn using the origin as an additional point. The gradient of the line was calculated. Each plot represented an "analysis line" for a particular PFA sample, or ash fraction.

Preparation of reference lines

Quartz (approximately 1 g) was blended with rutile and interground in cyclohexane (10 cm³) in a McCrone mill for 24 minutes. The cyclohexane was removed by pouring the slurry from the mill into a petri dish and oven drying at 378 ± 2 K for 10-15 minutes. A range of powder specimens was made with quartz/rutile weight ratios ranging from 0.83 to 7.63. The same procedure was used to produce powder specimens containing mullite (mullite/rutile ratios 1.01 to 10.53), magnetite (magnetite/rutile ratios 0.84 to 10.68) and haematite (haematite/rutile ratios 0.91 to 2.02).

Each powder specimen was prepared and analysed in the Siemens manner as described above. Identical operating conditions were used, but the 2θ angle range scanned was different for each mineral phase:

- quartz: 26° to 28° 2θ angle
- mullite: 25° to 28° 2θ angle
- magnetite: 27° to 32° 2θ angle
- haematite: 27° to 35° 2θ angle
Since sharp, well defined peaks were generally achieved, triangular peaks could be assumed. Peak areas were, therefore, calculated by multiplying widths by half heights. Peak intensities, compared to rutile, were plotted against weight ratios for each mineral phase. A "best fit" straight line was drawn using the origin as an additional point and the gradient of each line was calculated. Each plot represented a "reference line" for that mineral phase.

Peak intensities were plotted against weight ratios for each mineral phase. A "best-fit" straight line was drawn using the origin as an additional point. The gradient of each line was calculated. Each plot represented a "reference line" for that particular mineral phase. The reference materials were assumed to be pure (Appendix 4) and, therefore, no correction factor was required for the "ratio of slopes".

3.8 Classification of PFA samples

The suitability of centrifugal classification as a means of improving the hydrothermal performance of the Ratcliffe and Drakelow ashes was investigated.

3.8.1 Centrifugal air classifiers

Centrifugal air classifiers are the most common means of classifying "run of station" ash (18). The Minisplit™ (British Rema Limited) is a small scale classifier (Fig. 3.8), designed to operate in a similar manner to a full-scale unit. Ash fractions produced using the device should have comparable particle size distributions to those obtained from a commercial classifier. The throughput of the Minisplit™ is claimed to be between 1 to 50 kg h⁻¹ depending on the cut size required. A cut-point ranging from 1 to 75 μm is quoted in the manufacturer's literature.
3.8.2 Operation of a centrifugal air classifier

The cut-point achieved between fine and coarse material is dependent on the rotation speed of the rotor and the air flow through the unit. The principle of centrifugal air classifiers may be understood by considering a particle in a circular path within an air vortex (Fig. 3.9)

Fig. 3.9    A particle within a centrifugal classifier
The simplest approach is to consider two forces acting on the particle. Frictional drag \((D)\) of the air spiralling towards the central outlet draws the particle inwards. Due to the rotation, a centrifugal force tends to throw the particle towards the walls of the unit.

Under conditions of streamline airflow (laminar flow), the frictional drag \((D)\) is given by Stoke's equation:

\[
D = 2\pi \mu dv
\]

where, \(\mu\) = viscosity of air  
\(d\) = diameter of particle  
\(v\) = velocity of air

Streamline airflow within the classifier cannot, however, be assumed. Indeed, the design of the unit encourages turbulent flow since this breaks up agglomerates of particles within the feed material. Under these more realistic conditions, frictional drag may be calculated from an equation given by Klumpar (19).

\[
D = c \pi \left(\frac{d}{2}\right)^2 \mu(u - v)^2 / 2
\]

\(c\) = drag coefficient

The drag coefficient within a turbulent region is approximately constant and has a value of 0.44 (20). The centrifugal force \((c)\) experienced by a particle is given by the equation:

\[
c = mv^2 / r
\]

where, \(m\) = mass  
\(v\) = tangential velocity  
\(r\) = radius of circular plate

Assuming a spherical particle, of diameter \((d)\) and specific gravity \((\rho)\), then:

\[
\text{volume} = \frac{\pi d^3}{6}
\]
its mass is, therefore:

\[
\text{mass} = \rho \frac{\pi d^3}{6}
\]  

(23)

Displacement of air causes a small opposing force due to the Archimedes effect. Strictly, therefore, the difference between the particle density and air density (\(\Delta \rho\)) should be considered. Consequently, the centrifugal force may be calculated as:

\[
c = (\Delta \rho) \frac{\pi d^3 \cdot v^2}{6 \cdot \rho}
\]  

(24)

Since the density of air is low (0.0182 x 10^{-4} g cm^{-3} at 293 K), the effect may often be ignored. If frictional drag and centrifugal force are balanced, a particle will occupy an "equilibrium orbit" within the classifier. This is the condition which defines the cut-point. At a particular rotation speed and a given specific gravity, only particles of a certain diameter can exist in the "equilibrium orbit". Small particles will have insufficient mass for the centrifugal force to balance the frictional drag. Therefore, these particles will be drawn to the centre of the classifier and collected as fines. Conversely, large particles, with greater mass, experience sufficient force to overcome the frictional drag and will eventually collide with the outer wall of the classifier, fall down inside the cone to be collected as the coarse fraction.

In practice, however, any PFA sample has particles with a range of densities as well as different diameters. Therefore, the cut-point will not be sharply defined and significant overlap occurs. Dense particles, finer than the nominal cut-point will experience less frictional drag, but possess increased momentum. Such particles will be thrown to the outside of the classifier and will be collected in the coarse fraction. Conversely, low density particles coarser than the nominal cut-point, will be subjected to increased frictional drag, but will have less momentum. These particles will be swept towards the central outlet and collected with the fine fraction.

Increasing the rotor speed will reduce the cut-point achieved, since a greater number of relatively small particles will experience sufficient centrifugal force to be thrown to the walls of the classifier. The volume of primary and secondary air flow are also important factors which affect separation.
Secondary air flow creates turbulence in the classifier and this ensures de-agglomeration of particles within the airstream. However, the feed rate to the cyclone unit must also be controlled below a certain rate in order to aid de-agglomeration of the ash particles. Once these parameters are fixed, a particular cut-point is achieved. This is the nominal particle diameter below which the fine particles are carried through with the air stream from the cyclone. Material below the cut-point is collected by gravity below the cyclone.

Commercially, the classification of PFA is a single stage process. The cut-point is set to achieve ash of a particular fineness for a particular concrete mix design, or more usually to meet a specific standard (e.g. BS 3892:Part 1). It is possible, however, to undertake multi-stage separations of PFA, thereby, producing different ash fractions of distinct particle size distributions.

Preliminary experiments were undertaken to determine a set of operating conditions which gave separation of the bulk ash into well defined ash fractions.

The material was processed sequentially. At each stage the sample to be fractionated was manually loaded into the feed hopper and allowed to flow into the vibrating feed chute. The feed rate was adjusted to between 100 to 300 g min\(^{-1}\) by means of a cardboard "gate" placed across the feed chute. This allowed a 5 mm deep and a 30 mm wide stream of material to fall into the inlet. All fractionation runs used 100% primary air, but the secondary air was restricted to 30% by a choke. The processing of the two PFA samples through the Minisplit\textsuperscript{TM} is described in Table 3.4.
Table 3.4  Processing scheme for PFA samples using the Minisplit™

<table>
<thead>
<tr>
<th>Stage</th>
<th>Rotor speed (rpm)</th>
<th>Feed material</th>
<th>Fate of fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>fine</td>
</tr>
<tr>
<td>1</td>
<td>6,000</td>
<td>PFA sample</td>
<td>collected as sample [A]</td>
</tr>
<tr>
<td>2</td>
<td>4,000</td>
<td>coarse material from stage 1</td>
<td>collected as sample [B]</td>
</tr>
<tr>
<td>3</td>
<td>2,000</td>
<td>coarse material from stage 2</td>
<td>collected as sample [C]</td>
</tr>
<tr>
<td>4</td>
<td>850</td>
<td>coarse material from stage 3</td>
<td>collected as sample [D]</td>
</tr>
</tbody>
</table>

A limited amount of work has been reported in the literature regarding the reactivity of ash particles of particular particle sizes. The hydrothermal reactivities of ash fractions have been reported using various methods. However, the separation procedures used to obtain the ash fractions are unrealistic commercially. Procedures here included "float and sink" procedures using dense liquids, dry sieve, wet sieving and isolation of the magnetic portion. These methods may give fractions which differ either physically or chemically by either specific gravity or particle size, but are not commercially realistic. The only industrial significant process is air separation which is cost effective and produces a dry ash, but with slightly less rigorously defined particle size.

3.9 Scanning electron microscopy of ash fractions

Micrographs of the ash fractions obtained from the Minisplit™ classifier were obtained using a Cambridge Instruments Streoscan™ No. 4 scanning electron microscope (SEM).

Preparation

A conducting stud was thinly coated with PVA adhesive, which was allowed to dry until tacky. A small quantity of dry ash fraction was lightly dusted onto the stud. Once dry, the ash fraction sputter was coated to a depth of about 10 to 15 nm.
3.10 References


6. BS EN 196-2: 1995


17. Monshi, A., Messer, P.F., Ratio of slopes method for quantitative x-ray

18. Edwards, P., Foster, A., Making the most of a national resource, *Concrete*,


20. Scarlett, B., Sampling from gas streams, Course on Particle
Characterisation and Collection, Newark, N.J. and Chicago, 1972.
Chapter 4

Hydrothermal reactions of two pulverised fuel ashes within ash/lime pastes.

4.1 Significance of ash/lime pastes

Both Ratcliffe and Drakelow ashes were initially evaluated within ash/lime pastes, which were autoclaved at 457 K. The autoclaving conditions were considered to be comparable to commercial practice.

4.2 PFA samples

Sub-samples of Ratcliffe PFA and Drakelow PFA were obtained from bulk samples collected from each power station (see section 3.1). These sub-samples were used to obtain chemical analyses and to prepare the ash/lime pastes.

4.2.1 Physical properties

A particle size distribution was obtained for each PFA sample using a Malvern 3600E particle sizer and the method described in section 3.2.1. Specific gravity measurements were carried out using the ASTM procedure given in section 3.2.2.

4.2.2 Elemental analysis

Elemental analysis (XRF) was undertaken at UK Analytical Ltd. Carbon was not measured directly, but loss on ignition values were determined for each ash.

4.2.3 Mineralogy

Samples (100 g) of each ash were submitted to Dr. H.S. Pietersen of Delft University, Netherlands. A quantitative XRD procedure using calcium fluoride as an internal standard was used to determine the mineralogy of each ash (1). That is, the amounts of the crystalline phases, quartz, mullite,
haematite and magnetite. In conjunction with the loss on ignition value, the amount of glass within each ash was also calculated.

The particle size distributions determined for each ash are given in Fig. 4.1. Specific gravity results, elemental analysis and mineralogy are summarised in Table 4.1.

Fig 4.1 Particle size distribution of Ratcliffe PFA and Drakelow PFA

4.3 Preparation of pastes

Ash/lime pastes were prepared as outlined in section 3.5.1. Analytical grade calcium hydroxide and PFA were mixed together and distilled water added to form a paste with a water/solid (w/s) ratio of 0.82.

One experiment assessed the effects of mix proportions by investigating a set of pastes with lime/ash weight ratios from 0.25 to 0.97. Each paste was cured using an autoclaving cycle of 10 minutes purge for air removal, 10 minutes linear pressurisation to 1100 kN m\(^{-2}\) (457K), a dwell time of 360 minutes and 10 minutes linear depressurisation to atmospheric pressure.
A more extensive experiment involved the preparation of pastes, with a lime/ash ratio of 0.484 autoclaved for dwell times ranging from 15 to 720 minutes. The other stages of the autoclave cycle have been described above.

### Table 4.1 Analysis of Ratcliffe PFA and Drakelow PFA

<table>
<thead>
<tr>
<th>Elemental analysis (%)</th>
<th>Ratcliffe PFA</th>
<th>Drakelow PFA</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>50.60</td>
<td>45.50</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>26.00</td>
<td>25.80</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>8.90</td>
<td>11.40</td>
</tr>
<tr>
<td>CaO</td>
<td>1.70</td>
<td>6.50</td>
</tr>
<tr>
<td>MgO</td>
<td>1.70</td>
<td>2.10</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.50</td>
<td>0.90</td>
</tr>
<tr>
<td>K₂O</td>
<td>3.40</td>
<td>2.40</td>
</tr>
<tr>
<td>TiO</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.70</td>
<td>1.20</td>
</tr>
<tr>
<td>loss on ignition</td>
<td>4.50</td>
<td>3.20</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mineralogy (%)</th>
<th>Ratcliffe PFA</th>
<th>Drakelow PFA</th>
</tr>
</thead>
<tbody>
<tr>
<td>quartz</td>
<td>4.00</td>
<td>3.90</td>
</tr>
<tr>
<td>mullite</td>
<td>6.10</td>
<td>4.60</td>
</tr>
<tr>
<td>magnetite</td>
<td>0.80</td>
<td>1.90</td>
</tr>
<tr>
<td>haematite</td>
<td>0.60</td>
<td>1.10</td>
</tr>
<tr>
<td>glass</td>
<td>84.00</td>
<td>85.30</td>
</tr>
<tr>
<td>loss on ignition</td>
<td>4.50</td>
<td>3.20</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Ratcliffe PFA</th>
<th>Drakelow PFA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si/Al ratio</td>
<td>1.72</td>
<td>1.56</td>
</tr>
<tr>
<td>Si/Al molar ratio</td>
<td>1.65</td>
<td>1.47</td>
</tr>
<tr>
<td>Si/Fe ratio</td>
<td>3.80</td>
<td>2.66</td>
</tr>
<tr>
<td>Si/Fe molar ratio</td>
<td>7.56</td>
<td>5.31</td>
</tr>
<tr>
<td>Specific gravity (g cm⁻³)</td>
<td>2.12</td>
<td>2.44</td>
</tr>
</tbody>
</table>
4.4 Results

The results are given below.

4.4.1 PFA samples

The particle size distributions are shown in Fig. 4.1, which shows that Drakelow PFA has a greater proportion of smaller particles than Ratcliffe PFA.

Elemental analysis results for the ashes are given in Table 4.1. The compositions fall within the range observed for UK ashes (2). Differences in mineralogy are also clear. Ratcliffe PFA has a slightly higher silica content, but the ashes have similar quartz and glass contents. Ratcliffe PFA has more mullite, whereas Drakelow PFA has higher magnetite and haematite contents. Estimates of glass composition show that Ratcliffe PFA has a higher Si/Al ratio, but a lower Si/Fe ratio than Drakelow PFA.

4.4.2 Influence of ash/lime proportions

Results for calcium hydroxide/ash ratios of 0.97 and 0.48 are shown in Fig. 4.2

![Graph showing calcium hydroxide consumption](image_url)

**Fig. 4.2** Calcium hydroxide consumption for pastes with lime/ash ratios of 0.97 and 0.48.
Drakelow PFA is clearly more reactive than Ratcliffe PFA in the low-lime paste, and the consumption of calcium hydroxide is complete in about 360 minutes. More complex behaviour is noted in the lime-rich paste up to 180 minutes. Ratcliffe PFA consumes calcium hydroxide more rapidly than does Drakelow PFA.

With further autoclaving the reaction with Ratcliffe PFA slows, so that Drakelow PFA reacts to a greater extent. In these lime-rich pastes, with both ashes at this paste composition, calcium hydroxide consumption is incomplete, even after 720 minutes autoclaving. Reaction may be limited by the availability of "soluble silica" from PFA particles or by the formation of insoluble phases.

The influence of paste composition on calcium silicate hydrate formation is illustrated in Figs. 4.2 and 4.3. A sharp maximum is noted for the formation of semi-crystalline CSH from Ratcliffe PFA at a lime/ash weight ratio of 0.48. A broad maximum in tobermorite formed from Ratcliffe PFA is also observed, but the amount of tobermorite formed from Drakelow PFA is not greatly affected by the ash/lime ratio above about 0.5. More of these phases were produced from Ratcliffe PFA than from Drakelow PFA.

![Graph showing effect of lime/ash weight ratio on formation of semi-crystalline CSH](image-url)

Fig. 4.2 Effect of lime/ash weight ratio on formation of semi-crystalline CSH
4.5 Hydrothermal reactions PFA pastes at a fixed lime/ash ratio

The results in section 4.4.2 show that the lime/ash weight ratio of pastes have a significant influence on the hydrothermal reactions which occur at 457 K. An lime/ash weight ratio of 0.48 was chosen as the most appropriate composition for further study, since there is evidence that CSH formation is encouraged at this ratio. Pastes of this composition were prepared and autoclaved for dwell times ranging from 17 to 720 minutes.

4.5.1 Consumption of lime

Drakelow PFA is more reactive than Ratcliffe PFA in respect to lime consumption. With either type of ash, however, the consumption of calcium hydroxide is complete within 360 minutes.

4.5.2 Consumption of PFA

Fig. 4.4 shows that with both ashes the reaction reaches a plateau within 360 minutes, which parallels the lime consumption, although only about half of each ash has reacted.
Fig. 4.4 Reaction of Ratcliffe PFA and Drakelow PFA at 457 K

The results from the element dissolution experiments are shown in Figs. 4.5, 4.6 and 4.7. Again, 360 minutes dwell time produces a plateau for each element, although there are differences between the ashes. Silicon is initially liberated more readily from Drakelow, but with prolonged autoclaving, greater solubilization of the element is achieved from Ratcliffe. The release of alkali is complex in the early stages. Ratcliffe loses sodium much more rapidly than potassium, while Drakelow shows the reverse. The release of sodium from Ratcliffe becomes erratic and is exceeded by that from Drakelow after about 240 minutes. The release of potassium from each ash is slower than that of sodium after about 120 minutes, and smaller proportions are liberated. With the exception of sodium, no more than about 50% of each element is released, with Drakelow being more reactive throughout.
Figs 4.5 Solubilisation of silica

Figs 4.6 Solubilisation of alumina
4.5.3 Phase identification

Various phases were identified by XRD analysis.

4.5.3.1 Portlandite

The 0.310 nm peak was used to assess the change in portlandite concentration in addition to chemical analysis. This peak was present at short reaction times, but was not detectable against the background after 90 minutes for Drakelow and 180 minutes for Ratcliffe. These results are obviously different from those obtained from chemical analysis due to the high XRD background.

4.5.3.2 Calcium silicate hydrates

Fig. 4.8 shows the growth of the 0.307 nm peak for a mixture with a calcium hydroxide/ash ratio of 0.48. This peak may be attributed largely to the formation of calcium silicate hydrate phases (CSH), but there is also a significant contribution from hydrogarnet. More reliable indicators of CSH
formation are the peaks at 0.297 nm, due to a semi-crystalline phase, and at 1.13 nm, due to crystalline tobermorite (Fig. 4.9).

These show the formation of a less crystalline CSH, which then levels off as tobermorite is formed at longer times. A peak at 0.303 nm, which is apparent after 15 minutes autoclaving with both ashes, has been assigned to CSH gel. This peak persists until 90 minutes for Drakelow and 120 minutes for Ratcliffe. Consideration was given to this peak being due to calcite, caused by carbonation of the specimens. Apart from the general precautions taken to minimise this reaction, no decomposition of carbonate was detectable in TG/DTA runs carried out.

**Fig. 4.8**  
Growth of 0.307 nm peak at 457 K

**Fig. 4.9**  
Formation of CSH phases at 457 K
4.5.3.3 Hydrogarnet

A striking feature of the XRD traces is the growth, from a flat base line, of a peak at 0.274 nm. This indicates the formation of a hydrogarnet phase during autoclaving. The presence of hydrogarnets in autoclaved materials has been reported previously (3, 4). The formation of this phase is rapid and it is obviously stable, since a plateau is reached. Drakelow produces more hydrogarnet with time and across the range of lime/ash ratio studies (Fig. 4.10).

![Graph of hydrogarnet formation](image)

**Fig. 4.10** Formation of hydrogarnet

4.6 Reactivity of starting materials

The rapid consumption of calcium hydroxide within the pastes agrees with previously reported results for autoclaved products containing amorphous silica (5). The completeness of lime removal is obviously important for the overall reaction. The ashes do not show comparable reactivities, however, Drakelow generally reacts more quickly and to a greater overall extent than Ratcliffe. Consumption of ash ceases at approximately 60% for Drakelow and 40% for Ratcliffe, whereas the glass content is close to 85% in each case. These differences suggest that the reactivity is not related to the glass content of the ash. A calculation of the Potential Pozzolanic Index (K_2O/Al_2O_3) mass ratio x 100 (6) gives a value of 1.13 for Ratcliffe and 0.93 for Drakelow, suggesting that Ratcliffe ash should be more reactive; this is obviously contrary
to the present observations. It is possible that insoluble reaction products are inhibiting solubilisation of some of the elements, particularly silicon (7). Examination of Figs. 4.8 and 4.9 shows that there is a change of slope in the production of CSH phases between 120 and 240 minutes, which would be expected if such inhibition took place.

4.7 Solubilisation studies

It is clear from Figs. 4.5, 4.6 and 4.7 that various elements are released at different rates from the two ashes. However, because of the limited reaction of the ashes, accurate comparisons are difficult. Plots of ash reacted versus individual element release were produced, and linear regression analysis gave the information in Table 4.2. For such plots, a slope of unity shows identical rates of ash consumption and element release, which suggests a uniform distribution of the element throughout the ash. A slope greater than unity indicates surface enrichment, while a value less than unity shows surface depletion. The data in Table 4.2 suggests that sodium is strongly enriched whilst potassium is more variable, but tends to be depleted at the surface of Ratcliffe PFA. This observation is contrary to the results of work at 293 and 301 K, which indicates similar rates of release for both alkalis (8). Silicon appears to be depleted at the surface, but aluminium is less so.

Table 4.2 Element release from PFA versus ash reaction

<table>
<thead>
<tr>
<th>Element</th>
<th>Slope</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ratcliffe PFA</td>
<td>Drakelow PFA</td>
</tr>
<tr>
<td>Al</td>
<td>0.90</td>
<td>0.96</td>
</tr>
<tr>
<td>Si</td>
<td>0.71</td>
<td>0.78</td>
</tr>
<tr>
<td>Na</td>
<td>1.56</td>
<td>1.32</td>
</tr>
<tr>
<td>K</td>
<td>0.75</td>
<td>1.07</td>
</tr>
</tbody>
</table>
4.8. Reaction products

Formation of CSH phases is apparent from the appearance of the 0.307 and 0.297 nm peaks, the growth of which coincides with the most rapid consumption of the ashes. A plateau is reached at 360 minutes, which suggests that most "soluble silica" from the PFA has reacted with the limited amount of calcium hydroxide to form CSH phases. Increasing crystallinity is evident as autoclaving proceeds, since CSH gel is initially detected, but is not resolved after 90 minutes with Drakelow, or 120 minutes with Ratcliffe.

Formation of a semi-crystalline CSH phase is evident from the development of the 0.297 nm peak for up to 360 minutes, followed by a decline, suggesting the crystallisation of CSH to tobermorite. The ashes behave differently, Ratcliffe showing a much greater decline in semi-crystalline CSH than Drakelow. The 1.13 nm peak of tobermorite increases linearly for Ratcliffe, roughly matching the more rapid decline in CSH, while for Drakelow, the growth of tobermorite is deceleratory. These results obtained at various lime/ash ratios shown in Figures and indicate that the amount of CSH phase is maximised at a nominal C/S ratio of 0.78 for Ratcliffe (using the stated assumptions for the silica content and the calcium hydroxide purity). This ratio is lower than that observed by Sauman (9), who found that maximum tobermorite formed at a C/S ratio of about 1.2. No comparable maximum is evident for Drakelow, indeed, between a C/S of 0.78 and 1.53 the amount of CSH which forms is effectively constant. The formation of hydrogarnet also reaches a plateau at about 360 minutes with Drakelow, whereas 400 minutes is required with Ratcliffe. The d-spacings observed for this phase suggest a low-silicon type, with a composition close to that of katoite (10). Higher concentrations of hydrogarnet forming with increasing lime content are confirmed in Fig.4.11.
4.8.1 Comparison of the reactivity of ashes

The two ashes were chosen for this work because of their similarities, and it is clear from the analytical data in Table 4.1 that the main difference between the two lies in the lime content, and to a lesser extent in iron content. It is clear, however, that Drakelow PFA reacts more quickly, and to a greater extent than Ratcliffe PFA. This also applies to the more detailed element release data, with the exception of sodium release from Ratcliffe PFA. In the present study, it is unlikely that the high lime content of Drakelow PFA explains this variation in reactivity. In addition, the mineralogy of both ashes is similar. The major difference between the two lies in the particle size distributions, with Drakelow PFA having a uniformly smaller size distribution than Ratcliffe PFA. Assuming that the smaller particles in each ash react more quickly than the large, this would give greater reactivity to Drakelow PFA. It is also possible that the limited reaction of both ashes is due to a differentiation in the chemistry of the various fractions (11).
4.8.3 CSH versus hydrogarnet

Fig. 4.12 shows the Si/Al ratio of solubilised material plotted against dwell time. Both ashes give approximately the same low rate of release of silicon and aluminium after 240 minutes. The curves converge between 120 and 180 minutes, at a time when some lime remains as does a considerable amount of glassy phase. Differences in the rates of formation of the crystalline phases may be related to the varying amounts of silicon and aluminium liberated from the ashes. Significantly, Ratcliffe PFA provides more silicon than aluminium during the early stages of autoclaving. This favours the formation of CSH phases rather than hydrogarnet.

![Fig. 4.12 Silicon and aluminium release at 457 K](image)

4.9 Overview

The extent of the reaction in this low-lime study is controlled by the amount of lime present. Differences in the behaviour of the two ashes are observed with Drakelow PFA being the more reactive, whatever measure is used. Between 40 to 60% of the PFA samples reacts under hydrothermal conditions comparable to that used in the manufacture of AAC. The ashes have similar oxide and glass contents, and the most marked difference between the...
two is in lime content and the particle size distribution. The formation of hydrogarnet and calcium silicate hydrate phases may be related to the release of silica relative to alumina from the ash particles in the early stages of autoclaving.
4.10 References

1. Pietersen, H.S., Reactivity of Fly Ash and Slag in Cement, Doctoral Thesis, Chapter 4, Materials Science Section, Faculty of Civil Engineering, Delft University of Technology, Delft, The Netherlands, 1993


Chapter 5
Investigation of the ash fractions

5.1 The Minisplit\textsuperscript{TM} classifier

A Minisplit\textsuperscript{TM} classifier was used to separate approximately 21 kg of Ratcliffe PFA and 29 kg of Drakelow PFA each into 5 fractions. The throughput varied, depending on the particular fraction being processed. A typical flowrate of the machine was 12 kg h\textsuperscript{-1}. Overall, successful fractionation of the two ashes was achieved using the device.

5.1.1 Yields of ash fractions

The amounts of each ash fraction obtained are summarised in Table 5.1

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Weight (kg)</th>
<th>%</th>
<th>Fraction</th>
<th>Weight (kg)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>RC[A]</td>
<td>6.30</td>
<td>29.30</td>
<td>DK[A]</td>
<td>11.20</td>
<td>38.50</td>
</tr>
<tr>
<td>RC[B]</td>
<td>3.50</td>
<td>16.20</td>
<td>DK[B]</td>
<td>5.40</td>
<td>18.70</td>
</tr>
<tr>
<td>RC[C]</td>
<td>6.00</td>
<td>28.10</td>
<td>DK[C]</td>
<td>6.50</td>
<td>22.30</td>
</tr>
<tr>
<td>RC[D]</td>
<td>2.40</td>
<td>11.20</td>
<td>DK[D]</td>
<td>2.70</td>
<td>9.40</td>
</tr>
<tr>
<td>RC[E]</td>
<td>3.20</td>
<td>15.20</td>
<td>DK[E]</td>
<td>3.20</td>
<td>11.10</td>
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<tr>
<td>Total</td>
<td>21.40</td>
<td>100.00</td>
<td>Total</td>
<td>28.90</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Drakelow PFA has the largest proportion of fine ash particles, with approximately 39% being designated DK[A]. This compares with 29% of Ratcliffe PFA being composed of the same fraction. This agrees with the particle size distributions measured for each original ash in Chapter 4 which showed Drakelow PFA to be finer than Ratcliffe PFA.
5.2 Characterisation of ash fractions

Experimental work was undertaken to identify differences between the two sets of ash fractions and to determine if significant relationships existed between the particle size of ash fractions and their physical, chemical or mineralogical properties.

5.2.1 Particle size distribution

The particle size distribution of each ash fraction obtained from the Minisplit™ classifier was determined with the Malvern laser particle sizer, using the methods described in section 3.2.1. Selected data from the Malvern laser particle sizer results have been listed in Tables 5.2 and 5.3 (see also Appendix 5). Specific statistics listed for particle diameter are the lower decile (d10), upper decile (d90) and median (d50). The d10 and d90 values may be considered as indicators of the breadth of the particle distribution. The median particle diameter will be considered as the most appropriate single statistic which is representative of the particle size at each fraction and used in subsequent discussions.

Table 5.2 Selected particle size distribution data for Ratcliffe fractions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle diameter statistic (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>median (d50 value)</td>
</tr>
<tr>
<td>Ratcliffe PFA</td>
<td>14.20</td>
</tr>
<tr>
<td>RC[A]</td>
<td>4.60</td>
</tr>
<tr>
<td>RC[B]</td>
<td>10.00</td>
</tr>
<tr>
<td>RC[C]</td>
<td>24.40</td>
</tr>
<tr>
<td>RC[D]</td>
<td>41.20</td>
</tr>
<tr>
<td>RC[E]</td>
<td>51.70</td>
</tr>
</tbody>
</table>
Table 5.3  Selected particle size distribution data for Drakelow fractions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle diameter statistic (μm)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Median (d50 value)</td>
<td>Lower decile (d10 value)</td>
<td>Upper decile (d90 value)</td>
</tr>
<tr>
<td>Drakelow PFA</td>
<td>10.60</td>
<td>2.60</td>
<td>45.90</td>
</tr>
<tr>
<td>DK[A]</td>
<td>4.20</td>
<td>1.70</td>
<td>7.20</td>
</tr>
<tr>
<td>DK[B]</td>
<td>9.70</td>
<td>6.20</td>
<td>21.30</td>
</tr>
<tr>
<td>DK[C]</td>
<td>21.30</td>
<td>11.00</td>
<td>53.60</td>
</tr>
<tr>
<td>DK[D]</td>
<td>34.50</td>
<td>16.70</td>
<td>72.00</td>
</tr>
<tr>
<td>DK[E]</td>
<td>45.90</td>
<td>22.30</td>
<td>81.80</td>
</tr>
</tbody>
</table>

Particle size distributions obtained from the Malvern particle sizer, or indeed, any instrument based on laser diffractometry, are volume distributions. The algorithms calculate the distribution of diameters in a particular volume, over a specified period. Therefore, results are not directly comparable with sieve analyses, which are weight distributions. By entering a specific gravity value, nominal weight distributions may be calculated. However, this is of limited value for materials under test, since within a PFA sample, or ash fraction, numerous particles exist with a range of densities.

The particle size distributions based on laser diffractometry are appropriate for the project, because comparative results are required. There is no need to correlate with specifications based on sieve analyses. The algorithm used by the Malvern device assumes spherical particles. Using volume distributions, such as provided by the Malvern device, is more appropriate than sieve analysis, since results are to be compared with SEM micrographs.

5.2.2 Density determinations

Specific gravity determinations were carried out on each ash fraction and the original raw ashes, using the ASTM method described in Chapter 3. Duplicate results were in agreement to within ± 0.05 g cm$^{-3}$. Mean specific gravity values for each ash fraction have been included with the other analytical data in Tables 5.4 and 5.5.
5.2.3 Elemental analysis of ash fractions

The concentrations of ten elements (Si, Al, Fe, Ca, Mg, Ti, Na, K, Mn, and P) in each ash fraction were determined by XRF analysis at the Geology Department of Leicester University. Carbon and sulphur were determined using the LECOTM apparatus. Results of the elemental analysis are given in Tables 5.4 and 5.5. Carbon is reported as the element, all other elements are reported as nominal oxides. Each analysis has been normalised to give a total of 100%.

Table 5.4 Summary of analytical data for Ratcliffe fractions

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Table 5.5 Summary of analytical data for Drakelow fractions

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<tr>
<td>Loss on ignition</td>
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(μm)

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<th>Median diameter</th>
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<th>4.20</th>
<th>9.70</th>
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5.2.4 SEM analysis

Each ash fraction obtained from the Minisplit™ classifier was studied by SEM. Of particular interest was to assess the range of particle morphologies which occur at each particle size and to determine if significant differences exist between fractions derived from Ratcliffe PFA, compared with those obtained from Drakelow PFA. For each ash fraction, micrographs were produced using the procedures described in section 3.9. Generally, a low magnification view
was obtained in order to observe a large number of particles. This should indicate the typical range of particles within an ash fraction. Micrographs using higher magnification were also obtained so that specific features could be observed.

Selected micrographs obtained from each ash fraction are reproduced in section 5.2.4.1. The structures seen within individual fields of view are also discussed in the section. Median particle diameters quoted are those figures obtained from the Malvern laser particle sizer. The dimensions referred to in discussions about micrographs are approximate only and are estimated from the dark reference bar seen at the bottom of each frame.

5.2.4.1 SEM micrographs

Racclife ash fractions

RC[A] (d50 = 4.6 μm)

Fig. 5.1

Fig. 5.1 A field of view containing PFA spheres with diameters from 1 to 3 μm. However, dominating the frame is a flat structure, approximately 20 by 50 μm. It may be a portion of the "striated structure" observed in coarser fractions. The presence of this large particle illustrates how centrifugal classification does not give a precise cut point.
Fig. 5.2

Fig. 5.2 is a high magnification view of PFA spheres, which are the dominant particle type within fraction RC[A]. Particles with diameters ranging from 0.5 to 5 µm are visible. Typical of the finer fractions, the PFA spheres are tightly clumped together in agglomerates.

Fig. 5.3

Fig. 5.3 shows a field of view dominated by spheres ranging from 0.5 to 5 µm. The most interesting feature, in the right of the picture, is a small fragment of the "pumice-like" structures observed in coarser fractions (RC[D] and RC[E]).
Fig. 5.4

Fig. 5.4 is a general view of an assemblage of PFA spheres, with diameters ranging from 2 to 15 μm, but with most around 10 μm. Fragments of "pumice-like" particles are evident. Each fragment consists of a porous matrix into which small PFA spheres are embedded.

Fig. 5.5

A fragment of a "pumice-like" particle is shown in the top left corner of Fig. 5.5. The particle is 50 by 30 μm in size. As noted previously, smaller spheres, 5 to 10 μm across are embedded in the main particle.
A shard of material, 35 by 15 \( \mu m \) is shown in Fig. 5.6. This type of particle is rare in the Radcliffe ash fractions. The conchoidal fracture surfaces suggest that the particle may be quartz. It is interesting that no signs of fusion can be seen.

RC[C] \((d_{50} = 2.4 \mu m)\)

Fig. 5.7 is a relatively low magnification view. PFA spheres, ranging in diameters from 5 to 80 \( \mu m \) are the most numerous particle types. Most particles appear to have a diameter of about 20 \( \mu m \). Some fragments of hollow PFA spheres are apparent. There is little evidence of agglomerates.
A field of view composed almost exclusively of PFA spheres is given in Fig. 5.8. Particle diameters between 2 and 20 μm are evident. As in Fig. 5.7, the spheres are separated, with no agglomerates.

Fig. 5.9 shows a collection of spheres ranging in diameter from 2 to 25 μm. An interesting feature is an elongated particle 12 by 20 μm. There is evidence of blistering on its surface and the fragment may have been derived from an angular particle which has partially fused, softening its contours. The particle may have formed from a quartz fragment.
A general view of fraction RC[D] is shown in Fig. 5.10. There are two dominant types of particles, glass spheres of 20 to 150 µm diameter, and irregular “pumice-like” particles 50 to 70 µm across. A significant number of fractured hollow spheres are also evident.

Fig. 5.11 shows a range of particles which are typical of fraction RC[D]. Smooth spheres with diameters ranging from 10 to 50 µm are common. Several of the irregular “pumice-like” particles are in view. These are complex structures with significant porosity and contain numerous small spheres. Several fragments of broken glass spheres are evident.
Fig. 5.12 shows a PFA sphere of approximately 125 μm. An “imprint” left by contact with another particle during the fusion stage is evident.

Several fractured hollow spheres are seen in Fig. 5.13. The central fragment is derived from a hollow particle of approximately 150 μm. Its wall thickness ranges from 2 to 20 μm. Significant porosity exists within the walls, with pores 1 to 15 μm across. Fragments of thin walled spheres are also shown, as are small complete spheres ranging in diameter from 5 to 20 μm.
Fig. 5.14 is a general view of fraction RC[E]. Two main particle types are visible. Large "pumice-like" particles predominate. These are typically 300 μm across, but with some up to 600 μm across. Spheres with diameters between 50 and 175 μm are also common. Several fractured spheres with wall thicknesses of 20 to 25 μm are evident.

Fig. 5.15

A "pumice-like" particle is shown in detail in Fig. 5.15. The complexity of the particle type is evident. A highly porous matrix exists into which small spheres of 25 micrometers diameters are embedded. This could represent a char structure, as discussed by Flagan (1).
Fig. 5.16.

A group of broken hollow spheres, common in fraction RC[E], are shown in Fig. 5.16. The diameters range from 20 to 100 μm. The central fractured sphere has a wall thickness of about 10 μm, but contains numerous pores, some up to 5 μm across.

Fig. 5.17

Fig. 5.17 is a close-up of the fractured sphere shown in Fig. 5.16. Its wall thickness ranges from 5 to 10 μm, but considerable porosity exists, with pores ranging from 0.5 to 5.0 μm. Structure can be seen within the inner surface of the sphere. Elongated crystals, 5 micrometers long by 0.1 μm thick (aspect ratio 50), are evenly distributed. These structures may be mullite crystals, formed within the glassy matrix during cooling of the particle after combustion.
Drakelow ash fractions

DK[A] (d50 = 4.2 μm)

Fig. 5.18

Fig. 5.18 is a general view showing the spherical PFA particles which are predominant in the fraction. The particles have diameters ranging from 2 to 15 μm with a typical sphere being 8 to 10 μm across. It is notable that the particles are aggregated.

Fig. 5.19

A view of the typical agglomerates of spherical particles is shown in Fig. 5.19. Spheres with diameters ranging from 0.5 to 10 μm are evident.
Fig. 5.20 shows a small cluster of approximately 10 spherical particles, with diameters ranging from 1 to 5 \( \mu \text{m} \). Spheres as small as 0.5 \( \mu \text{m} \) are visible outside the cluster.

Fig. 5.21 shows a shard of material which is approximately 20 by 5 \( \mu \text{m} \). This may be a fragment of quartz. Also, in view, are spherical particles between 0.5 to 5 \( \mu \text{m} \) across.
A general view of fraction DK[B] is given in Fig. 5.22. Angular particles are rare and spherical particles 2 to 15 μm across predominate. A typical particle diameter is about 10 μm.

Fig. 5.23 shows an interesting flat structure, 60 μm long by 20 micrometers across. It is grooved, possibly a fragment of "striated structure" observed in coarse fractions. Numerous spherical particles 5 to 15 μm across are also visible. An angular fragment, 14 μm long may be a piece of quartz.
DK[C] (d50 = 21.3 μm)

Fig. 5.24

Fig. 5.24 is a low magnification view of fraction DK[C]. It shows that spherical particles predominate, but angular particles and other fragments are significant. The spheres have diameters ranging from 5 to 75 μm. A large, poorly formed sphere, approximately 80 μm across, can be seen at the centre of the field of view.

Fig. 5.25

A close-up of the poorly formed sphere noted above is given in Fig. 5.25. The particle is quite complex. From its surface contours it appears to be partially fused. There are numerous voids, or pores, some of which contain small smooth spheres of approximately 10 μm diameter.
Fig. 5.26

Fig. 5.26 illustrates some of the types of particles found within DK[C]. Spherical particles ranging in diameter from 2 to 30 μm are obvious. In the bottom right of the micrograph is a shard which is 40 μm across and 20 μm, which shows no signs of fusion and may be a fragment of quartz.

\[ \text{DK[D]} \quad (x.50 = 34.5 \text{ μm}) \]

Fig. 5.27

A low magnification view of the fraction is shown in Fig. 5.27. Spheres make up most of the field of view, but numerous angular and irregular particles can also be seen. The spheres have diameters ranging from 10 to 70 μm, whereas several of the other particles are larger than 100 μm.
An interesting composite structure. The particle itself is approximately 150 μm across. It has a large amount of porosity. However, contained within voids, or channels, are small spherical particles, 5 μm across. It is uncertain whether these small spheres have become entrapped during collection and storage of the ash. Alternatively, the large particle may be a char structure, which during combustion forms the smaller PFA spheres.

A PFA sphere of 40 μm diameter encrusted with a deposit is shown in Fig. 5.29. The deposit may be similar to the mixture of sulphate salts noted by Tidy (2).
Several PFA spheres ranging in diameters from 5 to 50 μm across are shown. The most prominent feature appears to have been derived from an angular particle, but the contours have been softened by fusion. This may be a partially fused fragment of quartz.

DK[E] (d50 = 45.9 μm)

A general view of fraction DK[E]. The striking feature of the micrograph is the variety of particles present. The particles may be categorized into three types, intact or fractured spheres, non-porous angular fragments and porous angular
fragments. Few agglomerates of particles are visible. Intact spheres are rare, but
diameters ranging from 40 to 125 μm may be observed, with a "typical"
dimension being 75 μm. The fragments of broken spheres have a wall thickness
ranging from 10 to 50 μm. Non-porous angular fragments appear to be more
abundant than PFA spheres. Some shards of an apparently dense material are
also present which could be fragments of quartz. Porous angular fragments
predominate the field of view. However, this is a very broad description and
does not assume that the particles are structurally similar. Indeed, a wide range
of complex structures are evident, ranging from angular fragments containing
voids and vesicles, and open "pumice-like" particles, to highly structured
fragments made up of numerous channels.

Fig. 5.32

A close-up view of a particle which is common in fraction DK[E]. The particle
is 450 μm long, by 260 μm across. It is highly structured, composed of
numerous axially aligned channels. The channels are regular in size and shape,
each being between 10 to 20 μm wide. An interesting feature of this complex
particle is the associated small PFA spheres, with diameters from 10 to 15 μm.
Several spheres are contained within the channels. This close association
suggests that the spheres may be formed from the larger particle. If this is true,
the particle represents a char structure discussed by Flagan (1). The structure of
the particle is reminiscent of the vascular system of plant material. It may be an
artefact from a mineralised fossil in the original coal seam.

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One of the intact spheres observed in fraction DK[E] is shown in Fig. 5.33. The particle has a diameter of approximately 170 μm and a relatively smooth surface. However, "blisters" on its surface are visible, suggesting internal porosity produced by condensing and evaporation of material.

Fig. 5.34 shows a fractured hollow sphere of 200 μm diameter. The particle has a relatively thick wall, averaging 50 μm. Considerable porosity in the walls can also be seen, with voids ranging from 1 to 20 μm. An interesting feature is a small sphere, 20 μm across, in the top left of the micrograph. It is surrounded by a fracture ridge which has a similar curvature as the small sphere. This seems to be an unlikely coincidence and suggests that the small sphere may have formed within the wall of the larger sphere.
5.2.4.2 Summary of SEM analysis

Some general observations may be made regarding the SEM micrographs detailed in section 5.3.4.1. In the three finer ash fractions, derived from both Ratcliffe and Drakelow ashes, spheres are the dominant particle type and angular particles are generally rare. In the finest ash fractions (RC[A] and DK[A]) the spheres are clustered together in agglomerates. In the coarser fractions, however, agglomerates are uncommon.

The coarser fractions, derived from either Ratcliffe or Drakelow ashes, (RC[D], RC[E], DK[D] and DK[E]), have large numbers of irregular and angular particles. Indeed, in the most coarse fraction derived from Drakelow PFA (DK[E]), angular particles probably account for greater than 50% of the particles visible. It is evident from the SEM micrographs that the cut point achieved with centrifugal classification is not precise, since a broad range of particle size is observed in each ash fraction. This may be confirmed by reference to the data obtained from the Malvern laser particle sizer which is summarized in Tables 5.2 and 5.3.

If the d10 and d90 values are taken to indicate the range of particle sizes measured, it is notable that ash fractions derived from Ratcliffe PFA have broader distributions than those obtained from Drakelow PFA. This may be related to the density range of particles in the original PFA samples. Ash fractions derived from Drakelow PFA have similar specific gravities (2.44 to 2.53 g cm⁻³), suggesting a narrow spread of densities in the original ash. Conversely, fractions obtained from Ratcliffe PFA have a wide range of specific gravities (1.80 to 2.48 g cm⁻³). This indicates a collection of particles with a significant range of densities within the original ash. Centrifugal classification as described in section 3.8.1, assumes particles of uniform density, if a distinct cut-point is to be achieved. However, fine particles which are dense, have sufficient momentum to be thrown to the outside of the classifier and collected with the coarse fraction.

Several of the ash fractions have complex structures which appear to contain small spherical particles. Such features may be similar to the char structures which Flagan considered were responsible for the formation of the majority of PFA particles. The “striated structures”, with numerous regular
channels are evident in Drakelow fractions (Figs. 5.23, 5.31 and 5.32). The largest examples of this particle type were found in DK[E], the coarsest fraction derived from Drakelow PFA. However, fragments were also apparent within DK[B], a finer fraction. The "striated structure" may be a fusein, an ancient charcoal fragment, from the original coal seam, which has survived combustion. These can contain clay, which may fuse to form the fine spheres associated with the fragment (3).

"Pumice-like" particles make up a large amount of the two coarser fractions derived from Ratcliffe PFA (RC[D] and RC[E]). Fragments of these particles type are also present in finer fractions, such as RC[B] and RC[B]. With both these types of particles it is the apparent close association of fine spheres which suggests generation of smaller PFA particles from larger fragments. There are other particles, observed in various fractions, which also may be the site for the formation of small PFA spheres (see Figs. 5.25, 5.28 and 5.32).

Shards of material are evident in several micrographs in the finest fractions. Conchoidal fracture surfaces sometimes may be seen (see Fig. 5.6). These shards may be fragments of unfused quartz.

Particles, as small as 0.5 μm in diameter, are resolved in the finest ash fractions (RC[A] and DK[A]) by SEM, beyond the resolution of the Malvern laser particle sizer. However, the median particle diameter (d50 value) obtained from the apparatus appears to be a reasonable measure of the size distribution within each fraction.

The presence of long thin structures, such as the fragment in Fig. 5.1, alongside fine spherical particles is significant. It demonstrates that centrifugal classification does not give ideal separation. Relatively large particles, with high aspect ratios can align with the airflow and be swept into the fine fraction.

5.2.5 Mineralogy of ash fractions

The mineralogy of an ash fraction may have a significant influence on its hydrothermal performance. Glass contents of ashes may influence the pozzolanic reactions which occur in mortar and concrete. However, the significance of the glass content within autoclaved products such as AAC has not been reported. It is possible that the relative amounts of quartz to glassy material within a PFA
sample, or ash fraction, affects the rate at which silicate ions are liberated during autoclaving. It is, therefore, important to assess quantitatively, or at least semi-quantitatively, the mineralogy of each ash fraction obtained from classification using the Minisplit™ apparatus. Of particular interest is to determine if the mineralogy changed systematically from each ash fraction. That is, to assess whether mineralogy was related to the fineness of the ash fractions. XRD analysis, using the "ratio of slopes" method described in section 3.7.2.5, was chosen as an appropriate quantitative method for assessing mineralogy.

UK power stations generally burn bituminous coal, or anthracite. Low-lime PFA samples are obtained as a by-product, with the four main crystalline phases being quartz, mullite, magnetite and haematite. Assuming these phases are present and that either carbon contents, or loss on ignition results are available, it is possible to estimate the amount of glass within the sample:

\[
\% \text{ glass} = 100 - \text{carbon content} - (\text{quartz} + \text{mullite} + \text{magnetite} + \text{haematite})
\]

In line with the "ratio of slopes" method, reference samples of quartz, mullite, magnetite and haematite were obtained. A sample of rutile was also acquired as an internal standard. Three specimens from each ash fraction were prepared containing various amount of rutile (section 3.7.3.1). XRD scans were undertaken to obtain data from which the analysis lines were produced (Appendix 6). Similarly, reference lines were obtained for the mineral phases (Appendix 7).

5.2.6 Assessment of the "ratio of slopes" method

Satisfactory analysis lines and reference lines were achieved. Plots were taken through the origin, as in the original paper by Monshi and Messer (4). Straight lines were obtained with high correlation coefficients, from 0.98 to 0.99. If the origin was not used, slightly lower correlation coefficients were noted, with the lowest being 0.94. The slopes from the analysis and reference lines are summarised in Appendix 8. Calculating the "ratio of slopes" gives an estimate of the weight fraction of particular phases within the specimens. These are listed in Table 5.6 for Ratcliffe fractions and Table 5.7 for Drakelow fractions.
Table 5.6  Mineralogy of Ratcliffe fractions

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Table 5.7  Mineralogy of Drakelow fractions

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According to Monshi and Messer the "ratio of slopes" method can be accurate and provide good estimates of the amount of each crystalline phase present within a sample. In this project, the main benefit of the technique is that it provides a measure of the relative differences in the mineralogy of the ash fractions.

5.3 Relationships between the properties of ash fractions and fineness

Using data reported in section 5.2.3 and 5.2.5, it is possible to determine how the physical and chemical properties of ash fractions vary, depending on
particle size. The median particle diameter (d50 value) obtained from particle size distributions may be taken as a representative measure of the fineness of each ash fraction. Thus, the d50 value (μm) may be plotted as the x-values, whilst various measured properties are plotted as y-values.

5.3.1 Density

Fig. 5.35 has plots of specific gravity against d50 value, for both Ratcliffe and Drakelow fractions.

The densities of the finest ash fractions are similar, irrespective of the original PFA sample. With d50 values of 10 μm or less (RC[A], RC[B], DK[A] and DK[B]) have specific gravities ranging from 2.3 to 2.6 g cm⁻³. Watt and Thorne (5), in a detailed analysis of selected ashes, observed microscopically that PFA particles of this density were generally clear solid glassy spheres. SEM studies in the project (section 5.2.4.1), show that the fine ash fractions are composed of small spheres which are assumed to be solid.

Differences in the two types of ash fractions are most evident in the coarser fractions. Ratcliffe fractions of 25 μm, or larger (RC[C], RC[D] and RC[E]), have progressively lower specific gravities. Indeed, the plot of specific gravity versus d50 value is almost linear for Ratcliffe ash fractions. This trend has been reported in other studies (6). The lower density of coarse Ratcliffe fractions may be explained by referring to the SEM micrographs, particularly those for RC[D] and RC[E]. Numerous "pumice-like" particles are evident. These are highly porous and, therefore, of low density. Ratcliffe PFA is clearly composed of particles with a wide range of densities. This has consequences for the centrifugal classification of PFA, as discussed in section 5.2.4.2.

The coarse Drakelow fractions DK[C], DK[D] and DK[E], have similar densities to the fine material. Indeed, the range of densities measured throughout the Drakelow fractions is surprisingly small. Therefore, density and the particle size of Drakelow fractions appears to be unrelated. Reference to the SEM micrographs is interesting, in the coarser fractions there are many angular particles which appear to be non-porous. Some highly porous particles may be observed, as can hollow spheres, but these are not as numerous as in the Ratcliffe fractions. The coarse Drakelow fractions also have high levels of iron.
Iron-rich particles will be relatively dense. An increase in the number of these iron-rich particles may offset any general increase in the porosity of particles in the coarse grades.

Fig. 5.35  Relationship between density and particle size of ash fractions

5.3.2 Elemental analysis

Eight of the twelve elements measured by XRF were considered of particular importance. These elements were silicon, aluminium, iron, calcium, sodium, potassium, sulphur and carbon.

5.3.2.1 Carbon

Fig. 5.36 shows that with the Drakelow fractions there is a clear relationship between carbon content and particle size, with the finest fraction DK[A] having the least carbon, and coarse fractions having progressively more. High carbon is normally associated with the coarser carbonaceous material. Indeed, a significant advantage cited for classification is removal of the coarse ash particles, which contains the high carbon material.

Any relationship between carbon content and the fineness of Ratcliffe fractions is less obvious than that noted for Drakelow fractions. However, a trend may be observed, RC[A] has the least carbon, whilst RC[E] has the most.
Fraction RC[D], with a median particle size of 41 μm, appears to have less carbon than would be predicted from the general trend.

**Fig. 5.36** Relationship between carbon and particle size of ash fraction

### 5.3.2.2 Silica (silicon)

Differences between Ratcliffe and Drakelow fractions are evident in Fig. 5.37. The silica content remains constant for all the Ratcliffe fractions, despite median particle diameters ranging from 4 to 52 μm. In the case of Drakelow fractions, however, a 47 % SiO₂ content is measured at a d50 value of 4 μm but this reduces to 39 % SiO₂ at 46 μm. High silica contents may be associated with fine particles.

### 5.3.2.3 Alumina (aluminium)

As with silica, significant differences between Ratcliffe and Drakelow fractions may be observed (Fig. 5.38). There is a marginal reduction in the alumina content of Ratcliffe fractions with increasing median particle diameters, from 27 % Al₂O₃ for RC[A], to 25 % for RC[E]. A more significant reduction in alumina takes place across the Drakelow fractions. A 20 % Al₂O₃ content is observed for DK[A] (d50 = 4 μm) which reduces to 17 % for DK[E] (d50 = 46 μm).
Fig. 5.37  Relationship between silica and particle size of ash fraction

Fig. 5.38  Relationship between alumina and particle size of ash fraction

5.3.2.4 Iron

A small increase in the iron content is noted with increasing d50 values in the Ratcliffe fractions (Fig. 5.39). Within the Drakelow fractions, however, a linear rise in the iron content with increased particle size is observed. This increase in iron content for the coarse fraction explains the corresponding
reduction in silica and alumina. The coarser Drakelow fractions may either increase in magnetite or haematite, or contain iron-rich glasses. Section 5.3.3 discusses the mineralogy of the ash fractions.

![Graph showing relationship between iron and particle size of ash fraction](image)

**Fig 5.39** Relationship between iron and particle size of ash fraction

### 5.3.2.5 Calcium (lime)

Fig. 5.40 shows how the lime content (%CaO) varies with the particle size of the ash fractions. In the case of Ratcliffe fractions, the lime content in only increases marginally with particle size. By contrast, all the Drakelow ash fractions have relatively high lime contents and there is a strong relationship with particle size. There is a rise in the lime content, from 5% CaO for DK[A] (d50 = 4 μm) to 9% CaO for DK[E] (d50 = 46 μm).

The lime content of the coarsest Drakelow fraction DK[E], approaches that of Class C PFA, which is derived from lignite or subbituminous coal. Lime may be combined in high-lime glasses, as portlandite or calcite, or within other phases.
Fig 5.40  Relationship between calcium and particle size of ash fraction

5.3.2.6 Alkalis

Figs. 5.41 and 5.42 show the relationships between the alkali (Na$_2$O and K$_2$O) and the particle size of the ash fractions. Ratcliffe fractions have consistently higher sodium and potassium, compared with Drakelow fractions.

A reduction in the concentration of both elements occurs with an increase in particle size. This is apparent for both sets of ash fractions. It is clear that most of the alkali salts are associated with the fine particles of PFA. This has been observed by other workers (7) and is due to the mechanism of PFA formation. The alkali metal salts volatalize readily during combustion, but condense as fine particles, or onto the surface of existing spherical particles.
Fig. 5.41  Relationship between sodium and particle size of ash fraction

Fig. 5.42  Relationship between potassium and particle size of ash fraction

5.3.2.7 Sulphur

Sulphur (reported as SO₃), occurs at higher concentrations in the fine ash fractions (Fig. 5.43). Higher sulphur contents are apparent in the Drakelow fractions, compared with the Ratcliffe fractions. Sulphur concentrations decline steadily with increasing particle size. Sulphate salts will account for the majority
of the sulphur. As noted by Tidy (8), a complex blend of mixed sulphates (calcium, magnesium, sodium, potassium and aluminium) form on fine particles, or as a surface coating on larger ash fractions. There is an association between the alkali metals and the sulphur content, indicating the sodium and potassium sulphates are probably the compounds present in the finest fractions.

![Graph showing the relationship between sulphur and particle size of ash fraction](image)

**Fig. 5.43** Relationship between sulphur and particle size of ash fraction

### 5.3.3 Mineralogy and glass composition

Using the "ratio of slopes" method (section 3.7.2.5), it has been possible to estimate by XRD analysis the amount of the crystalline phases which occur within each ash fraction (quartz, mullite, magnetite and haematite). Calculations of the amount of glass have also been undertaken. The results are summarised in Tables 5.6 and 5.7. Of particular interest in the project was to determine how the mineralogy varied between ash fractions. Can trends in the mineralogy be observed? Any significant relationships may have a bearing on the hydrothermal reactivities of the ash fractions. This would allow the effectiveness of the classification to be assessed as a means of modifying the performance of PFA within autoclaved products. The data within Table 5.6 and 5.7 was used to derive plots of phase composition against median particle diameters (Figs. 5.44 to 5.48 inclusive).
5.3.3.1 Quartz

Ash fractions derived from Drakelow PFA contain more quartz than corresponding fractions obtained from Ratcliffe PFA (Fig. 5.44). The coarser fractions have significantly more quartz than the fines, whatever the source of the original PFA. With the Ratcliffe fractions there is a steady rise in quartz content with increasing particle size. Hence, RC[A] (d50 = 4 μm) has 2% quartz which rises 4% for RC[E] (d50 = 52 μm). For the Drakelow fractions the relationship between quartz and particle size is more complicated. DK[A] has a similar amount of quartz to its Ratcliffe counterpart, but this rises steeply to 5% for DK[C] (d50 = 21 μm). The quartz content is at a maximum of 6% with DK[E] (d50 = 45 μm). It is noteworthy that the amount of quartz within an ash fraction bears no relationship to its silica content, as measured using XRF. Thus, Drakelow fraction DK[E] has the most quartz (6%), but the least amount of total silica (39%).

![Graph showing relationship between quartz and particle size of ash fraction](image)

**Fig. 5.44** Relationship between quartz and particle size of ash fraction

5.3.3.2 Haematite

The finest Ratcliffe and Drakelow fractions have a similar haematite content of approximately 1% (Fig. 5.45). Coarser fractions have more of the mineral. With the Ratcliffe fractions, haematite rises from nearly 2% in RC[C] (d50 = 25 μm) and remains constant within the two coarsest fractions (RC[D]
and RC[E]). With the Drakelow fractions, however, there is a steady increase in the haematite content within the coarser fraction. In DK[E] (d50 = 46µm) a haematite content of 3 % is reached.

![Relationship between haematite and particle size of ash fraction](image)

**Fig 5.45**  Relationship between haematite and particle size of ash fraction

### 5.3.3.3 Magnetite

Magnetite was not detected in the two finest Drakelow fractions, or Ratcliffe fractions (RC[A], RC[B], DK[A] and DK[B]) (Fig. 5.46) This corresponds to a median particle diameter of 10 µm or less. Measurable amounts of magnetite were detected in the three coarse fractions for each PFA source. That is, with median particle diameters of 20 µm or greater. Significantly more magnetite is observed in those ash fractions derived from Drakelow PFA, compared to those obtained from Ratcliffe PFA. Magnetite within the Ratcliffe PFA fractions increases from 4 % m/m for RC[C] (d50 =24 µm), to 6 % for RC[E] (d50 = 52 µm). With the Drakelow fractions, however, the magnetite content rises from 10 % for DK[C] (d50 = 21 µm) to nearly 18 % for DK[E] (d50 = 46 µm).

The absence of magnetite in the fine ash fractions is interesting, since elemental analysis (Tables 5.4 and 5.4) shows that there is sufficient iron for the phase. Indeed, a similar amount of iron exists in the two finest Ratcliffe fractions.
as in the three coarsest fractions. Yet, magnetite is detected in the coarse fractions, but not in the fines. An explanation may be centrifugal classification within the Minisplit™ apparatus. Magnetite is dense (S.G. = 5.2 g cm⁻³), so too are particles which contain appreciable amounts of the phase. Therefore, even quite small magnetite-rich particles in the rotating airstream of the classifier will experience significant centrifugal force and, thereby, acquire considerable momentum. These particles will be thrown to the walls of the classifier, to be collected with the coarse fractions. There will, therefore, be a tendency for small magnetite-rich particles to be collected with the coarse fractions.

Fig. 5.46 Relationship between magnetite and particle size of ash fraction

5.3.3.4 Mullite

Mullite was not detected within coarse ash fractions derived from Drakelow PFA (DK[E]) (Fig. 5.47). The mullite content of the other Drakelow fractions is relatively constant, at between 9 to 10 %. Thus, the distribution of mullite appears to be independent of the particle size of the ash fractions. Conversely, with Ratcliffe fractions, there is a rise in mullite, from 8 % for RC[A] (d₅₀ = 4 μm) to 11 % for RC[E] (d₅₀ = 52 μm). One fraction RC[D] (d₅₀ = 41 μm) appears to give a dip in the trend with a mullite content of 9 %. Differences in the relative cooling rates of molten ash particles during combustion may help to explain the slightly higher mullite content observed in the coarser Ratcliffe fractions. Small particles, such as RC[A], cool rapidly,
allowing little time for crystallisation of mullite. Rather, glass formation is encouraged. However, coarse fragments cool more slowly perhaps, allowing time for the formation of mullite crystals. Alkalis (Na$_2$O and K$_2$O) may also influence mullite formation since these act as glass modifiers, which encourage vitrification and inhibit crystallisation. Both the Na$_2$O and K$_2$O content of the ash fractions reduce with particle size.

![Fig. 5.47 Relationship between mullite and particle size of ash fraction](image)

5.3.3.5 Glass content

The relationship between glass content and the fineness of the ash fraction is summarised in Fig. 5.48.

![Fig. 5.48 Relationship between glass content and the particle size of ash fraction](image)
Glass content is significantly reduced in the coarser ash fractions, compared with the fines. This is true for ash fractions derived from both PFA sources. A steady reduction in glass content is noted for Ratcliffe fractions, from 86% for RC[A] (d50 = 5 µm) to 71% for RC[E] (d50 = 52 µm). A steeper reduction in glass with particle size is observed for the Drakelow fractions, from 85% for DK[A] (d50 = 4.2 µm), to a minimum of 64% for DK[D] (d50 = 35 µm). Drakelow fractions have significantly less glass than corresponding Ratcliffe fractions. Interestingly, the two finest ash fractions have similar glass content, whether derived from Ratcliffe PFA or Drakelow PFA. Thus, RC[A] and DK[A] have a glass content of approximately 84%. Whereas, RC[B] and DK[B] have a glass content of around 82%. This agrees with SEM results which show that the finer ash fractions are largely made up of spherical particles assumed to be composed of aluminosilicate glass.

There are no simple relationships between the elemental analysis and mineralogy of the ash fractions. For example, a high alumina content does not indicate increased mullite. Similarly, the silica content may not be used to predict either the amount of glass or quartz.

Pietersen (9) considered that the amount of network modifiers, CaO, Na₂O, K₂O and MgO, within PFA samples affects the amount of glass present, since these species encourage vitrification, rather than crystallization. The iron content (Fe₂O₃) may also influence the glass formation. There appears to be a correlation between the glass content (as determined by XRD) and the total alkali (measured by XRF). This may not be a direct relationship between alkali and glass, rather it simply indicates that most of the alkali salts are associated with fine particles, precisely where most of the glassy spheres exist.

No strong correlation exists between the combined network modifiers and the glass content. It is difficult to envisage how increased amounts of the network modifiers could lead to a reduction in the glass content of fractions. The "pozzolanic potential index" (PPI), proposed by Hubbard et al (10), may be calculated from the elemental analysis (Tables 5.4 and 5.5). The PPI is obtained by calculating the molar ratio of silica to alumina, multiplied by 10 (K₂O/Al₂O₃ x10). A strong positive correlation between PPI and the glass contents of PFA samples has been claimed by Hubbard et al. The PPI values for Ratcliffe and
Drakelow ash fractions have been calculated in Appendix 9. Within a set of ash fractions, a positive correlation is achieved, 0.92 for Ratcliffe and 0.95 for Drakelow. However, if both sets of data are combined only a very weak correlation is found, with a correlation coefficient of 0.58. If the PPI expression is only valid within a particular set of ash fractions, it is of limited analytical worth. Any relationship should be of general applicability, allowing calculations to be made directly from XRF results, without any knowledge of the PFA.

5.5 Overview

The Ratcliffe and Drakelow ashes are typical of PFA currently available from UK power stations. Superficially, the differences between the two materials are modest. Elemental analysis results do not show large differences. However, the reactions of the raw ashes described in Chapter 4 demonstrate that the hydrothermal behaviours of the ashes are different.

The results presented in this chapter show that the classification of the two ashes, using a method similar to commercial practice, further accentuates the differences. Fractions of comparable fineness may have significantly different elemental compositions and mineralogies. However, the fine fractions derived from each of the two PFA samples are most similar in composition, whereas there is greatest divergence of compositions in the coarse material. Thus, up to a median particle diameter of about 10 μm, except for higher sulphur and lime in the Drakelow fractions, similar elemental distributions are evident.

The two finest fractions are also similar mineralogically, with glass contents of about 85%. Comparable amounts of mullite and haematite are also noted, but magnetite is not observed in either fraction. Inspection of the SEM micrographs shows that fine spheres are the dominant particle type. The density range measured 2.32 to 2.53 g cm⁻³ is consistent with the solid aluminosilicate glassy spheres observed by Watt and Thorne (5). The Drakelow fine fractions, DK[A] and DK[B], however, have higher quartz than the equivalent Ratcliffe fractions.

Differences between the two ash sources are most evident in the fractions with median particle diameters above 20 μm (RC[C] and DK[C]), or coarser. With the coarse Ratcliffe fractions there is surprisingly little difference in
elemental analysis, except for a modest reduction in sulphur as the particle size increases. There are considerable changes in the elemental composition of the coarse Drakelow fractions with increasing particle size. The most notable changes are reduced silica, but increased alumina and calcium. Differences in mineralogy occur within both sets of ash fractions. A notable effect is the reduction in aluminosilicate glass content with increasing median particle diameter. This is most significant with the Drakelow fractions. Increased quartz is associated with the coarse Drakelow fractions, but the effect is less marked with Ratcliffe PFA. Both magnetite and haematite contents increase significantly in the coarser Drakelow fractions, whereas the rise is modest for Ratcliffe fractions.

Surprisingly, the measured density of the Drakelow fractions is unaffected by particle size. The specific gravity remains the same across the complete range of particle sizes. Conversely, the specific gravity of Ratcliffe fractions reduce steadily with the median particle diameter. An explanation is the large number of porous particles in the coarsest Ratcliffe fractions.

SEM micrographs show differences in typical particle morphologies of the two sets of ash fractions. This is particularly true in the coarser fractions. Several particles types are visible in the coarse Drakelow fractions, many of which are angular, but with some porosity. Any relationship between elemental composition and mineralogy is tenuous. It is not possible, therefore, to infer mineralogy from XRF results. This is contrary to the idea of the PPI (10). In both sets of ash fractions, SEM micrographs show particles with complex structures, which appear to act as sites for the formation of smaller spherical particles. These larger particles may be similar to the char structures, outlined by Flagan (1).
5.6 References


3. Gibbins, J., Imperial College, Private communication.


Chapter 6
Evaluation of autoclaved ash/lime specimens

6.1 Background

Ratcliffe PFA, Drakelow PFA and ash fractions were evaluated within autoclaved specimens from which strength measurements were obtained. Autoclaving in saturated steam at 457 K (1114 kN m⁻²), for dwell times up to 1260 minutes (21 h) has been studied. A fixed purge time, pressurisation rate and depressurisation rate has been used throughout the experimental work, but the effects of varying the dwell time at 457 K have been studied. Where an autoclave time is quoted in the text it refers to the dwell time.

6.2 Autoclaved ash/lime discs

Results for discs made with Ratcliffe PFA or Drakelow PFA, and tested by the "Brazilian" method, are given in Fig. 6.1. A lime/ash weight ratio of 0.48 was used and dwell times ranging from 0 to 1260 minutes (21 h) tested. A dwell time of "0" represents specimens, which have been hydrothermally cured by pressurisation to (457 K) and immediately depressurised to atmospheric pressure.

![Fig. 6.1 Relationship between the diametral compressive strength and autoclaving time at 457 K for ash/lime discs](image-url)
Autoclaving for dwell times up to 360 minutes produces similar diametral compressive strengths for both sets of specimens. Subsequently, the strengths achieved with the two PFA samples diverge. Strength development begins to level off in those discs made with Ratcliffe PFA between 480 and 720 minutes. Discs made with Drakelow PFA increase in strength with further autoclaving up to a maximum of approximately 8 MPa, achieved after 720 minutes (12h). Autoclaving for a further 360 minutes produces a reduction in strength. However, the strength achieved within discs made with Drakelow PFA is still greater than that obtained with Ratcliffe PFA. At maximum strength, after 720 minutes autoclaving, discs made with Drakelow PFA are approximately 18% stronger than equivalent discs made with Ratcliffe PFA.

Results on the variability of the “Brazilian” method are summarised in Table 6.1. The coefficient of variance measured for each set of discs is given (n = 8 to 10). Values ranging from 0.04 to 0.18 were obtained for specimens containing Ratcliffe PFA and 0.05 to 0.14 for those made with Drakelow PFA. This variability is greater than that measured for autoclaved ash/lime cubes in section 3.6.2.3. The presence of unseen flaws within the discs is a possible explanation for this relatively high variability.

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Table 6.1 Variability of diametral compressive strength for ash/lime discs
The low water content of the discs, compared to AAC mixes and the high variability in strength measurements were reasons for alternatives to the "Brazilian" method being used. It was also difficult to produce discs with sufficient green strength from the coarse ash fractions. This was attributed to low cohesion between ash particles, because of relatively low surface areas.

6.3 Relationship between compressive strength and lime/ash ratio

With autoclaved cementitious products made with finely divided quartz, the bulk molar lime/silica ratio (C/S) is a prime factor in determining strength. Therefore, a relationship between the proportions of calcareous and siliceous raw materials to strength may be expected for the specimens used in the project. The influence of the bulk calcium hydroxide/ash ratio of specimens to compressive strength was investigated. It was necessary to define a single lime/ash weight ratio, which may be used to characterise the performance of ash fractions obtained from the Minisplit™ classifier.

Two sets of cylindrical specimens were produced, one using Ratcliffe PFA, the other Drakelow PFA. These were prepared and tested in accordance with the method given in section 3.6.2.2. Lime/ash weight ratios from 0.424 to 0.605 were assessed. The results are illustrated in Fig. 6.2.

![Graph showing relationship between compressive strength and lime/ash ratio](image)

**Fig. 6.2** Relationship between compressive strength and lime/ash weight ratio of cylinders autoclaved for 360 minutes at 457 K
Interestingly, the behaviour of the two ashes are different. The compressive strength of Ratcliffe specimens is not greatly influenced by the lime/ash ratio. There is, however, a marginal rise in strength at higher lime contents. By contrast, the strength of specimens made with Drakelow PFA is significantly influenced by the lime/ash weight ratio. A sharp maximum is noted at a lime/ash weight ratio of 0.48. Over the complete range of lime/ash ratios, higher saturated compressive strength is achieved with those cylinders made with Drakelow PFA, rather than those produced with Ratcliffe PFA. Based on these result, ratio of 0.48 was chosen as the "optimum" value for further experimental work. In particular, this composition was used to assess the hydrothermal performance of ash fractions obtained from the Minisplit™ classifier.

As the silica content of each ash fraction is known from elemental analysis (section 3.2.3), in principle, the lime/ash ratio may be adjusted to give the same C/S ratio within each specimen. This approach was not adopted because it assumes that any silica, whether derived from quartz, or aluminosilicate glass, has the same solubility during autoclaving. Also, PFA samples are assessed on a weight for weight basis industrially, since elemental analysis are not routinely available.

In section 6.5, cube specimens have been used to investigate the rate of strength development during autoclaving with both PFA samples and to assess the hydrothermal performance of the ash fractions. These specimens are easier to produce than cylinders, since the "three gang" mould can be readily clamped to the vibratory table in order to remove air voids.

6.4 Development of compressive strength with autoclaving time

An experiment was conducted to assess how compressive strength develops within ash/lime specimens during autoclaving at 457 K. Cubes were produced from both Ratcliffe PFA and Drakelow PFA with an lime/ash weight ratio of 0.484 in accordance with the method given in section 3.6.2.3. The results of the experiment are given in Fig. 6.3. Throughout autoclaving, the saturated compressive strength of cubes made with Drakelow PFA is consistently higher than those made with Ratcliffe PFA. Smooth curves have
been drawn, but it is noticeable that the individual points for the cubes made with Drakelow PFA are quite scattered.

As illustrated in Fig. 6.4, strength develops rapidly during the early stages of autoclaving. For example, with cubes made with Ratcliffe PFA, 68% of the final strength is achieved after only 60 minutes (1 h) and 78% after 240 minutes (4 h). The comparable figure for cubes made with Drakelow PFA are 65 and 84%.

Fig. 6.3 Development of compressive strength in ash/lime cubes autoclaved at 457 K

Fig. 6.4 Percentage gain in compressive strength for ash/lime cubes autoclaved at 457 K
This observation agrees with the other properties measured in simple ash/lime pastes discussed in Chapter 4. An analogous reaction profile is noted, a rapid rise in a measured property, followed by a levelling off (e.g. lime consumption). This phenomenon suggests that the attainment of compressive strength may be governed by an underlying diffusion controlled process. A possible mechanism is the silica solubilisation.

The profiles in Fig 6.4 were used to define autoclaving times for investigations of the hydrothermal reactions of ash fractions obtained from the Minisplit™ classifier. A dwell time of 120 minutes was chosen as a short autoclaving time, whereas 360 minutes was selected as a medium period and 720 minute judged to be prolonged curing. Autoclaving times beyond 720 minutes were considered to be inappropriate, since little change in strengths were expected and such curing periods are not normally undertaken commercially.

6.5 Hydrothermal reactions of ash fractions

From the five ash fractions derived from both Ratcliffe PFA and Drakelow PFA, three series of 50 mm cubes were cast and autoclaved at 457 K. As noted in section 6.3, dwell times of 120, 360 and 720 minutes were studied. The "three gang" mould described in section 3.6.2.3 was used to produce a set of three 50 mm cubes. Two cubes were soaked in distilled water for 4 days and the mean saturated compressive strength determined. A third cube was retained for further analysis and test. Of particular interest was to compare the behaviour of the ash fractions under conditions typical of those encountered in the manufacture of AAC. Data on lime consumption, compressive strength and XRD analysis were plotted against the median particle diameter (d50 value) for each ash fraction.

Lime consumption, a measurement of ash reactivity, was calculated from free lime results obtained by the Franke method. XRD analysis was used to identify reaction products formed during autoclaving. An important aspect of the experimental work was to assess the technical benefits, if any, of classification for PFA intended for AAC manufacture. Compressive strength measurements allowed this to be determined.
6.5.1 Compressive Strength

Figs. 6.5 and 6.6 illustrate how the compressive strength of autoclaved cubes alters with the ash fraction used and autoclaving time.

Fig. 6.5 Compressive strength of ash/lime cubes made with Ratcliffe fractions

Fig. 6.6 Compressive strength of ash/lime cubes made with Drakelow fractions
Both sets of ash fractions give a similar performance within cubes autoclaved for 120 minutes. Higher strength is measured in the cubes produced with fine ash fractions, RC[A], RC[B], DK[A] and DK[B] (d50 = 10 μm or less) and coarser ash fractions give weaker cubes. With Ratcliffe ash fractions, the compressive strength declines from about 10 MPa for RC[A] and RC[B], to 4 MPa for RC[E]. The comparable figures for Drakelow ash fractions are 12 MPa for DK[A], to MPa for DK[E].

Autoclaving for 360 minutes produces cubes with higher compressive strength. However, the behaviour of the two sets of ash fractions differs considerably. For the cubes which contain Ratcliffe ash fractions, maximum strength occurs with RC[C] (d50 = 24 μm). The strength of cubes made with coarse ash fractions RC[D] and RC[E] (d50 = 41 and 51μm) is considerably higher than that measured after 120 minutes. Autoclaving for 720 minutes produces a further general increase in strength, except for cubes containing RC[E] which are unchanged. Two features of these results are noteworthy. Firstly, maximum strength is not achieved with the fine ash fractions, rather this occurs with intermediate particle size, RC[C] (d50 = 24 μm). Secondly, the three intermediate ash fractions RC[B], RC[C] and RC[E] give very similar cube strengths. Hence, comparable compressive strengths are achieved with d50 values of 10, 24 and 41 μm. The low strength associated with RC[E] (d50 = 52 μm) is probably due the coarseness of the ash fraction and its low surface area available for hydrothermal reaction. However, the relatively low strength associated with RC[A] (d50 = 4 μm) is not be readily explained.

The plots relating to cubes made with Drakelow ash fractions are considerably different from those which contain Ratcliffe ash fractions. A general increase in strength occurs with autoclaving for 360 minutes. The biggest strength gain, compared to 120 minutes, occurs in cubes which contain DK[B] and DK[C] (d50 = 10 and 21 μm). Autoclaving for 720 minutes gives relatively small changes in strength, except for DK[A] (d50 = 4 μm), where a significant increase occurs. Cubes made with the three fine ash fractions DK[A], DK[B] and DK[C] (d50 = 4, 10 and 21 μm) have the highest compressive strengths. There is very little difference between the values, all are
around 20 MPa. Strength reduces considerably in cubes which contain the two coarse ash fractions DK[D] and DK[E] (d50 = 35 and 40 µm).

Differences in compressive strength achieved with Ratcliffe and Drakelow ash fractions are highlighted in Fig. 6.7, which compares results for 720 minutes dwell time at 457 K. Cubes made with the three fine Drakelow ash fractions, are from 22 to 65 % stronger than cubes made with the corresponding Ratcliffe ash fractions. However, cubes made with DK[D] (d50 = 35 µm) are about 14 % weaker than those made with RC[D].

![Compressive strength of ash/lime cubes autoclaved at 457 K for 720 minutes made with Ratcliffe and Drakelow fractions](image)

**Fig. 6.7** Compressive strength of ash/lime cubes autoclaved at 457 K for 720 minutes made with Ratcliffe and Drakelow fractions
6.5.2 Lime consumption

Lime consumption for a set of ash fractions after 120, 360 and 720 minutes autoclaving are given in Fig. 6.8. Results obtained after 120 minutes are not surprising. Fine ash fractions consume lime more rapidly than do the coarse fractions. This can be directly correlated to the higher surface area of the fine fractions and the predominance of reactive aluminosilicate glass. After 120 minutes autoclaving, approximately 97 % of the lime has reacted with the fine ash fractions, derived from either Ratcliffe PFA or Drakelow PFA. Even with the coarse ash fractions nearly 70 % of the lime has reacted after only 2 h of autoclaving. Autoclaving for 360 minutes gives almost complete consumption of the lime.

![Fig. 6.8 Lime consumption in autoclaved ash/lime cubes](image)

6.5.3 Mineralogy of ash/lime cubes

XRD analysis was used to assess the mineralogy of the autoclaved cubes. Quantitative analysis was not attempted, unlike the investigation of ash fractions undertaken in Chapter 5. Rutile was used as an internal standard and interground with each dry specimen at a fixed addition level. Five peaks were identified as being characteristic of the autoclaved cubes:
1.13 nm: A peak arising from the basal plane of tobermorite. Its presence is diagnostic of the phase.

0.336 nm: The main diffraction peak of quartz. Its presence is diagnostic of the phase.

0.307 nm: A strong peak which is associated with most common semicrystalline and crystalline CSH phases. It is not truly diagnostic, since hydrogarnet also contributes to the peak intensity.

0.297 nm: A strong peak associated with tobermorite. The peak may be taken to be indicative of a crystalline CSH phase.

0.275 nm: This is the main diffraction peak of a low-silica hydrogarnet, similar to katoite and its presence is diagnostic of the phase.

The graphs obtained by plotting relative intensities for these selected peaks are complex and anomalies exist. However, useful information regarding the hydrothermal reactions of ash fractions may be obtained.

0.336 nm peak

Fig. 6.8 Relationship between 0.336 nm peak intensity within autoclaved cubes and the particle size of Ratcliffe fractions
Fig. 6.9 Relationship between 0.336 nm peak intensity within autoclaved cubes and the particle size of Drakelow fractions

The performance of the Ratcliffe and Drakelow ash fractions differ considerably in regard to the quartz peak. For a particular autoclaving time, the 0.336 nm peak intensities observed for cubes made with Ratcliffe ash fractions are unaffected by particle size. However, the intensities of the quartz peak are generally lower with dwell times of 360 and 720 minutes, compared to 120 minutes. This demonstrates consumption of quartz as hydrothermal reactions occur. A single point, relating to RC [C] (d50 = 24 μm), autoclaved for 360 minutes, is anomalous.

Distinct trends are evident for those cubes made with Drakelow fractions. With a dwell time of 120 minutes, the 0.336 nm peak intensity is highest in those cubes which contain coarse ash fractions (Fig. 6.9). In fact the profile is strikingly similar to the plot of quartz content versus median particle diameter for Drakelow fractions obtained from quantitative XRD analysis in Chapter 5. This suggests that after 120 minutes of autoclaving only a limited amount of quartz has reacted. The plot obtained after 360 minutes at 457 K shows lower 0.336 nm peak intensities and still further reduction in the quartz peak occurs with 720 minutes autoclaving.
A considerable reduction in quartz peak intensity occurs after 720 minutes autoclaving, compared to 120 minutes. This is particularly evident with the coarse Drakelow ash fractions and shows that significant amounts of quartz undergo hydrothermal reactions.

0.307 nm Peak

Fig. 6.10 Relationship between 0.307 nm peak intensity within autoclaved cubes and the particle size of Drakelow fractions

Fig. 6.11 Relationship between 0.307 nm peak intensity within autoclaved cubes and the particle size of Ratcliffe fractions
Autoclaving produces changes in the intensities of the 0.307 nm peak in cubes made with Drakelow fractions (Fig 6.10). After autoclaving for 120 minutes, relatively low intensities are associated with the coarse ash fractions, whereas higher intensity are observed in cubes which contain the fine ash fractions. Autoclaving for 360 minutes results in a growth in peak intensity and this is particularly associated with the two coarse fractions DK [D] and DK [E] (d50 = 35 and 46 μm). Prolonged autoclaving, for 720 minutes, gives further growth in peak intensity, but only in those cubes made with the fine ash fraction. A maximum intensity for the 0.307 nm peak occurs in cubes which contain DK [C] (d50 = 21 μm).

The graph, (Fig. 6.11), obtained from cubes made with Ratcliffe ash fractions is difficult to interpret as few clear trends are detected. The intensity of the 0.307 nm peak does increase with autoclaving. Surprisingly, the most significant increases are associated with the coarse ash fractions.

Growth of the 0.307 nm peak may be assumed to be due to the formation of reaction products. These are likely to be predominantly CSH phases, but there will be some contribution from hydrogarnet. Therefore, reaction products continue to form as a result of the hydrothermal reactions of calcium hydroxide with the fine ash fractions DK [A], DK [B] and DK [C] throughout autoclaving at 457 K. However, in cubes made with either of the two coarse Drakelow fractions, DK [D] and DK [E], formation of reaction products reduces significantly between 360 and 720 minutes.

1.13 nm Peak

The 1.13 nm peak was not generally well developed in the cubes analysed by XRD (Figs. 6.12 and 6.13). In some specimens a peak could not be distinguished against the background. There is no clear correlation between the intensity of the 1.13 nm peak and either autoclaving time or the particle size of the ash fractions used. However, within cubes made with Drakelow ash fractions, the maximum intensity of the 1.13 μm peak was associated with the coarse ash fractions. Anomalously high intensities were observed in cubes.
containing the three coarse Ratcliffe ash fractions, autoclaved for 360 minutes. Quite well developed intense 1.13nm peaks were evident.

Fig. 6.12  Relationship between 1.13 nm peak intensity within autoclaved cubes and the particle size of Ratcliffe fractions

Fig. 6.14  Relationship between 1.13 nm peak intensity within autoclaved cubes and the particle size of Drakelow fractions
Fig. 6.14 Relationship between 0.297 nm peak intensity within autoclaved cubes and the particle size of Ratcliffe fractions

Fig. 6.15 Relationship between 0.297 nm peak intensity within autoclaved cubes and the particle size of Drakelow fractions
There are no clear trends in the appearance of the 0.297 nm peak in cubes containing any of the Ratcliffe fractions (Fig. 6.14). For dwell times ranging from 120 to 720 minutes, the intensities measured are similar for each ash fraction. An exception is the coarse fraction RC [E] \((d_{50} = \mu m)\), where the measured intensity of the 0.297 nm peak increases with the autoclaving time.

Well defined trends are evident in autoclaved cubes which contain Drakelow ash fraction (Fig. 6.15). The intensity of the 0.297 nm peak increases with the medium particle diameter of the ash fraction, for all three autoclaving times. Longer autoclaving time also increases the intensity of the 0.297 nm peak associated with a particular ash fraction.

Increased amounts of crystalline CSH phase, perhaps tobermorite, appears to form due to the hydrothermal reaction of the coarse fraction, rather than from the fine fractions. Prolonged autoclaving also increases the amount of crystalline CSH phase which forms. It is interesting that formation of the crystalline CSH phase is not maximised with the fine ash fractions, which contain the most aluminosilicate glass and, therefore, may be expected to provide solubilised silica rapidly. Rather, the phase forms more readily within cubes made with coarse ash fractions, which contain the least aluminosilicate glass, but the most quartz.

0.275 nm Peak

Similar trends are observed, whether the autoclaved cubes contain Ratcliffe or Drakelow ash fractions (Figs. 6.16 and 6.17). For a dwell time of 120 minutes, higher levels of hydrogarnet occur in cubes made with fine ash fractions. The intensity of the 0.275 nm peak falls with increasing particle size of the ash fractions. Further autoclaving, however, for 360 or 720 minutes, increases the hydrogarnet content in cubes made from coarse ash fractions to similar levels as associated with the fine ash fractions. After 720 minutes autoclaving, the hydrogarnet level is comparable whatever the ash fraction used.
Fig. 6.16  Relationship between hydrogarnet formation within autoclaved cubes and the particle size of Ratcliffe fractions

Fig. 6.17  Relationship between hydrogarnet formation within autoclaved cubes and the particle size of Drakelow fractions
These results show that the hydrogarnet forms rapidly from the fine ash fractions in the early stages of autoclaving. Formation of the phase does not appear to proceed beyond a certain amount.

Hydrogarnet formation may be determined by the rate of solubilisation of silica and alumina from the ash particles. The phase therefore forms more readily from the fine ash fractions in the early stages of autoclaving, because high surface areas of aluminosilicate glass are exposed for hydrothermal reaction. The levelling off in hydrogarnet formation with prolonged autoclaving may be due to a reduction in the rate of dissolution of either silica or alumina. The composition of the underlying ash particles may alter, reducing solubility. Alternatively, deposition of insoluble reaction product on particle surfaces may inhibit the further solubilisation of silica and alumina. The hydrothermal reaction of the coarse Drakelow ash fractions with calcium hydroxide does not lead to formation of increased amounts of hydrogarnet, despite elemental analysis showing these fractions to have increased aluminium (% Al₂O₃). This suggests that the availability of aluminium is not the rate determining step in the formation of hydrogarnet.

Development of compressive strength within autoclaved specimens is due to the hydrothermal reaction of lime with aluminosilicate glass to form a semi crystalline CSH phase. This is demonstrated by the growth of a XRD peak at 0.307 nm. It is assumed that the phase is voluminous, compared to the reaction products, and crystallises with many points of contact form throughout the autoclaved matrix. There is evidence for the formation of crystalline CSH, but this does not significantly influence the gain in strength associated with the fine ash fractions (d50 = 20 μm or less). The formation of the crystalline CSH may, however, contribute to the strength of specimens made with coarse ash fractions.

Differences in compressive strength of test cubes are not related to the hydrogarnet content. Similar amounts of the phase are observed in various specimens which have significantly different compressive strength.
6.4 Overview

The three fine Drakelow fractions give autoclaved specimens with significantly higher compressive strength, compared to corresponding Ratcliffe fractions. SEM micrographs show that these ash fractions are composed of similar types of particles, mostly solid spheres. Differences in elemental composition and mineralogy are generally modest. The ash fractions are mostly aluminosilicate glass. Therefore, the differences in compressive strength cannot be readily explained. Within the glass of the Drakelow fraction the calcium content is likely to be higher. This may make the material more reactive during hydrothermal curing.

Generally, higher quartz contents exist within the Drakelow fractions, compared with the Ratcliffe fractions. This difference may be significant. It is well documented that the reaction products formed from amorphous silica are different to those which form from crystallised silica, such as quartz. It has been observed that the rate of formation of semi-crystalline phases is more rapid from a glassy material. However, transformation of this phase into the more crystalline tobermorite may be relatively slow.

Although CSH phases form more slowly from quartz, there is evidence that the crystallisation stage to form tobermorite is achieved more readily. There are two possible explanations for this effect. Firstly, the rapid liberation of silicate ions from an amorphous silicate surface may give rise to a thin layer of reaction products, which precipitates onto the silicate surfaces and prevents further solubilisation. However, alternatively the nature of the CSH phase which forms from amorphous silica may
be significantly different. It is likely to be more highly polymerised with longer, silicates chains. It is more difficult for such a structure to transform into tobermorite.
Chapter 7

Conclusion

7.1. General

The experimental work undertaken in the project will be reviewed in the context of the aims and objectives given in Section 1.5.

7.2. Test Methods

Physical, chemical and mineralogical methods have been used to assess the hydrothermal behaviour of PFA samples, or ash fractions. Tests were either applied to the ashes themselves or autoclaved ash/lime specimens.

Autoclaved ash/lime pastes are useful specimens from which basic information on the hydrothermal reactions of PFA, or ash fractions, may be obtained. If used in combination with other analytical techniques, an outline reaction profile in respect to the appearance of CSH phases and hydrogarnets may be derived. However, ash/lime pastes are limited because strength measurements are not obtained. Since the development of compressive strength is of significance in any commercial autoclaved product, this is a considerable drawback.

Autoclaved ash/lime discs tested for strength using the "Brazilian" method have advantages regarding ease of production. However, these specimens were prone to severe damage during autoclaving which meant that a realistic w/s value could not be used.

Autoclaved ash/lime cubes performed satisfactorily. It was possible to produce autoclaved specimens of accurate dimensions with w/s values comparable to those used in AAC manufacture. Tests suggest that the variability of the method is acceptable. Experiments based on the cubes demonstrate significant differences between PFA samples or ash fractions.

Monitoring calcium hydroxide consumption by measuring free lime (Franke method) is a relatively quick and easy means of assessing "reactivity" of siliceous materials during hydrothermal curing. Differences due to fineness or
glass content have been observed. Measurement of free lime helps to assess the early reaction rates of lime with PFA. However, free lime measurements become less appropriate in the later stages of hydrothermal cure when most of the lime has been consumed. At this stage changes in the crystallinity of the CSH phases formed is the most significant process.

Infrared spectroscopy was unsatisfactory for the analysis of reaction products or raw materials and was, therefore, not developed beyond initial experiments.

The solubilisation studies, based on autoclaved ash/lime pastes have proven to be useful in estimating the rates of ash consumption. Valuable information on the dissolution of elements from the aluminosilicate glass within PFA has been gained. It would be worthwhile to develop the technique, particularly using modern methods of experimental analysis.

X-ray diffractometry has been one of the most useful techniques to study the hydrothermal reactions of PFA, despite being used qualitatively, rather than quantitatively.

Quantitative x-ray diffractometry was used to study the mineralogy of ash fractions obtained from a centrifugal classifier. The "ratio of slopes" method adopted proved useful for the comparison of the various ash fractions. This method is worthy of further development. It would be useful to assess the method using an x-ray diffractometer with step scanning facility, an automatic sample changer and modern data acquisition software. This would allow the necessary "analysis lines" to be obtained automatically, thus greatly increasing the efficiency of the technique. Analysis of a suite of PFA samples of known mineralogy (by other techniques) by the "ratio of slopes" method would serve to validate the method.

7.3 Comparison of the hydrothermal reactions of two UK PFA samples.

The hydrothermal reactions of two UK ashes, typical of the material currently used to manufacture AAC have been studied and compared using several techniques. Methods of test used for conventional concrete and mortar proved to be unsuitable for autoclaved products. Significant differences in the
behaviour of the two ashes during autoclaving were noted. Such differences are evident from the results of several test methods, as noted in the text.

There are several ways in which the hydrothermal reactivity of a PFA sample may be assessed, the rate of consumption of lime, rate of reaction of the PFA itself, the appearance of particular reaction products, or the development of compressive strength. These measures of hydrothermal reactivity may not, however, be necessarily related.

The conventional view that PFA is largely composed of spherical aluminosilicate silicate particles with small amounts of crystalline phases applies to the two ashes tested. However, straightforward measurements based on this approach, such as silica content, the amount of glass present, alkalis within the ash, or particle size distribution are not useful in predicting behaviour during autoclaving.

7.4 Reaction products formed during autoclaving

Rapid reaction of PFA particles with calcium hydroxide characterises the early stages of autoclaving. It can be assumed that aluminosilicate silicate glass is rapidly solubilised from the ash particles. Results show between 40 to 60% of a PFA may be solubilised and takes part in the formation of reaction products. The hydrothermal process may be diffusion limited, possibly governed by the rate of silica solubilisation. Several measured properties show a similar profile, that is a period of rapid change followed by a plateau. This is evident in quite diverse measurements such as the appearance of specific CSH phases, or the development of compressive strength.

The appearance of a CSH phase and a hydrogarnet similar to katoite are the initial reaction products observed with x-ray diffractometry. Differences in the rates of formation of these reaction products may be affected by the relative rate of solubilisation of silica and alumina from PFA.

After the formation of the initial semi-crystalline CSH phase, transformation to crystalline tobermorite occurs. It is difficult to assess the extent of this crystallisation stage, but significant amounts of the semi-crystalline phases probably persist even with prolonged autoclaving. The relatively small
amount of quartz within a PFA, or ash fraction, may be significant in regards to
the formation of tobermorite.

The hydrogarnet which form at a similar rate to the CSH phases persists
with prolonged autoclaving and, therefore, can be judged to be stable.

7.5 Classification

The classification method was chosen because of its industrial relevance,
rather than the precision of fractionation. Indeed observations by SEM confirm
that particles with diameters significantly different from the median exist in each
fraction. Air classification deviates from the ideal because of density variations
in the PFA source. There is no simple relationship between the fineness of ash
particles and the compressive strength achieved in autoclaved specimens. This
observation is of significance if the industrial classification of PFA intended for
AAC is to be considered. Classification of a PFA, to produce a finer product
may not necessarily improve the compressive strength. Any technical benefit
will be PFA source dependent. One of the PFA sources investigated in the
project had fines which if incorporated into an autoclaved ash/lime cube gave
increased strength compared to the coarse fraction. By the correct choice of
cut-point, classification of this material may result in increased compressive
strength. Conversely, fines within the other PFA source investigated did not
give significantly higher strength within autoclaved specimens if compared with
the coarse fraction. In this case classification may not lead to an increase in the
compressive strength achieved in autoclaved products.

Successful air classification of two British PFA samples was achieved
and five ash fractions were derived from each source. Differences between the
two "raw ashes" were accentuated in the ash fractions. These differences were
particularly evident with the coarser fractions. The fines of each set of ash
fractions were similar with respect to particle size and morphology. Mineralogical measurements also show similar amounts of aluminosilicate glass
exists in the fines, yet the behaviour of these fractions during hydrothermal
reactions with lime may be quite different. Therefore, particle size distribution,
bulk elemental analysis, or indeed, mineralogical analysis are not sufficient
parameters by which the autoclaved performance of ash fractions may be judged.

Investigations of the microstructure within ash fractions would be valuable. Variations in the glass chemistry of ash particles on the "nanoscale" may provide better methods for predicting the behaviour of ash fractions during autoclaving. Such an approach is technically difficult, because considerable effort would be required to relate the varied chemistry of a large number of ash particles to a macroscopic property such as strength.

Autoclaved ash/lime specimens made with Drakelow PFA are consistently stronger than those made with Ratcliffe PFA. This is true whatever the specimen type, lime/ash ratio, and at both high and low w/s values. There would appear, therefore, to be an intrinsic strength which a particular PFA sample can achieve during autoclaving. This agrees with the author's experience with the manufacture of AAC. However, this hydrothermal behaviour of the PFA cannot be readily explained in terms of elemental analysis or mineralogy. It is surprising that this difference also is evident with the fractions derived from both these PFA samples.

7.6 Recommendations

It would be worthwhile to undertake quantitative x-ray diffractometry of the autoclaved specimens. The "ratio of slopes" method could be used. This requires standard crystalline reaction products to be synthesised hydrothermally, in particular, tobermorite and hydrogarnet.

Further investigations of ash fractions to determine specific relationships between particle types, elemental composition and mineralogy would be valuable.

Experiments on the autoclaved ash/lime cubes measuring the pore size distribution would be valid. This may establish a correlation between the microporosity of the specimens and compressive strength.
Appendix 1

Facsimile Cover Sheet

To: Jo Deeley
Company: Marley Building Materials Ltd
Phone: 01675 462 314
Fax: 01675 462 314

From: Andy Smith
Company: LUGS
Phone: 0116 252 3629
Fax: 0116 252 3918

Date: 23/04/96
Pages including this cover page: 1

Comments: FTAO Jo Deeley/Rob Carroll

Jo, can you please pass this information on to Rob Carroll,

RE- LECO

Carbon/Sulphur analysis by LECO CS-125. Sample weight range 0.5 - 1 gram depending on the C/S content expected. Detection limits to 3 decimal places up to 6 wt %. Rock powders mixed with Lecocell II accelerator (0.5 grams) and Iron Chip Accelerator (0.5 grams). Accelerator weights not included in the analytical weight. Calibration set daily based on 5 standard analyses for C and S. Standards used are steel rings of known C/S content. Actual composition used is dependent upon the sample range expected i.e. we use a low calibration standard if the C/S values are expected to be low, etc. C standard range 3.04 % to 0.052%, S standard range 0.224% to 0.004%. We also use a mineral standard for high (upto 6% S) S contents.
Detection of the C/S is by conversion to CO2 and SO2 and then detected by passive IR. Combustion is in a low C crucible, in a RF furnace in pure Oxygen atmosphere.

Hope these answer all your questions, if not give me a call and I'll do my best to help you out. All the best for the submission. I'm in the same boat at the moment.

Regards
Andy Smith
Appendix 2

REPORT FILE

Analysis of Fly Ash for Sodium & Potassium by flame photometry, and Aluminium & Silicon by Atomic Absorption Spectroscopy.

IAN HART

Chemical Management Services Limited
Sodium and potassium were determined by flame photometry and aluminium and soluble silicon by atomic absorption spectroscopy on the 20 samples of fly ash supplied by Thermalite. All elements are those soluble in 0.1 mol dm$^{-3}$ Hydrochloric Acid at room temperature.

Determination of acid soluble material.

1.0000g of the sample was weighed and transferred quantitatively into a 400 ml beaker. Hydrochloric Acid, 270 ml, 0.1 mol dm$^{-3}$ hydrochloric acid was added carefully. The suspension of fly ash in the acid was stirred for 1 hour at room temperature. The suspension carefully filtered into a 500 ml volumetric flask. The filtrate was made up to 500 ml with deionised water and stored in plastic bottles for analysis. The weight loss was recorded after drying the filtrate at 50 - 60 °C. See table in Appendix 1.

Determination of Sodium & Potassium by Flame Photometry.

The analysis was as set out in BS4550 Pt 2 (1970), Method 16.2. Method recommended for UK internal purposes. An aluminium solution was prepared from very pure Aluminium Chloride (low in Sodium), Puratronic(R) Grade, from Johnson Matthey. The solution contained 17g/litre of Al$^{3+}$. The Sodium and Potassium stock solutions were prepared from Analar Grade reagents that had been dried at 250 °C for 1 hour prior to use. Sodium contained 0.1866g NaCl per litre and the Potassium 0.1583g per litre KCl. Aristar Grade Nitric Acid was used.

A series of standards was prepared from these solutions.

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# Volumes of reagent in cm$^3$ per litre.

Results in Table 2, Appendix 1.
Determination of Aluminium and Silicon by Atomic Absorption Spectroscopy.

Aluminium is linear in the range 0 to 60 ppm Al\(^{3+}\) and silicon in the range 0 to 150 ppm Si. Suitable standard solutions within these ranges were prepared from 1000 ppm standard solutions. A SpectrosoL Grade aluminium standard solution was used to prepare the aluminium calibration standards. For silicon the standard solution was prepared by dissolving 10.1119g sodium metasilicate (Na\(_2\)SiO\(_3\).9H\(_2\)O) in 500 ml deionized water, adding 10 ml concentrated hydrochloric acid and diluting quantitatively to 1000 ml with deionized water, 1000 ppm Si. Aluminium was determined at 309.3 nm (working range 40-200 \(\mu\)g mL\(^{-1}\)) and Silicon at 251.6 nm (working range 70-280 \(\mu\)g mL\(^{-1}\)), both elements required a fuel-rich nitrous oxide-acetylene flame. Multiple readings, 4 second manual integration, were taken for both the standards and the soluble ion in the solutions. If the reading of the samples was outside the linear range for that ion then the sample was suitably diluted, pipette and volumetric flask. The signal strength can vary with flame conditions, aluminium being a refractory metal, but this was most evident with the silicon analysis. The Silicon standards gave different linear readings from day to day and even during the same day, see graphs in Appendix 2. Two Ratcliffe and two Drakelow samples were therefore re-analysed with the changed conditions and the resultant figures are shown in brackets in table 3, Appendix 1. Errors of up to 10% for the soluble silicon should therefore be expected.
Appendix 1

Table 1

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<td>108</td>
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<tr>
<td>112</td>
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<td>0.2605</td>
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<td>0.5144</td>
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<td>0.3373</td>
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<td>0.3450</td>
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<td>0.3137</td>
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<tr>
<td>106</td>
<td>0.9999</td>
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<td>1.0002</td>
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<td>113</td>
<td>1.0002</td>
<td>0.2276</td>
</tr>
<tr>
<td>174</td>
<td>1.0002</td>
<td>0.2313</td>
</tr>
<tr>
<td>182</td>
<td>1.0000</td>
<td>0.1989</td>
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</table>
Table 2

Soluble ion in mg per 500 ml solution.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Sodium</th>
<th>Potassium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ratcliffe PFA</td>
<td>1.1</td>
<td>0.4</td>
</tr>
<tr>
<td>122</td>
<td>0.7</td>
<td>0.4</td>
</tr>
<tr>
<td>116</td>
<td>2.5</td>
<td>0.6</td>
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<td>94</td>
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<td>3.1</td>
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<td>98</td>
<td>3.9</td>
<td>4.9</td>
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<tr>
<td>104</td>
<td>5.3</td>
<td>6.9</td>
</tr>
<tr>
<td>108</td>
<td>6.0</td>
<td>7.4</td>
</tr>
<tr>
<td>112</td>
<td>6.5</td>
<td>7.9</td>
</tr>
<tr>
<td>176</td>
<td>6.9</td>
<td>8.0</td>
</tr>
<tr>
<td>184</td>
<td>6.6</td>
<td>8.3</td>
</tr>
<tr>
<td>Drakelow PFA</td>
<td>0.9</td>
<td>0.5</td>
</tr>
<tr>
<td>124</td>
<td>1.2</td>
<td>1.4</td>
</tr>
<tr>
<td>118</td>
<td>2.2</td>
<td>4.4</td>
</tr>
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<td>96</td>
<td>3.5</td>
<td>5.7</td>
</tr>
<tr>
<td>102</td>
<td>3.1</td>
<td>5.9</td>
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<td>106</td>
<td>4.4</td>
<td>6.3</td>
</tr>
<tr>
<td>110</td>
<td>3.6</td>
<td>7.3</td>
</tr>
<tr>
<td>113</td>
<td>3.3</td>
<td>7.5</td>
</tr>
<tr>
<td>174</td>
<td>4.2</td>
<td>7.9</td>
</tr>
<tr>
<td>182</td>
<td>4.0</td>
<td>7.9</td>
</tr>
</tbody>
</table>
Table 3
Soluble ion in mg per 500 ml solution.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Aluminium</th>
<th>Silicon</th>
</tr>
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<tr>
<td>Ratcliffe PFA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>122</td>
<td>2</td>
<td>0 (0)#</td>
</tr>
<tr>
<td>116</td>
<td>11.5</td>
<td>4.6</td>
</tr>
<tr>
<td>94</td>
<td>17.8</td>
<td>30.2</td>
</tr>
<tr>
<td>98</td>
<td>25</td>
<td>40.5</td>
</tr>
<tr>
<td>104</td>
<td>40.5</td>
<td>52.0 (44.8)#</td>
</tr>
<tr>
<td>108</td>
<td>46.5</td>
<td>72.9</td>
</tr>
<tr>
<td>112</td>
<td>46.5</td>
<td>66.4</td>
</tr>
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<td>176</td>
<td>46.5</td>
<td>74.2</td>
</tr>
<tr>
<td>184</td>
<td>46.5</td>
<td>76.5</td>
</tr>
<tr>
<td>Drakelow PFA</td>
<td>0.5</td>
<td>5.5 (5.1)#</td>
</tr>
<tr>
<td>124</td>
<td>11.5</td>
<td>17.4</td>
</tr>
<tr>
<td>118</td>
<td>26</td>
<td>45.6</td>
</tr>
<tr>
<td>96</td>
<td>35</td>
<td>60.6</td>
</tr>
<tr>
<td>102</td>
<td>35</td>
<td>61.7 (1.4)#</td>
</tr>
<tr>
<td>106</td>
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<td>66.6</td>
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<tr>
<td>110</td>
<td>46.5</td>
<td>68.7</td>
</tr>
<tr>
<td>113</td>
<td>49.3</td>
<td>64.7</td>
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<tr>
<td>174</td>
<td>50</td>
<td>68</td>
</tr>
<tr>
<td>182</td>
<td>49.3</td>
<td>70.2</td>
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</table>

# Results from analysis of solution on Day 2.
Table 4

Redrying of selected samples.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Weight taken</th>
<th>Dried Weight</th>
<th>Weight Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>98</td>
<td>0.2553</td>
<td>0.2376</td>
<td>0.0177</td>
</tr>
<tr>
<td>116</td>
<td>0.2385</td>
<td>0.2370</td>
<td>0.0015</td>
</tr>
<tr>
<td>122</td>
<td>0.4166</td>
<td>0.4163</td>
<td>0.0003</td>
</tr>
<tr>
<td>176</td>
<td>0.2073</td>
<td>0.1859</td>
<td>0.0214</td>
</tr>
</tbody>
</table>
KRONOS 3025

Titanium dioxide

non-surface-treated coarse rutile TiO₂ without pigmentary properties, readily soluble in melts

KRONOS 3025 is a special grade for rutile ceramics.

Applications

KRONOS 3025 is particularly suitable for the manufacture of electro-ceramics, vitreous enamels, glass, glass fibres, ceramics and welding electrodes. In addition, it can be used with advantage in glazes.

Attributes

KRONOS 3025 titanium dioxide has excellent fusibility in vitreous enamels and glass increases the UV absorption in sheet and container glass improves the mechanical, thermal and electrical properties of glass fibres increases the mechanical and thermal resistance of glazed ceramic articles

improves sintering in ceramics and enhances resistance to acids and thermal stability; permits certain colour effects to be achieved ensures excellent ionisation in electric arc welding ensures consumption of the electrode without spattering and easy re-ignition of the electrode allows control of slag fluidity enables welding electrode coatings to be colour-coded

Characteristics

KRONOS 3025 is an untreated coarse rutile TiO₂.

It is practically free from phosphorus, sulphur and impurities, such as vanadium, iron and chromium compounds, which discolor the melt.

Chemical and Physical Data

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ content</td>
<td>99%</td>
</tr>
<tr>
<td>Density</td>
<td>4.2 g/cm³</td>
</tr>
<tr>
<td>Sieve analysis</td>
<td></td>
</tr>
<tr>
<td>DIN 53195</td>
<td></td>
</tr>
<tr>
<td>&gt; 0.2 mm</td>
<td>&lt; 1 %</td>
</tr>
<tr>
<td>&gt; 0.1 mm</td>
<td>&lt; 10 %</td>
</tr>
<tr>
<td>&gt; 0.063 mm</td>
<td>&lt; 30 %</td>
</tr>
<tr>
<td>&gt; 0.04 mm</td>
<td>&lt; 40 %</td>
</tr>
<tr>
<td>&gt; 0.025 mm</td>
<td>&lt; 50 %</td>
</tr>
</tbody>
</table>

* Trademark of KRONOS TITAN-GMBH

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Appendix 4

Reference lines for the ratio of slopes method
Quartz reference line

\[ y = +1.28x^1 - 0.0212, \text{ } R^2 = 0.0688, \text{ max dev: } 0.112 \]
Mullite reference line

\[ y = +0.280x - 0.137, \text{ R}: 0.119, \text{ max dev: 0.158} \]
Haematite reference line

\[ y = 0.937x + 0.0185, \quad R: 0.0585, \quad \text{max dev}: 0.103 \]
Magnetite reference line

\[ y = 0.182x^1 + 0.0715, \quad R: 0.110, \quad \text{max dev}: 0.131 \]
Particle size distributions of fractions from RC1 ash

Particle size distributions of fractions from DK1 ash
Appendix 6

Analysis lines
RC[A]

\[ y = +0.0250x' + 0.00621, \text{R:} 0.0122, \text{max dev:} 0.0116 \]  (quartz)

\[ y = +0.0227x' + 1.10E-5, \text{R:} 0.00203, \text{max dev:} 0.00229 \]  (mullite)

\[ y = +0.0120x' - 0.00798, \text{R:} 0.0135, \text{max dev:} 0.0148 \]  (haematite)
quartz $y = +0.0329x^1 + 0.0324$, $R: 0.0518$, max dev: 0.0524
mullite $y = +0.0247x^1 - 0.00203$, $R: 0.0105$, max dev: 0.0109
haematite $y = +0.0107x^1 + 0.00974$, $R: 0.0176$, max dev: 0.0160
quartz \( y = +0.0477x^1 -2.49E-4, R:0.0137, \text{max dev:}0.0157 \)
mullite \( y = +0.0288x^1 -0.0133, R:0.0307, \text{max dev:}0.0302 \)
haematite \( y = +0.0181x^1 -0.00409, R:0.0159, \text{max dev:}0.0176 \)
magnetite \( y = +0.00709x^1 +0.00809, R:0.0148, \text{max dev:}0.0129 \)
2. Quartz: $y = +0.0469x + 0.0128$, $R: 0.0514$, max dev: 0.0618
   Mullite: $y = +0.0260x + 0.0194$, $R: 0.0319$, max dev: 0.0319
   Haematite: $y = +0.0182x - 6.35E-4$, $R: 0.0184$, max dev: 0.0202
   Magnetite: $y = +0.00956x + 0.0247$, $R: 0.0408$, max dev: 0.0410
RC[E]

quartz  \[ y = +0.0522x' +0.00310, R:0.0473, \text{max dev:0.0530} \]
mullite \[ y = +0.0311x' -0.0170, R:0.0270, \text{max dev:0.0232} \]
haematite \[ y = +0.0179x' -0.00773, R:0.0198, \text{max dev:0.0225} \]
magnetite \[ y = +0.0127x' -0.00429, R:0.0163, \text{max dev:0.0193} \]
quartz  \[ y = +0.0301x^1 +0.0131, R:0.0478, \text{max dev:}0.0567 \]
mullite  \[ y = +0.0270x^1 +0.00947, R:0.0283, \text{max dev:}0.0329 \]
haematite  \[ y = +0.0121x^1 +0.00407, R:0.00999, \text{max dev:}0.0110 \]
DK[B]

quartz \( y = +0.0421x^1 +0.0223, \ R:0.0406, \ \text{max dev:0.0340} \)
mullite \( y = +0.0253x^1 +0.0300, \ R:0.0554, \ \text{max dev:0.0664} \)
haematite \( y = +0.0178x^1 +8.62E-4, \ R:0.0179, \ \text{max dev:0.0209} \)
DK[C]

quartz  \( y = +0.0686x' -3.19E-4, R:0.0271, \text{ max dev:0.0310} \)
mullite  \( y = +0.0275x' +0.0136, R:0.0236, \text{ max dev:0.0272} \)
haematite  \( y = +0.0225x' +0.0163, R:0.0312, \text{ max dev:0.0378} \)
magnetite  \( y = +0.0193x' -0.0175, R:0.0308, \text{ max dev:0.0255} \)
DK[D]

quartz  \( y = +0.0714x^1 + 0.0724, R:0.120, \text{max dev:}0.132 \)
mullite  \( y = +0.0272x^1 + 0.0121, R:0.0201, \text{max dev:}0.0218 \)
haematite  \( y = +0.0290x^1 + 0.0285, R:0.0466, \text{max dev:}0.0489 \)
magnetite  \( y = +0.0247x^1 + 0.0115, R:0.0334, \text{max dev:}0.0387 \)

Weight ratio (mineral/rutile) vs. Peak height ratio (mineral/rutile) graph showing the regression lines and data points for quartz, mullite, haematite, and magnetite.
quartz $y = +0.0780x^1 + 0.0495, \ R: 0.106, \ max\ dev: 0.109$
haematite $y = +0.0315x^1 + 0.0248, \ R: 0.0513, \ max\ dev: 0.0508$
magnetite $y = +0.0328x^1 - 0.0136, \ R: 0.0340, \ max\ dev: 0.0376$
Appendix 7

Mineralogy of ash fractions by the ratio of slopes method

Information derived from analysis lines of ash fractions

<table>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>0.025</td>
<td>0.329</td>
<td>0.048</td>
<td>0.047</td>
<td>0.052</td>
<td>0.030</td>
<td>0.042</td>
<td>0.069</td>
<td>0.071</td>
<td>0.078</td>
</tr>
<tr>
<td>Mullite</td>
<td>0.227</td>
<td>0.247</td>
<td>0.029</td>
<td>0.026</td>
<td>0.031</td>
<td>0.027</td>
<td>0.027</td>
<td>0.028</td>
<td>0.027</td>
<td>nd</td>
</tr>
<tr>
<td>Magnetite</td>
<td>nd</td>
<td>nd</td>
<td>0.007</td>
<td>0.010</td>
<td>0.013</td>
<td>nd</td>
<td>nd</td>
<td>0.019</td>
<td>0.025</td>
<td>0.033</td>
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<tr>
<td>Haematite</td>
<td>0.120</td>
<td>0.011</td>
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<td>0.018</td>
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<td>0.018</td>
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<td>0.032</td>
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Information derived from reference lines

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<tr>
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<th>Correlation coefficient</th>
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<tr>
<td>Mullite</td>
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<td>0.990</td>
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<tr>
<td>Magnetite</td>
<td>0.182</td>
<td>----</td>
</tr>
<tr>
<td>Haematite</td>
<td>0.937</td>
<td>0.980</td>
</tr>
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<td></td>
<td>SiO₂</td>
<td>TiO₂</td>
</tr>
<tr>
<td>----------------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>Mullite</td>
<td>23.51</td>
<td>0.01</td>
</tr>
<tr>
<td>Rutile (silica added)</td>
<td>89.63</td>
<td>10.09</td>
</tr>
<tr>
<td>Silica</td>
<td>100.12</td>
<td>0.00</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>1.18</td>
<td>0.00</td>
</tr>
<tr>
<td>Hematite (silica added)</td>
<td>90.34</td>
<td>0.00</td>
</tr>
<tr>
<td>Hematite (out of calib')</td>
<td>4.04</td>
<td>0.01</td>
</tr>
</tbody>
</table>
Appendix 9

Relationship between glass content of ash fractions and PPI value

\[ y = +69.8x - 46.9, \text{ } R: 1.33, \text{ max dev: 1.42 } \]

1. Ratcliffe fractions

2. Drakelow fractions

3. All fractions

\[ y = +15.3x + 52.8, \]