INCORPORATION OF INORGANIC METAL SALTS IN COMPOSITE CEMENTS

A thesis presented for the degree of Doctor of Philosophy

by

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SUMMARY

The science associated with the incorporation of intermediate level toxic and radioactive waste into cement systems is an important field to understand for the safe and cost effective storage and disposal of these wastes. A fundamental understanding of the effects of different wastes and, possibly, a prediction of their effects, is necessary to fully utilise the material. Composite cement systems are an attractive alternative to Portland cement for a number of reasons. The use of mineral additions consumes a waste product which would otherwise need a disposal route and, due to the decreased amount of Portland cement used, reduces cost and energy consumption. Strength of the cemented waste is not of primary importance so the lower strength of the composite cements should not pose a problem. However, one of the main advantages of composite cements over Portland cements is that they evolve less heat during hydration, which is a useful property especially for the storage of cements in an underground repository where the ambient temperature could be significantly higher than usual.

A Portland cement and three composite cements (3:1 BFS:OPC, 9:1 BFS:OPC and 3:1 PFA:OPC) were studied with the Portland cement acting as a reference material. To these cements five inorganic metal salts were added. These were $ZnCl_2$, $SnCl_2.2H_2O$, $SnCl_4.5H_2O$, $AlCl_3.6H_2O$ and As_2O_3 and they were added at levels of 0.1%, 1.0% and, in some cases, 5% by weight of metal. To allow the study of the effects of zinc chloride and the two tin chlorides to be carried out in depth, the number of samples to be studied was selectively reduced during the project. The kinetics of early hydration, the formation of non-standard hydration products and the location of the metals within the microstructure were investigated using such techniques as isothermal conduction calorimetry, X-ray diffraction, and scanning electron microscopy with energy dispersive spectroscopy analysis.

It was not possible to generalise the effects of the metal salts on the hydration of the cement as the variation between the different cement systems was considerable. Zinc chloride caused a retardation of set and hydration in all cement systems, the severity of which increased with increased loading of metal salt. Tin(II)

chloride also caused a retardation of set but this was not as great as in the zinc system. Tin(IV) chloride had mixed effects which were dependent on the amount of salt present in the system. All the additions affected the various cement systems to different extents, with the 9:1 BFS:OPC being the most retarded. The formation of calcium hydroxo stannate, $CaSn(OH)_6$, and calcium zincate, $CaZn_2(OH)_6.2H_2O$, was identified in the appropriate cement systems with the formation of Friedel's salt, $Ca_3Al_2O_6.CaCl_2.10H_2O$, also apparent alongside the appearance of these phases. The identification of the metals (zinc or tin) within the microstructure revealed that the metal did not locate in grains of the mineral addition but, in all cases, was incorporated in the Portland cement phases.

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CONTENTS

ABBREVIATIONS

MATERIALS

OPC	Ordinary Portland cement
BFS	Blast furnace slag
PFA	Pulverised fuel ash

TECHNIQUES

ICC	Isothermal conduction calorimetry
XRD	X-ray diffraction
DTA	Differential thermal analysis
SEM	Scanning electron microscopy
EDS	Energy dispersive spectroscopy

CHEMISTRY

HYDRATION PHASES

CH	$Ca(OH)_2$	Calcium hydroxide
CC	$CaCO_3$	Calcium carbonate
C-S-H		Calcium silicate hydrate of unknown stoichiometry
E	$Ca_6Al_2(OH)_{12}(SO_4)_3.26H_2O$	Ettringite
FS	$Ca_3Al_2O_6.CaCl_2.10H_2O$	Friedel's salt
X	$CaSn(OH)_6$	Calcium hydroxo stannate
Z	$CaZn_2(OH)_6.2H_2O$	Calcium zincate

ANHYDROUS CEMENT PHASES

C_3S	Ca_3SiO_5	Tricalcium silicate (Alite)
C_2S	Ca_2SiO_4	Dicalcium silicate (Belite)
C_3A	$Ca_3Al_2O_6$	Tricalcium aluminate
C_4AF	Ca_2Al,Fe,O_5	Calcium aluminoferrite

ANHYDROUS REPLACEMENT MATERIALS PHASES

G	$Ca_2Al(Al,Si)_2O_7$	Gehlenite
Q	SiO_2	Quartz
M	$3Al_2O_3.2SiO_2$	Mullite

OTHER ABBREVIATIONS

BEI	Backscattered electron imaging
SEI	Secondary electron imaging
OP	Outer product
LLW	Low level waste
ILW	Intermediate level waste
HLW	High level waste
w:c	water:cement ratio
w:cp	water:cement powder ratio

CHAPTER ONE

1. INTRODUCTION

The work undertaken for this research was carried out in conjunction with British Nuclear Fuels Ltd, Sellafield and was one part of a much larger research plan. The overall aim was to incorporate inorganic metal salts into four cement systems and study the effects of the salts on the hydration and microstructural properties of the cements. The reason for the work was to increase fundamental understanding of the systems with a view to the incorporation of toxic and radioactive waste into the cements for disposal of these wastes, primarily from the Sellafield site although with a view to extending this to other companies and countries. Other aspects of the study of immobilisation of the wastes, such as leaching, were carried out at Sellafield and the results of all parts of the research would be combined to give an overall picture of the effects of different inorganic metal salts on composite cement systems.

A composite cement is a hydraulic cement composed of one or more inorganic materials that take part in the hydration reactions and, therefore, make a substantial contribution to the hydration product.[1] For this research the mineral additions were blast furnace slag (BFS) and pulverised fuel ash (PFA) which are waste materials arising from the production of iron and coal burning power stations respectively. Whilst these mineral additions are not unusual, the replacement levels used for this work were comparatively high. The slag was used at 75 and 90 % replacement levels and the ash at 75%. This was done in conjunction with British Nuclear Fuels Ltd. to be comparable with work in progress at Sellafield. An ordinary Portland cement (OPC) was studied alongside the composite cements to use as a reference as there have been more studies made on this cement than any composite cement.

When the project was set up it was decided that there would be five inorganic metal salts added to each of the four cement systems. These salts were: $ZnCl_2$, $SnCl_2.2H_2O$, $SnCl_4.5H_2O$, $AlCl_3.6H_2O$ and As_2O_3. With the exception of the arsenic compound, the anion was kept constant so as to eliminate a variable that could complicate the system and the metals were chosen for a number of reasons. All the metals are common elements that could arise in waste streams produced by British Nuclear Fuels and the knowledge gained would, therefore, be of direct importance to them. Also, zinc is on a list supplied by the Environmental Protection Agency (EPA) in America as one of a number (along with arsenic) about which immobilisation information needs to be known. Tin was chosen as both Sn(II) and Sn(IV) so that the effects of variation in oxidation state could be investigated. The salts are all amphoteric which means that they can act as either a weak acid or a weak base. As well as considering the points just mentioned, it was also necessary to correlate the results of this project with the work at Sellafield and the salts were chosen on this basis.

The aims of the research were to assess the effects of the metal salt additions on the generation of heat during initial hydration kinetics which was an attempt to ascertain whether the composite cements had any effect in lowering the heat output and if the salts caused any significant changes to the heat output. This was important for consideration of storage in underground repositories as the temperature would be increased over that of ambient temperature to begin with and, therefore, it would be beneficial to have a cement system which would generate the lowest amount of heat possible. Secondly, to establish the presence and identification of standard and non-standard hydration phases and to examine the microstructures to investigate where and how the metal ions were incorporated into the hydration matrix. These were to establish the chemistry and the microstructure of the system and decide if the metal salts had any detrimental effects on the microstructure which could lead to the metals leaching out of the system.

The generation of heat during the first few days of the hydration was studied using isothermal conduction calorimetry and comparisons made between all the different systems. To identify the standard and non-standard hydration phases the primary technique employed was x-ray diffraction which allowed a study of the expected phases from the different cement systems alone. It also allowed a comparison of the salt-containing systems with the standard cement systems to identify any differences. At this stage it was deemed necessary to streamline the project as it became increasingly clear that there would be too many samples to allow a thorough study of all of them. Therefore, after consultation it was decided that only three metal salts would be investigated in detail. These were the zinc chloride and the two tin chlorides. The aluminium was eliminated from the study as there was already a significant amount present in the neat cement which would mean that identification of the metal would be the most difficult of all the salts. It was decided that it would be beneficial to keep the two tin salts as this provided a valence state comparison which left one salt to be chosen. The arsenic was dropped because this was the most difficult of the remaining salts to study from a safety aspect and the cation associated with it was an oxide whereas the tin salts were chlorides. Therefore, the salts remaining were $ZnCl_2$, $SnCl_2$ and $SnCl_4$ which allowed each of them to be studied in depth. In addition to the x-ray diffraction studies, a limited amount of differential thermal analysis was undertaken to amplify the results obtained with the x-ray diffraction. The final technique employed was scanning electron microscopy (SEM) which allowed a study of the microstructure and any differences due to the metal salts to be observed. Alongside this, electron dispersive spectroscopy (EDS) was used to locate where in the microstructure the metals were deposited.

Reported studies on the metal salts used here in the cement systems chosen are limited although there is a significant amount of literature on the subject of immobilisation of wastes in general. This is an important field of study as the potential benefits of encapsulating toxic and radioactive waste in cement systems are remarkable. Also, any study of composite cements can only add to the understanding of these systems.

CHAPTER TWO

2. LITERATURE SURVEY

2.1 BACKGROUND

The addition of inorganic metal salts to the different cement systems was carried out because these cements are currently in use, and being further investigated, for the immobilization and encapsulation of toxic and radioactive wastes from nuclear power stations. The wastes produced can be characterised into three types which, currently, have the following definitions:

High Level Wastes (HLW): Wastes from the reprocessing of irradiated fuel which generate heat and will be vitrified. These contain over 95% of all the radioactivity in wastes from the generation of electricity by nuclear power.

Intermediate Level Wastes (ILW): Wastes with radioactivity exceeding the boundaries for low level wastes, but of a lower activity and heat output than high level wastes.

Low Level Wastes (LLW): Wastes with a radioactivity not exceeding 4GBq*/tonne alpha activity or 12 GBq*/tonne beta/gamma activity, other than those acceptable for disposal with household refuse. These wastes do not normally require radiation shielding.[2]

*1Bq = 1 Bequerel = 1 disintegration s^{-1}

Historically, low level waste (LLW) has been sent for shallow land burial whereas intermediate level waste (ILW) and high level waste (HLW) streams have been stored on site in steel drums. This is now changing and waste is treated to facilitate transport, storage and disposal:

LLW will be reduced and containerised prior to disposal.

HLW will be immobilised by vitrification and then stored for 50 years to allow the radioactivity to decline before disposal.

ILW will be encapsulated in an inorganic cement matrix and sent for storage until such a time as a suitable disposal route is available. (such as a deep underground repository). [3]

To give some idea of the amounts involved, it is thought that by the year 2000, there will be around 60,000m^3 of ILW produced.[4] This, therefore, means that one of the major considerations for the encapsulating material is that it is cheap and production is simple. However, the considerations are not that straight forward. ILW covers a wide range of materials, for example metals, ion exchangers etc., each with differing chemical properties. Therefore, it is necessary that the encapsulated product properties are such that it:

1) develops and maintains sufficient strength to allow normal handling without damage
2) remains in a solid mass
3) minimises activity release under normal conditions or as a result of an accident.[4]

To gain some perspective on immobilisation it is necessary to give an explanation of physical immobilisation. Transport of a radionuclide through porous cementitious materials is mainly dependent on two properties: the diffusion coefficients and a capacity factor. The diffusion coefficient is controlled by the volume and continuity of capillary pores in the cementitious materials. The capacity factor accounts for retention of radionuclides due to physical adsorption, chemisorption, chemical binding and precipitation. This factor is finite for a given cementitious material so, if it is exceeded, transport becomes a process of simple diffusion.

Low diffusion rates can be achieved by using low w:c ratios and mineral admixtures - these minimise the volume and continuity of pores, thereby limiting diffusion. Where physical adsorption is significant for immobilisation, hydrated materials with a high surface area and large micropore volume are especially desirable, i.e. C-S-H gel with a high surface area. Materials with blast furnace slag seem particularly advantageous because they contain a high proportion of gel and the gel itself has a high micropore volume.[5]

Further consideration to those already mentioned are:

Leachability - it is necessary that the cements do not allow any leaching as this would allow radioactive/toxic species to escape into the surroundings.

Radiation stability - it is vitally important that the cement is not degraded by radiation.

Mechanical stability - for example, strength. These properties should not degrade over time or because of the surroundings.

Phase complexity of the matrix - that is, what chemical compounds are formed when the waste products react with the cement and will they have deleterious effects?[5]

There are, obviously, many more areas to be considered depending on the final outcome of the cemented waste. For example, if it were to be stored in steel drums then degradation of the steel and its effects would need to be assessed, or if the waste were to be placed in a repository, the effects of groundwater and temperature would be major concerns. However, cement has many attributes which make it a suitable material for encapsulation and immobilisation:

- It is inexpensive and readily available in required quantities.
- It helps to immobilise radionuclides by:
    a) acting as a diffusion barrier
    b) providing sorption and reaction sites

c) maintaining a high pH which in turn decreases radionuclide solubility.

- It provides radiation shielding which is not degraded by the radiation.
- Its permeation and diffusion characteristics are controllable over a wide range via selection of constituents and components.[5]

The applicability of different cement systems to immobilisation and encapsulation of wastes can be examined individually and comparisons made between them. Therefore, this literature survey can be broken down into three main parts: ordinary Portland cement (OPC) and cements containing blast furnace slag (BFS) and pulverised fuel ash (PFA) as replacement materials. It will then be necessary to look at the effects of inorganic salts on these systems in general.

2.2 ORDINARY PORTLAND CEMENT (OPC)

Portland cement is a hydraulic binder, i.e. a finely ground inorganic material which, when mixed with water, forms a paste which sets and hardens by means of hydration reactions and processes and which, after hardening, retains its strength and stability even under water.[6] It is made by heating a mixture of limestone and clay to a temperature of 1450°C when partial fusion occurs and nodules of clinker are produced. This clinker is then mixed with a few percent of gypsum to control setting and is then finely ground to make the cement. The typical composition of the clinker is: 67% CaO, 22% SiO_2, 5% Al_2O_3 3% Fe_2O_3 and 3% other components such as Na_2O, K_2O, MgO, TiO_2 etc.[1] The clinker usually contains four major phases: alite (C_3S), belite (C_2S), tricalcium aluminate C_3A) and a ferrite phase (C_4AF) which are shown in Table 2.1. There will also be other phases present, such as alkali sulphates and calcium oxide.

PRODUCTS	CEMENT NOTATION	CHEMICAL NAME
Ca_3SiO_5	C_3S	tricalcium silicate
Ca_2SiO_4	C_2S	dicalcium silicate
$Ca_3Al_2O_6$	C_3A	tricalcium aluminate
Ca_2AlFeO_5	C_4AF	tetracalcium aluminoferrite

Table 2.1 Constituents of Cement Clinker

Alite is the most important constituent and constitutes around 50 - 70 % of the Portland cement. It is tricalcium silicate whose composition and crystal structure are modified by the incorporation of foreign ions, especially Mg^{2+}, Al^{3+} and Fe^{3+}. It reacts quickly with water and is the most important of the phases for strength development, especially in the first 28 days. Belite constitutes 15 - 30% of the clinker and is dicalcium silicate again modified by the incorporation of foreign ions. It reacts relatively slowly with water which means it contributes very little to the early strength development but is important to the further increase in strength at later ages. Belite has been shown to have 5 polymorphs at ordinary pressures[1]:

$$\begin{array}{ccccccccc} \alpha & \rightleftarrows & \alpha'_H & \rightleftarrows & \alpha'_L & \rightleftarrows & \beta & \rightleftarrows & \gamma \\ & 1425^\circ C & & 1160^\circ C & & 630\text{-}680^\circ C & & <500^\circ C & \end{array}$$

All of the polymorphs are built from Ca^{2+} and SiO_4^{4-} ions and the arrangements of these are similar in all except the γ-C_2S. The most common polymorph present in the majority of clinkers is the β form as the high temperature polymorphs are not generally preserved on cooling and, in all normal Portland cement clinkers, there are enough stabilising ions to prevent the transformation to γ-C_2S from occurring.[1]

The aluminate and ferrite phases both constitute around 5 - 15% of the clinkers. Again they are modified in composition by foreign ions such as Si^{4+}, Fe^{3+}, Na^+ and K^+ and by variations in the Al/Fe ratio in the case of the ferrite phase. The aluminate phase reacts very quickly with water and can be responsible for rapid setting unless a set-controlling agent is added. The rate of reaction of the ferrite phase with water varies but can be generalised to being initially high and then intermediate between the alite and belite phases at later ages.[1]

There is some disagreement as to the nature of the mechanism of hydration of Portland cement. A definition of hydration given by Taylor[1] explains that in cement chemistry, the term hydration is used to explain the totality of changes which occur when an anhydrous cement, or one of its constituent phases, is mixed with water. The chemical reactions which take place during hydration are more complex than a simple conversion of the anhydrous compounds into the corresponding hydrates which complicates the explanation of the mechanism of hydration. There are two main theories of what occurs during hydration and a combination of both may provide the best explanation. The process of hydration can be broken down into the sum of those of the individual clinker materials[1,7] however, this does not really help when considering the hydration of cement in its entirety due to the complex mutual reactions occurring between the individual phases.

In 1887, Le Chatelier[8] proposed a hydration mechanism which involved the anhydrous material dissolving to form a solution of hydration products. When supersaturation is reached, the hydrates precipitate out as interlocking crystals which are responsible for the strength development of the paste. However, in contrast to this, Michaelis (1893) interpreted the reaction as the formation, cohesion and subsequent desiccation of a gel which provides the strength development[8]. There was a problem with these theories in that neither accounted entirely for complex reaction kinetics or the product structures observed and it is now accepted that the hydration of a cement is a combination of the two theories. It is believed that an understanding of the dormant period will assist in the explanation of the reaction mechanisms. Attempts to explain this phenomenon resulted in the formation of two different theories and then a third, which combines aspects of the other two.

Firstly, Young et al[9] suggested that Ca^{2+} ions leached out of the C_3S grains on contact with the water, which left a silica-rich layer on the surface of the grain. High local concentrations of Ca^{2+} ions inhibited further dissolution and, although calcium continued to dissolve, the rate slowed down to a level at which no large thermal changes were detectable. This was the dormant period and served the purpose of allowing the nucleus of the grain to reach the critical size required for growth to occur. When supersaturation of the liquid was attained, and the calcium hydroxide nuclei had reached their critical size, a rapid development of hydration products occurred. This was accompanied by a large evolution of heat which corresponds to the setting of the C_3S.

A modified view was described in a review by Skalny & Young[10]. There is a formation of a protective coating around the C_3S grains which acts as a barrier to further reaction and promotes the onset of the dormant period. However, the layer is unstable and permeable and, therefore, allows continued transfer of ions to and from the C_3S grain. This results in the protective layer converting to a 'second hydrate'. The C:S ratio of this hydrate was determined and it was found to be less than three. This suggests that the formation of the hydrate must be accompanied by simultaneous release of calcium hydroxide and the combined energy changes involved represents the second major heat evolution and, therefore, signals the end of the dormant period.

During the 1960's a suggestion was made by Powers[11] that osmotic effects may play an important role in the hydration of Portland cement. This suggestion was not really developed further until the late 1970's when two sets of researchers put forward a theory for a membrane/osmosis model to explain the hydration of cement[12,13] which incorporates elements of the previous two suggestions. According to Birchall et al[13], cement products can be considered as dispersions of solid particles in a matrix of hydration products. They made an attempt to explain the mechanism by which the morphology of cement arises and related this to the mechanical properties of a dense, hydrated cement paste. This was done by concentrating on the C-S-H phase as they believed that it was most likely to play the dominant role in the hardening process and the final mechanical properties. They followed the appearance of calcium and silicon (as the two major elements in cement) and, also, the effect of pH on the morphology. It was found that when cement is placed in contact with water, calcium ions are rapidly leached from the solid to form calcium hydroxide solution, but only traces of silica are found. However, an increase in the silica released from Portland cement was observed when the initial pH was reduced in an experiment using water of varying initial pH values.

This was investigated using scanning electron microscopy which showed an absence of the normal hydration feature (fibre-like morphology) observed by other workers, but evidence of considerable penetration by water into the grains. The authors found it difficult to agree with a dissolution, nucleation and particle growth mechanism for the appearance of C-S-H in the interstitial space of cement paste when one constituent (SiO_2) does not appear in the bulk aqueous phase. Under normal conditions the movement of SiO_2 is restricted to the vicinity of the original particle. This restriction can be removed by reducing the pH of the aqueous phase whereby the SiO_2 rises to saturation level but the normal formation of C-S-H is not observed. It is suggested that C-S-H is formed at the grain surface by the combination of dissolved calcium hydroxide and silicate anions. Changes around the cement grain have been reported by many workers. Initially, a gel-like phase forms around each grain which extends into the core. After 1-3 hours, fibre-like outgrowths radiate from the grain - a process resembling that of the 'silicate garden'[14] - where tubiform growths emanate from a crystal of a soluble polyvalent metal salt placed in a solution of sodium silicate. This is not directly analogous to the hydration of cement, because in the latter the aqueous phase is a solution saturated or supersaturated with respect to calcium hydroxide, with silicate confined to the region of the grain. Birchall et al[15] pointed out that the 'silicate garden' effect is not confined to silicates but is also given by borates, aluminates, stannates, zincates etc. and that the most essential feature is that a solid reaction product is formed which is gelatinous and able to form a continuous membrane between two solutions of different composition. From the work undertaken, Birchall et al[13] were able to construct a model for the hydration and setting of Portland cement. The early stage of hydration involves the rapid leaching of calcium into the bulk aqueous phase and the formation of a calcium depleted layer of orthosilicic species (from the orthosilicate structures of C_3S and β-C_2S) around the cement grains which increases in depth as hydration proceeds into the grain. It is proposed that combination occurs between dissolved calcium hydroxide and the dimeric silicate anions. Therefore, a membranous precipitate of C-S-H is formed at the interface through which water passes into the grain and calcium ions pass outwards to the bulk aqueous phase. Osmotic pressure rises within the membrane eventually causing its rupture at weak points and extruding the fluid contents. Continued formation of the C-S-H at the grain produces the tubiform growths observed. The proposed early setting and hydration of Portland cement is as follows:[13]

$$\text{cement clinker} + \text{water} \rightarrow \underset{\text{(surface)}}{\text{orthosilicate anions}} + \underset{\text{(dissolved)}}{\text{calcium hydroxide}}$$

$$\underset{\text{(surface)}}{\text{orthosilicate anions}} \xrightarrow[12.6]{\text{pH}} \underset{\text{(surface)}}{\text{disilicate anions}}$$

$$\underset{\text{(surface)}}{\text{disilicate anions}} + \underset{\text{(dissolved)}}{\text{calcium hydroxide}} \rightarrow \underset{\text{(formed outwards from surface)}}{\text{C-S-H}}$$

This confirms that crystallisation (nucleation and growth of solids having long range order) is not involved in the early formation of the major cementing phase in Portland cement.

In summary, the model described has the advantage over others mentioned for the following reasons:

1. It gives a reason for the onset and termination of the induction period observed with conduction calorimetry.
2. It explains the morphology of outer C-S-H products - tubular and others.
3. It is compatible with the variations which occur in the composition of the bulk aqueous phase during hydration.
4. It provides a transport mechanism for the silicate material from the cement core to the outer hydration products - without the need for diffusion through the bulk aqueous solution where the concentration has been found to be very low.[11]

2.3 COMPOSITE CEMENTS

According to Taylor[1], a composite cement is "a hydraulic cement composed of Portland cement and one or more inorganic materials that take part in the hydration reactions and thereby make a substantial contribution to the hydration product". He calls these inorganic materials mineral additions and the most important are, currently, pulverised fuel ash (PFA), ground granulated blast furnace slag (GGBFS), natural pozzolanas and microsilica (condensed silica fume). The ones used for this work were pulverised fuel ash and blast furnace slag and, therefore, this review will concentrate only on these additions. The mineral additions can be categorised as pozzolanic materials or latent hydraulic cements and neither material reacts significantly with water in the absence of anything else. Pulverised fuel ash is a pozzolanic material which is usually high in SiO_2 and, quite often in Al_2O_3, and low in CaO. When mixed with water and CaO (from Portland cement), pozzolanic materials are sufficiently reactive to form C-S-H and, therefore, to act as hydraulic cements. Latent hydraulic cements have a composition intermediate between pozzolanic materials and Portland cement and will act as a hydraulic cement when mixed with water and another substance which acts as an activator. Blast furnace slag is a latent hydraulic cement and will react with the calcium hydroxide produced by the Portland cement with which it is mixed.[1,16] Both blast furnace slag and pulverised fuel ash are waste materials arising from the production of iron and coal burning power stations, respectively. This means that their use as mineral additions for composite cements are advantageous both economically (as the amount of Portland cement required is decreased which reduces the amount of energy required in the cement production as well as keeping down cost of the composite cement itself[17]) and environmentally (utilising by-products of industry which would otherwise have to be disposed of elsewhere). Also, the addition of these materials can improve the properties of the cement.[16,18,19]

2.3.1 Blast Furnace Slag Cements

Blast furnace slag (BFS) is formed as a liquid at 1350 - 1550°C during the manufacture of iron. When it is cooled sufficiently rapidly to below 800°C, it forms a glassy material which is a latent hydraulic cement. Although this material possesses hydraulic properties, its reaction with water is very low at 20°C. To enable hydration to proceed at an acceptable rate, continued dissolution must be promoted by chemical or thermal activation[16,19]. The most popular method of achieving this is by blending the slag with an ordinary Portland cement - giving a composite cement. In this system it is thought that calcium hydroxide and gypsum act as activators. Calcium hydroxide, produced from the hydrating Portland cement, has an activating effect by providing hydroxyl ions which attack the glassy slag (see Figure 2.1). Gypsum, although not as activating as calcium hydroxide, is important for the formation of the AFt phase.[16] Blast furnace slags are composed of four main oxides, CaO, MgO, Al_2O_3 and SiO_2 with smaller amounts of iron oxide, TiO_2, Na_2O, K_2O and some substitution of S^{2-} for oxygen.[20]

The reaction of the glassy material yields hydrates which are similar in nature to Portland cement hydrates.[19] However, the proportion of calcium hydroxide formed is smaller, the lime/silica ratio of the C-S-H is lower and a hydrotalcite-type phase (magnesium aluminate hydrate) may be formed. These effects become more pronounced the higher the proportion of slag, but even at a ratio of nine parts slag to one part cement there is residual calcium hydroxide. A model for the early hydration of a slag cement is given by Roy and Idorn[19] which presupposes sufficient heat of hydration for initial alkali activation of the slag, and corresponds to these characteristics of the hydration mechanism and structure formation:

1. Dilution of Portland cement by slag reduces the quantity of calcium hydroxide to be precipitated in the pores of the cement.
2. The slag fraction hydrates alongside the Portland cement.
3. The Portland cement releases alkalis and lime during the hydration whilst the slag retains alkalis and lime in its hydration products.

Another proposed mechanism for the hydration of the slag is shown in Figure 2.1.

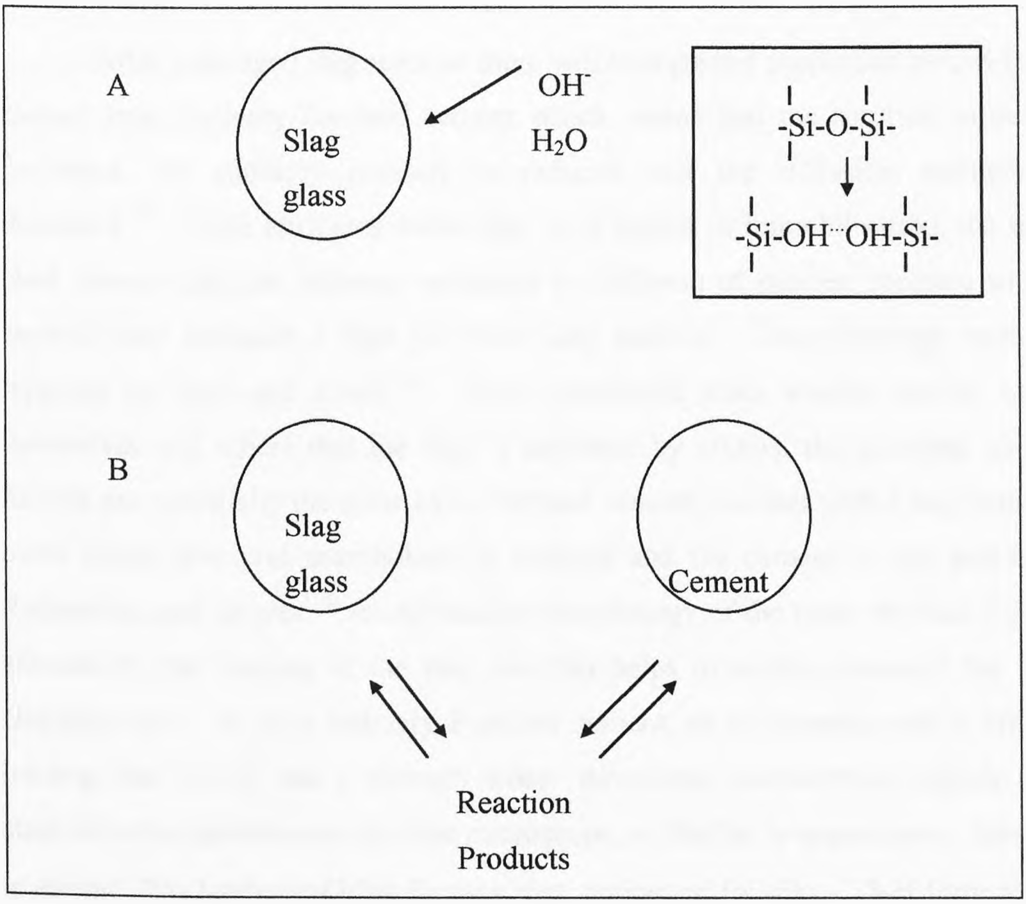

Figure 2.1 Hydration of slag in presence of Portland cement (adapted from reference 20)

Figure 2.1 shows the early stages of reaction between a slag particle and alkaline aqueous solution as a result of which, hydrolytic bond attack occurs on Si-O-Si linkages (A). The bottom section (B) shows how, subsequently, slag and cement particles react. The rate of reaction of the glassy phase is accelerated in alkaline solutions because the initial stage of the reaction requires hydrolysis (A). The glass contains Si-O-Si bonds that are hydrolysed by the OH^- ions provided by the calcium hydroxide from the hydrating cement. Once the glass network has been disrupted reaction between the components can occur and during the early stages material transport occurs through solution. However, as precipitation builds up a solid matrix and, as liquid water becomes increasingly confined to the pores, transport through the solid products of reaction dominates continuing production.[20]

This mechanism does not only apply to slag cements but to any glassy material (such as fly ash).

After prolonged slag reaction there will be a greater proportion of C-S-H than formed from ordinary Portland cement which means that the sorption capacity is increased, the capillary porosity is reduced and the diffusion resistance is increased.[5] These attributes mean that, with regard to immobilisation, the use of blast furnace slag can increase resistance to diffusion of species, increase sorption capacity and maintain a high pH over long periods. These findings were also reported by Roy and Idorn[19]. They concluded from studies carried out by themselves and others that the slag is activated by alkalis, the principal hydrates formed are essentially the same as in Portland cement, but that with a slag cement, a more dense structural morphology is induced and the cement is less permeable. Richardson and Groves[18] found that the morphology of the outer product C-S-H is affected by the loading of the slag and this helps to explain some of the above characteristics. In pure ordinary Portland cement, or in cements with a low slag loading, the C-S-H has a strongly linear directional characteristic which, when studied in the transmission electron microscope, is fibrillar in appearance. However, at around 75% loading of blast furnace slag, regions of foil-like C-S-H form without the linear characteristics and as the amount of blast furnace slag increases the foil-like morphology replaces the fibrillar morphology. This difference in morphology could account for the effect of a reduction in diffusion rates observed with slag. This is because, the fine porosity in the fibrillar morphology, observed in Portland cement, appears to leave coarse interconnected pores whereas the evenly distributed pores in the foil-like C-S-H of the slag cements are probably less well interconnected.

2.3.2 Pulverised Fuel Ash Cements

Pulverised fuel ash is a by-product of the combustion of pulverised coal in thermal power stations. It is removed by dust collection systems as a fine particulate residue from the combustion gases before they are discharged into the atmosphere. Fly ash particles are typically spherical, ranging in diameter from less than 1μm to more than 150μm, the majority being less than 45μm. The chemical composition of fly ash is determined by the types and relative amounts of incombustible matter in the coal used.[1,6] More than 85% of most fly ashes comprise compounds or glasses formed from SiO_2, Al_2O_3, Fe_2O_3, CaO and MgO. A typical analysis for a UK fly ash is shown in Table 2.2[6]

Component	**Percentage**
SiO_2	51.0
Al_2O_3	25.6
Fe_2O_3	9.6
CaO	1.7
MgO	1.6
K_2O	3.8
SO_3	0.7
Carbon	2.8

Table 2.2 Typical Composition of a UK Fly Ash

There are two classifications of fly ash (as specified by the American Standard): high lime and low lime content which can also be identified as class C and class F fly ash respectively. The above example is of a low lime fly ash and this is typical of an ash produced in the UK. As mentioned previously, it is widely accepted that fly ashes have pozzolanic properties which means that although it has little or no cementing action when existing alone it will, in the presence of lime and water, form insoluble cementitious compounds. In the case of fly ash blended with ordinary Portland cement, it is generally believed that the lime released by the hydrating cement reacts with the finely divided silica in the fly ash to form calcium silicate hydrates.[21]

The incorporation of mineral additions to Portland cement has been reported to have both accelerating and retarding effects on the hydration of the cement depending on the addition. However, in the case of PFA, different investigators have reported both accelerating[22-26] and retarding[22,27-29] effects. Through subsequent reading it became clear that it wasn't a case of PFA being either retarding or accelerating but a combination of both which appears to depend on the length of time the PFA has been hydrating. The results of Halse et al[22] and Taylor et al[30] agree closely and show that retardation appears to be restricted to the first 24 hours and then there is a subsequent acceleration. Halse et al[22] also showed that both class C and class F fly ashes retard both C_3S and C_3A hydration with the high lime fly ash causing the greater retardation.

It is suggested that the retardation phenomenon is related to the presence and condition of the fly ash surfaces because the surface acts like a calcium sink. That is, calcium in solution is removed by abundant aluminium associated with the fly ash, as an AFt phase preferentially forms on the surface of the fly ash. This depresses the Ca^{2+} ion concentration in solution during the first six hours of hydration which retards the formation of a calcium-rich surface layer on the clinker materials. Until diffusion or thickness of the calcium-rich layer on the fly ash slows the formation of the additional AFt phase, this calcium-rich surface does not form, resulting in a longer induction period. Taylor et al[30] and Halse et al[22] explained that the subsequent acceleration probably occurs because the fly ash particles provide additional sites on which the C-S-H and calcium hydroxide can nucleate. This is further corroborated by Diamond et al[31] who pointed out that in the fly ash cement paste the fly ash particles are often covered by a layer of fibrous hydrates termed 'duplex film'. He explained this as the deposition of cement hydration products such as calcium hydroxide and C-S-H phase. This phenomenon was further elucidated by Montgomery et al[21] as fly ash acting as the nucleation centres for cement hydration. However, Fraay et al[32] state that the pozzolanic reaction of the fly ash can only start after more than one week (at 20°C). This is because it is only after this time that the alkalinity of the pore water is high enough to dissolve the fly ash and that during this time the fly ash behaves as an inert material serving as a precipitation nucleus for calcium hydroxide and C-S-H gel originating from the cement hydration. However, they then state that the rate of the fly ash reaction is extremely sensitive to the pH of the pore water and is strongly temperature dependent. Therefore, it is possible that the fly ash could start to react before one week and, consequently, fall more in line with the findings of Halse et al[22] and Taylor et al[30].

With regards to the immobilisation of waste, the chemical reactions which occur are important. Fly ash contains silica and alumna in its glassy phases which are able to react with the calcium hydroxide that results from the normal Portland cement reactions. If enough fly ash is incorporated (>30%) then virtually all of the accessible calcium hydroxide could be consumed. As this occurs, the lime/silica ratio of the C-S-H may drop as low as 0.8 (typical Portland cement ≈1.7). Also, the pH of the aqueous pore solution starts to drop below the value associated with a saturated calcium hydroxide solution (≈12.5). This is not necessarily a good thing as a high pH helps to decrease radionuclide solubility. However, to ensure small quantities of calcium hydroxide remain after prolonged periods of reaction the amount of fly ash used could be minimised. However, the pozzolanic reactions form calcium silicate, calcium sulphoaluminate and calcium aluminate hydrates in addition to those formed from the Portland cement. Therefore, after substantial pozzolanic reaction, the sorption capacity is increased, the capillary porosity is decreased and the diffusion resistance is increased. Also, there is evidence to suggest that the C-S-H formed can be effective in reducing the capillary pore continuity and mass transport rates.[30] Another attribute of fly ash is that there can be an improvement in the workability of the cement. This means a lower w:c ratio can be used, which in turn increases resistance to permeation and diffusion.

2.4 THE USE OF CEMENT FOR IMMOBILISATION OF WASTES

In the UK, government policy is that radioactive wastes should be disposed of under strict supervision to high standards of safety and the periods of storage should be the minimum compatible with safe disposal. For heat generating wastes , i.e. high level wastes (HLW), this means storing them for at least 50 years to allow them to cool. For intermediate level waste (ILW) and low level waste (LLW), it is desirable to dispose of them as soon as possible and to avoid the creation of additional wastes and the need for expensive storage sites. The UK Nuclear Industry Radioactive Waste Executive (NIREX), therefore, discusses the need for underground repositories for these intermediate and low level wastes. However, until this is addressed new intermediate level waste will be immobilised by encapsulation and, in the UK, this will be in cement.[2] The choice of immobilisation matrix depends on the process and product fulfilling certain criteria. As far as the process is concerned this should be simple and cost effective and should not lead to the production of secondary waste streams. The product of the immobilisation process should be a monolith with acceptable mechanical, chemical and physical properties that are maintained over an appropriate time such that the release of the radioactive material from the wasteform is minimised. Cement was the first choice as the matrix for cementing intermediate level wastes because, from the processing point of view, it remains fluid for sufficient time to allow placement, processing is safe, it is a low temperature operation tolerant to water and the set cement has adjustable properties. Cement can also tolerate a wide range of wastes by adaptation of the cement composition to different physical, chemical and radiochemical properties of the waste which is essential as the intermediate level waste varies considerably, for example, metal ion exchangers and metal hydroxide flocs, each with different chemical properties.[2,33]

Encapsulation can take the form of immobilisation, fixation and solidification/stabilisation processes. Although these terms are sometimes used interchangeably they are different, but they do all relate to the encapsulation of waste and have similarities. Fixation is usually described as a product's resistance to leaching in the environment[34] whilst solidification is 'the act of tying up free water in a waste to improve its handling characteristics or to make it acceptable for landfill disposal'[35] and stabilisation refers to 'the treatment of a waste which results in the decrease of the mobility of contaminants in a landfill environment'.[35] Immobilisation is fundamentally the same as fixation. This project was concerned with the incorporation of metal salts into the cements and, therefore, the term immobilisation will generally be used although the above definitions should be considered at all times.

Solidification/stabilisation is an economical way of disposing of many types of hazardous waste. The process usually involves addition of a heavy metal waste to a cement binder with the heavy metals expected to precipitate as their respective insoluble hydroxides due to the high pH of the system. These hydroxides are then immobilised in the dense matrix of the cement where ionic transport is decreased as the porosity and permeability are reduced.[36]

A number of factors affect the degree of immobilisation of the constituents in the waste and usually there are several working at the same time which makes these systems complicated. However, a list of the main factors follows[34] with an explanation of some of the terms:

pH control It is widely accepted that cement based waste forms rely heavily on pH control for metal containment and, for most systems, is a necessary condition. Normally a high pH is desirable as metal hydroxides have minimum solubility in the range 7.5-11 but not all metals reach their minimum solubility at the same pH. Therefore, the optimum pH of a system has to be a compromise achieved by considering the solubility curves of the metal hydroxides with which a specific waste is associated.[34]

Redox Potential The redox potential, E_h, is the oxidation-reduction potential referred to the hydrogen scale, expressed in millivolts. It is usually measured against another reference electrode and then converted to E_h. The presence of strong oxidants or reductants can change the valence state of a number of metals, affecting their chemical speciation and, therefore, their mobilities. Hence, it is important to bear this possibility in mind and to consult E_h-pH diagrams to assess the possible effects of redox processes.[34]

Chemical reaction

Carbonate precipitation
Sulphide precipitation
Silicate precipitation
Ion specific precipitation
Complexation

Adsorption Adsorption occurs when a molecule or ion becomes attached to a surface, usually as a monolayer. Griffin et al[37] found that adsorption of the cationic metals (lead, cadmium, zinc, copper and chromium(III)) increased with increasing pH, while the opposite was true of the anionic metals (chromium(IV), arsenic and selenium).[34]

Chemisorption Close-range chemical or physical forces cause the retention of one species by another. The binding forces are greater than those of pure adsorption but not a true chemical bond.[34]

Passivation Metal ions dissolving from a solid surface may precipitate on the surface after being in contact with an anion in solution which forms a less soluble species. If the precipitate forms a tight impermeable layer, it may block or inhibit further reaction at the surface. These are specific to the constituents and the system as a whole and may not be permanent. One system is the formation of silica gel on the surface of metal salts exposed to a soluble silicate solution. The gel layer prevents further passage of metal ions into solution, thus slowing dissolution. However, it also acts as a semi-permeable membrane, allowing the passage of water which builds osmotic pressure on the solid side. Eventually, the membrane ruptures spilling concentrated metal solution into the liquid phase.[34]

Ion Exchange

Isomorphous Replacement When one element substitutes for another of similar size and charge in a crystalline lattice. This is also known as diodochy. An example of this would be zinc or manganese substituting for calcium in calcite.

Reprecipitation

Encapsulation Previously, encapsulation was used to describe many of the processes and encapsulation rarely occurs without other fixation mechanisms.

Microencapsulation Most waste particulate matter is held in a microencapsulated form and the sizes of the microencapsulated particles may range from very small occlusions to larger agglomerates visible, possibly, to the naked eye.

Macroencapsulation This term has been used to describe processes where a solid or cemented waste form is coated with, or contained in, an impervious layer to limit access of leachant to the waste itself. It is also used to describe the encapsulation of large agglomerates in a solidification matrix - a large version of microencapsulation. The degree of protection depends completely on the matrix, coating or container.

Embeddment Where it is necessary to incorporate discrete waste masses of large size into a solid matrix before disposal. For example, contaminated personal protective equipment from laboratories etc. and medical laboratory solid wastes (syringes etc.). An example of a matrix used for this purpose is concrete which is reinforced if necessary.

Alteration of waste properties In a lot of cases the highest degree of containment can be obtained by pre-treating the waste before fixation. For example, removal of immiscible organic phases to achieve acceptable leaching and neutralisation of acids.

All of these factors have to be taken into account when considering the immobilisation of a waste in a cement matrix. However, this was not the main point of the study but some of these will be mentioned again as all were considered during the work. The aims of the project were to study the effects of the metal salts on the rate of hydration and the products formed. Therefore, it would be pertinent to look at the effect that adding metal salts has on cement systems.

2.5 THE EFFECT OF METAL SALT ADDITIONS

The work carried out in this area appears to be extensive until one looks deeper and it then becomes apparent that the reported work has been on similar subjects which makes it difficult to find specific published work for the salts used in this project. However, an outline of the published work gives some insight into this project. The most widely studied species appears to be calcium chloride. This is a well known accelerator of C_3S/C_2S hydration. That is, it promotes the dissolution of the calcium cations and anions from cement, thus promoting the formation of C-S-H and calcium hydroxide.[38] Akhter et al[39] state that the accelerating effects have been rationalised in terms of the semi-permeable membrane model for cement hydration in the following way: chloride is incorporated into the colloidal hydration products resulting in a membrane coating that is more easily ruptured. Also, the high mobility of chloride allows more ready diffusion through the membrane, increasing internal osmotic pressure. Taylor[1] states that the accelerating effects are greater at lower temperatures. They increase with the amount of calcium chloride used and, at 4%, very rapid setting may occur; 2% may be a reasonable limit.

Mattus and Mattus[38] give a brief outline of accelerators and retarders of C_3S and C_3A as these phases play the most important role in the setting of neat cement. Listed as accelerators of C_3S hydration are: calcium chloride, aqueous solutions of various chlorides such as calcium, sodium and aluminium as well as aqueous solutions of alkali carbonates, aluminates and silicates. Also, sodium fluoride, sodium aluminate and potassium carbonate are known to be accelerators. With regards to C_3A hydration, they state that not much work has been done. However, an interesting point is that Skalny & Young[10] reported that fluoride, which is a retarder for C_3S hydration, is recognised as an accelerator for C_3A.

Retarding waste species will increase the length of the dormant period of C_3S hydration and delay calcium hydroxide precipitation. The mechanism by which this effect is thought to occur is related to the formation of a coating of insoluble amorphous gels around the C_3S grains preventing access to the solution. With C_3S hydration this is observed with fluorides and phosphates as well as some inorganic compounds. The retardation effect can also occur from interferences with the development of C_3A hydration. The presence of sodium and potassium ions in the pore solution produces a basic environment and acts as a retarder for C_3A because of the formation of an amorphous precipitate of calcium hydroxide.[38]

The effect of chloride on the set of cement is variable depending upon the nature of the cation it is associated with and the concentration of the salt. Lea[40] explains that calcium chloride has a dual effect upon set; at concentrations less than 1%, based on weight of cement, the action of calcium chloride is to retard the set of Portland cement while the addition of larger amounts produces an acceleration. Also, in a paper by Kondo et al[41], where the effects of various chloride salts on the hydration of alite were studied, the accelerating effects of the chloride ion on the overall hydration were clearly observed. However, they also pointed out that not all chlorides reduce the induction period and that the salts forming the least soluble hydroxides have the greatest retarding effect, while those forming intermediate solubility exhibit a smaller amount of retardation. The alkali metal salts which form soluble hydroxides act as accelerators. It is clear from the reviews so far that the question of a salt having the effect of either retarding or accelerating the set of the cement is not that straight forward. Trying to determine the effect of a specific cation or anion on the cement is not possible as, in either case, the effect depends on the combination of cation and anion. The reported work appears to have concentrated mainly on cadmium, chromium, lead, mercury etc. with some reports of zinc studies, although these have mainly been with nitrates not chlorides. The reason for the choice of metals to study appears to have come from a list drawn up by the Environmental Protection Agency (EPA) in America of the most toxic elements. Also, there are no reported studies of tin-containing cements. Therefore, without specific examples of the chloride which were used in this study, it may be difficult to give a full explanation using the literature but an attempt will be made to generalise the effects of the different metals used. There has also been little work done with composite cements and most of the literature relates to Portland cement. However, where a composite cement has been used, it will be mentioned specifically.

McWhinney & Cocke[42] carried out a surface study of Portland cement using x-ray photoelectron spectroscopy (XPS) with scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) to do topographical and bulk examinations respectively. $Zn(NO_3)_2$, $Cd(NO_3)_2$ and $Hg(NO_3)_2$ were added to the cements as aqueous solutions. The XPS results showed an increase in carbonation over the undoped cements. This may have been due to the presence of cations directly forming or indirectly inducing the formation of greater quantities of surface carbonate species. Carbonation at the 29% doping level was around half that at 10% for the zinc and cadmium. This increase in the formation of a carbonate phase was also observed by other researchers.[43,44] The SEM and EDS results showed similar morphologies for cadmium and zinc-doped cements. Both exhibited massive cracks throughout the matrix regardless of doping levels or curing times. There appeared to be a denser network of cracks with sheer walls in the zinc-doped cement and may have been due to the breakdown of the integrity of the cement matrix. On the other hand, the fissures in the cadmium-doped cements tended to be less sheer with the edges covered in a 'crystalline' type material resembling ettringite. EDS analysis revealed the presence of zinc throughout the matrix but with a low relative intensity whilst cadmium was observed throughout the surface with a relatively high intensity.[42]

The leaching of the metal species from the cement over time is an important factor as this determines whether the metal has been immobilised or not. Collecting leach test data was not part of this research project, but was carried out by British Nuclear Fuels. However, it is worth mentioning because a lot of the work reported in the literature is concerned with this aspect. Poon et al[44-47] incorporated a number of metal nitrates into OPC and OPC/PFA cements and found that the retention of the metals in increasing order were: Cd>Zn>Hg although the zinc leached only slightly more than the cadmium. Hamilton et al[48] also found that there was an increased retention of zinc when compared to lead in leach tests. In this case, the zinc was present as an oxide so it appears that the anion is not important when considering the retention of zinc as they all indicate a low leaching level.

Another area where the literature appears to agree, regardless of the anion associated with the zinc, is in the formation of a calcium zincate phase within the cement.[36,41,43,44,46,49-51] All of these papers mention, in some way, the formation of $CaZn_2(OH)_6.2H_2O$ when zinc has been added and this formation can be associated with the retardation effect also observed with these cement systems. A proposal for how this may occur is that the zinc retards the hydration and setting of cement by precipitating, at the surface, an amorphous layer of zinc hydroxide on the anhydrous clinker grains. This zinc hydroxide then reacts with the calcium hydroxide to form the calcium zincate.[44,49] The formation of calcium metal hydroxides is not confined to zinc, but also other cations which can form insoluble hydroxy compounds such as: lead, copper, cadmium, tin etc.[49]

In summary, it is not possible to cover all aspects of one particular cement system containing a specific metal salt but it can be seen that, especially for zinc, there has been enough work reported that a picture can be built up of processes which may be occurring. These findings can also, tentatively, be used to predict the behaviour of other systems.

CHAPTER THREE

3. EXPERIMENTAL

3.1 EXPERIMENTAL PLAN

Four cement systems were used in this project. These were:

100% OPC
3:1 BFS:OPC
9:1 BFS:OPC
3:1 PFA:OPC

The 100% OPC was used as a reference material whilst the main interest was in the other three systems. The OPC and BFS were supplied by Castle Cement plc and the PFA was provided by Pozzolanic Lytag plc. All the powders were prepared to specifications requested by British Nuclear Fuels Ltd (Sellafield). The chemical analyses for the OPC and BFS are shown in Table 3.1.1. There was no chemical analysis supplied for the PFA, therefore, it is only possible to quote the calcium oxide content which was 1.9%.

	OPC	**BFS**
CaO	64.1	41.4
SiO_2	21.0	32.9
Al_2O_3	5.1	13.5
Fe_2O_3	3.1	0.8
MgO	2.5	8.3
SO_3	2.2	-
K_2O	0.7	0.4
Na_2O	0.3	0.2
Chloride	0.03	0.03
Insolubles	0.3	-
Loss on ignition	0.6	0.5
Free Lime	0.8	-

Table 3.1.1 Chemical Analyses for OPC and BFS

Five metal salts were initially chosen to be added at different weight percentages to the cement systems. These were:

$ZnCl_2$
$SnCl_2.2H_2O$
$SnCl_4.5H_2O$
$AlCl_3.6H_2O$
As_2O_3

During the project it was decided that some work would also be carried out using $Zn(NO_3)_2.6H_2O$. This was as a direct comparison with $ZnCl_2$ to assess if the metal or the anion was responsible for any changes in the hydration of the cement.

Ten ageing times were chosen to cover the hydration of the cement for one year. A water:cement powder (w:cp) ratio of 0.35 was used throughout. However, this does not equate to a constant water:cement (w:c) ratio of 0.35 for the composite cement systems because of the different amount of OPC present in each. Table 3.1.2 shows the w:c ratios for all four cement systems.

Cement System	w:c ratio
100% OPC	0.35
3:1 BFS:OPC	1.4
9:1 BFS:OPC	3.5
3:1 PFA:OPC	1.4

Table 3.1.2 w:c Ratios For All Cement Systems

A summary of the experimental conditions is shown in Table 3.1.3

Condition	
Storage Temperature/°C	23±2
Relative Humidity/%	86±2
Number of days hydration	1, 3, 7, 14, 21, 28, 56, 90, 180, 360
Weight % of metal salt added	0.1, 1.0, 5.0

Table 3.1.3 Summary of Conditions

The number of samples involved was high - four cements, five additions (even without zinc nitrate) at two different weight percentages and ten ages. This gave a total of 400 samples (without including some later work, e.g. to produce some systems with 5% additions). Therefore, a numbering system was employed which allowed the cement type, age, metal salt addition and its weight percent to be identified. An example is shown in Figure 3.1.1.

↓type of addition

cement type→ $\mathbf{1\underline{180}B2}$ ←amount of addition

↑age (days)

1180B2 = 100% OPC at 180 days hydration with 1.0% $SnCl_2$ added.

Figure 3.1.1 An Example of the Sample Numbering System

Cement Type	Types of Addition	Amount of Addition
1 = OPC	A = $ZnCl_2$	1 = 5.0%
2 = 3:1 BFS:OPC	B = $SnCl_2$	2 = 1.0%
3 = 9:1 BFS:OPC	C = $SnCl_4$	3 = 0.1%
4 = 3:1 PFA:OPC	D = $AlCl_3$	
	E = As_2O_3	

The age of the sample is written as a number of days. Therefore, the above example would have been hydrated for 180 days. This means the second section (the one underlined) could be a one, two or three digit number.

Samples without any metal salt addition will be referred to as neat cements. This is not only applicable to the 100% system but also to all the composite systems when there is no metal salt present.

3.2 SAMPLE PREPARATION

3.2.1 Preliminary Mixes

All systems were prepared in the same way using a w:cp ratio of 0.35.

100±0.1g of powders were weighed out and, where necessary, were mixed thoroughly. 35±0.1g of distilled water was weighed, the correct amount of metal salt mixed with the water to form a slurry and the temperature of this slurry recorded (T_1). The cement powders were then gradually added to the slurry and, when all the powder had been added, the slurry was mixed manually for approximately two minutes. The temperature of the cement (T_2) was then recorded between 3-5 minutes after the cement powders were added to the slurry (i.e. on completion of mixing but less than 5 minutes) and any observations noted. All this was done in small plastic pots which had airtight lids. Once mixed, the lid was placed on the pot and the cement left to hydrate. Approximately every half to one hour the extent of the set was assessed by inserting a spatula into the cement.

3.2.2 Casting Prisms

500±0.1g powders were weighed out and, where necessary, thoroughly mixed. 175±0.1g of distilled water was weighed and the correct amount of metal salt weighed and placed in a glass beaker. The metal salt was added as a weight percent of the powders and was calculated such that it was the weight percent of metal (rather than the compound) which was used. To do this a correction factor was used:

$$\frac{RMM(compound)}{RAM(metal)} \text{ x percentage required}$$

This then gave the amount of compound required for 100g of cement powders. For example, $ZnCl_2$ added at 0.1%:

Metal RAM = 65.3 Compound RMM = 136.59

$$\therefore \quad \frac{136.59}{65.3} \text{ x } 0.1 = 0.201$$

∴ For this example: 0.201g $ZnCl_2$ / 100g powder

The amounts of metal salts used are shown in Table 3.2.1

	0.1%	1.0%	5.0%
$ZnCl_2$	1.04	10.4	52.0
$Zn(NO_3)_2.6H2O$	2.28	22.2	110.0
$SnCl_2.2H_2O$	0.95	9.5	47.5
$SnCl_4.5H_2O$	1.48	14.8	74.0
$AlCl_3.6H_2O$	4.47	44.7	223.5
As_2O_3	0.66	6.6	33.0

Table 3.2.1 Amount of metal salt addition g/500g cement powder

Table 3.2.2 shows the moles of metal used for 500g of cement powder and 175g of water. It can be seen that the $AlCl_3.6H_2O$ has significantly more moles of metal than either the zinc salts or the tin salts which are similar to each other although the zinc has more than the tin. Therefore, a classification can be drawn up which should be considered when comparing the different salt additions in the results section:

$$Al >> ZnCl_2 > Zn(NO_3)_2 > Sn(IV) = Sn(II) > As$$

	0.1%	**1.0%**	**5.0%**
$ZnCl_2$	0.008	0.076	0.382
$Zn(NO_3)_2.6H_2O$	0.008	0.075	0.370
$SnCl_2.2H_2O$	0.004	0.042	0.211
$SnCl_4.5H_2O$	0.004	0.042	0.211
$AlCl_3.6H_2O$	0.020	0.19	0.926
As_2O_3	0.003	0.033	0.167

Table 3.2.2 Moles of metal added /500g cement powder

The slurry was mixed in the glass beaker (as for the preliminary mixes) and the cement powders gradually added. Once all the powder had been added, the cement was mixed manually for approximately three minutes. The paste was then poured into PTFE moulds. It was possible to cast 16 prisms of 100mm x 10mm x 10mm from one batch of cement.

3.2.3 Curing

The temperature and relative humidity environment required for the continuing hydration of the cement samples was controlled by a cabinet in the laboratory. The cabinet was made of perspex and measured 690mm deep, 1030mm wide and 670mm high. It was lined on the inside with polystyrene sheets approximately 20mm thick. These served to conserve the heat and humidity. Access to the samples was gained by a sliding front door. The relative humidity was controlled using three 600ml jars filled with saturated K_2SO_4 solution. The aim was to keep the relative humidity around 80 - 90%. The temperature was controlled by means of three lamps connected to a thermostat which was adjusted to maintain a temperature of 21°C. A probe situated inside the cabinet measured the temperature and relative humidity. This was connected to a combined thermometer/hygrometer digital readout which was placed on the outside of the cabinet. The temperature and relative humidity were constantly monitored without opening the door of the cabinet which caused variations in the temperature and humidity. There were also two electric fans inside the cabinet which circulated the air to help maintain constant temperature and humidity throughout the cabinet.

Initially there were problems during the summer months keeping the temperature down to 21°C. This was overcome by installing a Peltier pump which could be switched on and off when the temperature was rising. The negative side to this was that this also decreased the humidity. Therefore, during the summer it was necessary to find a compromise between the temperature and the humidity. To do this the temperature was lowered sufficiently using the Peltier pump without allowing the humidity to drop too low ($\geq$ 70%). The pump was then switched off and both the temperature and humidity allowed to rise although the temperature was never allowed to exceed 25°C. However, the overall temperature variation was 23±2°C and the relative humidity, for most of the work period, was 86±2%.

The moulds were placed in the environmental cabinet for 24 or 48 hours and then the samples were demoulded. The samples were then returned to the cabinet and left for the required length of time. When removed from the cabinet the samples were quenched and stored in acetone to stop the hydration from proceeding further.

3.3 EXPERIMENTAL PROCEDURE

3.3.1 Isothermal Conduction Calorimetry

The equipment used was a JAF calorimeter supplied by Wexham Developments. External mixing was employed for all samples and the two temperatures used were 35±0.1°C (because this is the cave temperature when considering underground repositories) and 21±0.1°C, because this is more closely related to the temperatures used for curing the samples left in the environmental cabinet. Samples were usually left to run for 72 hours and the results were analysed using the Exel package to produce the traces shown in Chapter 4.

15±0.1g of cement powders were weighed and placed in a small plastic sample bag. 5.25±0.1g of distilled water and the correct amount of metal salt required were measured. 20ml of oil was placed in the calorimeter can which was left in the water bath for approximately 1 hour prior to the run to bring it to the correct temperature. Where necessary the metal salt was mixed with the water to form a slurry. The water (or slurry) was then poured into the bag of cement powders and mixed for 1 - 2 minutes. The bag was then sealed and placed in the can containing the oil which, in turn, was placed in the calorimeter cell. The cell was then placed in the water bath and the computer programme started. The amounts of metal salt used are shown in Table 3.3.1

	0.1%	**1.0%**
$ZnCl_2$	0.03	0.31
$Zn(NO_3)2$	0.07	0.68
$SnCl_2$	0.03	0.29
$SnCl_4$	0.04	0.44
$AlCl_3$	0.13	1.34
As_2O_3	0.02	0.20

Table 3.3.1 Amount of Metal Salt Used For Calorimetry g/15g cement powder.

3.3.2 X-Ray Diffraction

The system used was a Philips 1700 x-ray diffractometer using CuKα radiation tube. This is interfaced to a computer which runs the equipment using the Siehilt programme. The resulting traces were then analysed using the traces programme and identification of phases was achieved using the JCPDS card system. The parameters for the runs were as follows:

Sample	**Start Angle /°2θ**	**End Angle /°2θ**	**Speed /°2θmin^{-1}**	**Step Size/°2θ**
Anhydrous	10.0	65.0	2.0	0.02
Hydrated	5.0	65.0	1.0	0.02
Hydrated with >0.1% addition	5.0	80.0	1.0	0.02

Table 3.3.2 XRD Parameters

A cement prism was crushed in a percussion mortar and then placed in an agate mortar. An excess of acetone was added (to stop the cement hydration and to aid grinding) and the cement ground by hand to a size of <63μm. The powder was packed into back filled sample holders (to minimise preferred orientation) for use in the x-ray diffractometer.

3.3.3 Scanning Electron Microscopy

A JEOL JSM 6400 scanning electron microscope equipped with Link x-ray analytical facilities was used. Backscattered electron imaging was used throughout.

A cement prism was cut into cubes of approximately 10mm square, one side of which was ground flat. The samples were then placed in a vacuum desiccator for a minimum of three days. After this time, the sample was cold resin mounted and then ground and polished. The samples were polished manually using diamond paste from 6μm through to 1/2 μm. The finished sample was then carbon coated under vacuum to render them conducing for use in the microscope.

3.3.4 Differential Thermal Analysis

A Stanton Redcroft 760 DTA 673 - 4 linked to a chart recorder was used to obtain the DTA curves. 100mg of powdered sample (as prepared for XRD) and 100mg of fired alumina (reference) were weighed into platinum crucibles. The samples were heated from room temperature to 600°C at 10°/min with a nitrogen gas flow of 350ml /min.

CHAPTER FOUR

4. RESULTS

4.1 PRELIMINARY MIXES

Preliminary mixes were undertaken to gain some understanding about the ease of mixing and setting of the cement systems with the different metal salts. As mentioned in Chapter 3, 100g of cement powder was mixed with 35g of water and the cement allowed to set in airtight plastic pots. The pH of the slurry and the temperature of both the slurry (T_1) and the cement paste (T_2) were recorded along with initial and final set times. The final set was taken to be when the spatula no longer left an impression on the surface of the cement. If a cement had not set within seven days it was deemed to have no set.

4.1.1 pH Measurements

The control of the pH of the cement environment is widely known to be important for metal containment. It has also been shown to affect the leachability of some other organic and inorganic species. Normally, high pH is desirable because many metal hydroxides have minimum solubility in the range of pH from 7.5 to 11. However, some metals, for example chromium, which exhibit amphoteric behaviour have high solubility at both low and high pH. Also, not all metals reach minimum solubility at the same pH so the optimum pH of a system would have to be a compromise.[53]

Although there was no control of pH within the scope of this project, it was deemed necessary to have a record of the pH of the slurry as it was thought this may aid explanation of some of the phenomena observed. Table 4.1.1 shows the pH of the slurries measured using indicator paper.

METAL SALT	pH @ 5% ADDITON	pH @ 1% ADDITON
$ZnCl_2$	4	7
$Zn(NO_3).6H_2O$	3	4
$SnCl_2.2H_2O$	2	2
$SnCl_4.5H_2O$	1	1
$AlCl_3.6H_2O$	1	4
As_2O_3	7	7

Table 4.1.1 pH of Slurries

4.1.2 Neat Cement Systems

Table 4.1.2 shows temperature and setting data for all four cement systems without any metal salt addition. All systems were identical with regards water and mix temperatures and also had similar initial and final set times, with the exception of 3:1 BFS:OPC which had a longer initial set time. Therefore, any differences noted with the addition of metal salts can be assumed to be due to the salts. Where there are a range of times given for a set it means that the measurement was taken at the times stated but the cement had set between the measurement times.

Cement System	Water T/°C	Mix T/°C	ΔT	Initial Set Time/hrs	Final Set Time/hrs
100% OPC	22.0	24.0	+2	1	14 -20
3:1 BFS:OPC	22.0	24.0	+2	>6	14-20
9:1 BFS:OPC	22.0	22.0	0	1	14-20
3:1 PFA:OPC	22.0	24.0	+2	1	14-20

Table 4.1.2 Neat Cements

4.1.3 100% OPC System

Metal Salt	% Addition	T_1/°C	T_2/°C	ΔT	Initial Set Time/hrs	Final Set Time/hrs
$ZnCl_2$	5.0	41.0	60.0	+19	*	*
$ZnCl_2$	1.0	25.5	28.0	+2.5	_	2
$ZnCl_2$	0.1	22.0	22.0	+0	4.5	18-24
$SnCl_2$	5.0	17.0	53.0	+36	0.75	6.0
$SnCl_2$	1.0	17.0	23.0	+6	_	18-24
$SnCl_2$	0.1	22.0	24.0	+2	4.5	18-24
$SnCl_4$	5.0	26.0	90.0	+64	*	*
$SnCl_4$	1.0	19.0	32.0	+13	1	5
$SnCl_4$	0.1	22.0	25.0	+3	4.5	18-24
$AlCl_3$	5.0	42.0	>100.0	+>58	*	*
$AlCl_3$	1.0	29.0	55.0	+26	_	<0.5
$AlCl_3$	0.1	21.0	25.0	+4	2	8-22
As_2O_3	5.0	21.0	25.0	+4	_	0.25
As_2O_3	1.0	21.0	25.0	+4	0.5	5-21
As_2O_3	0.1	16.0	18.0	+2	0.75	8-20

* = no set within 7 days

_ = initial set not recorded

Table 4.1.3 100% OPC + All Metal Salts

At 0.1% loading, all systems appeared to take approximately 24 hours to reach final set which is similar to the neat cements (Table 4.1.2). However, at higher loadings there was not the same trend. With the exception of $SnCl_2$ and As_2O_3, all metal salts added at 5% loading caused the final set not to occur within 7 days. Both systems which did set appeared to achieve this fairly rapidly (6 hours for $SnCl_2$ and 0.25 hours for As_2O_3). At 1% loading the setting times varied the most, i.e. between 2 and 24 hours. The temperatures of the slurries and the mixes were also interesting. The water for the slurry was always at room temperature but the temperatures of the slurries varied substantially. Some additions of metal salts increased the temperature and others decreased it. Also, on adding the cement powders it can be seen that, in some cases, the temperature was particularly high (5% $SnCl_2$ and 5% $AlCl_3$ in particular). Set did not occur with these systems as the temperature rise resulted in insufficient water remaining to form a paste.

4.1.4 3:1 BFS:OPC Cement Systems

Metal Salt	**% Addition**	**T_1/°C**	**T_2/°C**	**ΔT**	**Initial Set Time/hrs**	**Final Set Time/hrs**
$ZnCl_2$	5.0	41.0	50.0	+9	40	*
$ZnCl_2$	1.0	27.0	28.5	+1.5	1	24-48
$ZnCl_2$	0.1	23.0	24.0	+1	1	48
$SnCl_2$	5.0	17.0	40.0	+23	40	*
$SnCl_2$	1.0	20.5	26.0	+5.5	_	48
$SnCl_2$	0.1	22.0	24.0	+2	>6	18-24
$SnCl_4$	5.0	26.0	50.0	+24	*	*
$SnCl_4$	1.0	23.0	35.0	+12	4	24-48
$SnCl_4$	0.1	22.5	25.0	+2.5	>6	18-24
$AlCl_3$	5.0	39.0	95.0	+56	*	*
$AlCl_3$	1.0	29.0	45.0	+16	*	*
$AlCl_3$	0.1	21.0	23.5	+2.5	0.75	8-22
As_2O_3	5.0	21.0	24.0	+3	_	0.25
As_2O_3	1.0	21.0	24.0	+3	0.33	5-21
As_2O_3	0.1	16.0	18.0	+2	2	8-20

* = no set within 7 days

_ = initial set not recorded

Table 4.1.4 3:1 BFS:OPC + All Metal Salts

4.1.5 9:1 BFS:OPC Cement Systems

Metal Salt	**% Addition**	**T_1/°C**	**T_2/°C**	**ΔT**	**Initial Set Time/hrs**	**Final Set Time/hrs**
$ZnCl_2$	5.0	40.0	41.0	+1	5	*
$ZnCl_2$	1.0	23.0	24.0	+1	0.5	*
$ZnCl_2$	0.1	22.0	23.0	+1	1.5	18-24
$SnCl_2$	5.0	15.0	37.5	+22.5	5	*
$SnCl_2$	1.0	17.0	22.0	+5	*	*
$SnCl_2$	0.1	22.0	23.0	+1	1.5	18-24
$SnCl_4$	5.0	22.0	76.0	+54	*	*
$SnCl_4$	1.0	22.0	23.0	+1	<6	18-24
$SnCl_4$	0.1	22.0	25.0	+3	4	18-24
$AlCl_3$	5.0	42.0	92.0	+50	*	*
$AlCl_3$	1.0	29.0	40.0	+11	*	*
$AlCl_3$	0.1	21.0	23.0	+2	<0.25	48
As_2O_3	5.0	21.0	23.0	+2	_	0.25
As_2O_3	1.0	21.0	23.0	+2	0.33	3
As_2O_3	0.1	16.0	17.0	+1	0.5	8-20

* = no set within 7 days

_ = initial set not recorded

Table 4.1.5 9:1 BFS:OPC + All Metal Salts

In the 3:1 BFS:OPC (Table 4.1.4) system at 0.1% all cements had set within 24 hours with the exception of $ZnCl_2$, although this had set within 48 hours. This is also the case for the 9:1 BFS:OPC (Table 4.1.5) although here it was the $AlCl_3$ which retarded the set the most. Also, at 5% loading both 3:1 and 9:1 BFS:OPC systems showed similar trends. No set was recorded for any of the systems apart from As_2O_3 which set very quickly (i.e. 0.25 hours). However, at 1% there was a substantial difference between the two systems. In the 3:1 BFS:OPC cement all systems had set within 48 hours, with the exception of the $AlCl_3$ system which showed no set. However, most additions in the 9:1 BFS:OPC cement caused no set at all although $SnCl_2$ set within 24 hours and As_2O_3 within 3 hours. This increase in the number of systems which exhibited no set within 7 days cannot be explained by a large increase in temperature as, in most cases, the temperature of the mix for the 9:1 BFS:OPC system was lower than that of the 3:1 BFS:OPC system. One explanation could be the amount of OPC present in the cement. Since there is only 10% present in the 9:1 system the lack of OPC may have caused a slower hydration reaction as slag cements hydrate more slowly than OPC due to their need to be activated by the calcium hydroxide produced from the hydration of OPC.

4.1.6 3:1 PFA:OPC Cement Systems

Metal Salt	**% Addition**	**T_1/°C**	**T_2/°C**	**ΔT**	**Initial Set Time/hrs**	**Final Set Time/hrs**
$ZnCl_2$	5.0	38.0	41.0	+3	7	*
$ZnCl_2$	1.0	24.0	27.0	+3	1	*
$ZnCl_2$	0.1	22.5	25.5	+3	1	48
$SnCl_2$	5.0	16.0	39.0	+23	7	*
$SnCl_2$	1.0	18.0	26.0	+8	1.5	24-48
$SnCl_2$	0.1	22.5	25.5	+3	1	48
$SnCl_4$	5.0	23.5	71.0	+44.5	*	*
$SnCl_4$	1.0	20.0	35.0	+15	1.5	24-48
$SnCl_4$	0.1	22.0	27.0	+5	1	18-24
$AlCl_3$	5.0	42.0	78.0	+36	0.25	8-20
$AlCl_3$	1.0	28.0	45.0	+17	0.5	*
$AlCl_3$	0.1	21.0	26.0	+5	<0.25	8-22
As_2O_3	5.0	21.0	25.0	+4	_	0.25
As_2O_3	1.0	21.0	25.0	+4	0.33	3
As_2O_3	0.1	16.0	20.0	+4	0.33	8-20

* = no set within 7 days

_ = initial set not recorded

Table 4.1.6 3:1 PFA:OPC + All Metal Salts

At 5% loading this system showed the same trends as observed in the 3:1 and 9:1 BFS:OPC systems. There was no set except for As_2O_3, which set very quickly. Other than this the system appears to fall somewhere between the two slag containing systems. At 0.1% all systems set within 48 hours although the $ZnCl_2$ and $SnCl_2$ systems were slower than the corresponding systems for either of the slag cements. At 1% there were more systems than in the 3:1 BFS:OPC system which did not set, but fewer than in the 9:1 BFS:OPC system. For those which did set the time was very similar to that in the slag cements.

To summarise, the addition of metal salts had an effect on all the cement systems, with the OPC being the least affected compared to the cements with mineral additions. However, what later became apparent was that when the mixes were scaled up for the casting of samples, some of the cements which had shown no set in these preliminary mixes did actually set within 7 days in the environmental cabinet. Therefore, the results here were used only to give an indication of possible difficulties which may have been encountered during casting.

4.2 ISOTHERMAL CONDUCTION CALORIMETRY

Isothermal conduction calorimetry provides valuable information about the hydration reactions which occur during the early stages of hydration of cements. The most obvious information given is the amount of heat released. However, the shape of the curves and other features in the plots can provide additional information on the relative rates of hydration and the occurrence of other reactions (such as slag hydration and pozzolanic reactions) which may occur in composite cements.

Fig 4.1[53] below is a model hydration plot for an OPC paste.

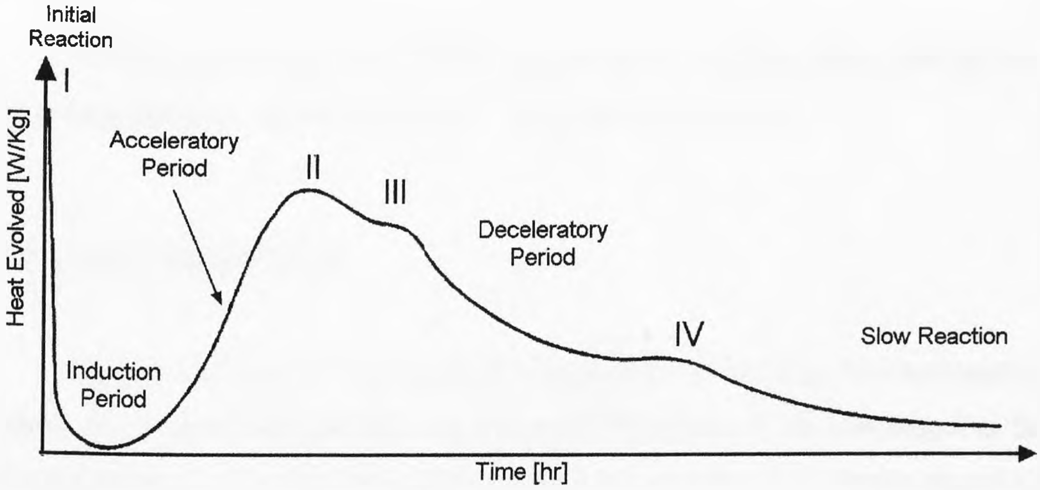

Figure 4.1 Model Hydration Curve for an OPC Paste

There is some disagreement as to the reactions associated with each peak but generally they are as follows. Peak I is due to the initial interaction of the cement powder with water and early stage reactions.[1] After this initial peak there is the dormant period (also known as the induction period) during which little heat is evolved and the stiffness of the paste increases, followed by an acceleration in heat evolution during which setting occurs.[54] The main peak, peak II, occurs after this acceleratory period and is generally believed to be due to the hydration of C_3S and generation of CH. Taylor[1] included two more periods, deceleratory and slow reaction periods. During the deceleratory period, peak III is well defined in some cements or can sometimes appear as a shoulder of peak II. A peak IV can also appear in some cements. There is disagreement as to the nature of peak III, although it has been suggested that it is due to the transformation of AFt to AFm or renewed formation of AFt. Also, in composite cements incorporating significant amounts of blast furnace slag, a peak 'S' occurring after peak II has been attributed to the hydration of the slag fraction because this requires activation by the alkali which, in this case would be the calcium hydroxide liberated during the hydration of the C_3S.[55] Peak IV is sometimes associated with the hydration of the ferrite phase [16,53] although this is by no means established. Setting is assumed to occur on the slope up to peak II (as shown below). The value for the heat output at the peak is known as Q_m and corresponds to the maximum amount of heat generated. The time at which this occurs is known as t_m.

All charts presented in this section show the rate of heat output and the total heat output and were carried out at 35°C unless stated otherwise.

4.2.1 Neat Cement Systems

Figures 4.2.2 and 4.2.3 illustrate the differences between the four neat cement systems and it an be seen that there were marked differences in the heat output of the different cements. It can be seen from Table 4.2.1 that the OPC system generated significantly more heat than any of the composite cements when considering absolute values of Q_m. Q_m was 7.26 Wkg^{-1} compared with 2.41 Wkg^{-1} for 3:1 BFS:OPC, 1.29 Wkg^{-1} for 9:1 BFS:OPC and 1.48 Wkg^{-1} for the PFA system (Table 4.2.1). However, t_m was approximately the same for all the cements with the exception of 3:1 PFA:OPC in that Q_m occurred at around 4 - 5 hours, but after 10.3 hours for the PFA system. The effect of this was that, although there was a reduction in the amount of heat generated by the slag cements compared to the OPC, there was no classic retardation of set as exhibited by the PFA system. Classic retardation of set involves a reduction in heat evolved accompanied by a peak shift to longer times. When the Q_m values were normalised, both slag cements showed significantly higher values than the OPC system whilst the PFA cement was lower. All of these trends were mirrored at 21°C although the values were different. Thus, t_m at 21°C was approximately double the value at 35°C and Q_m was approximately half (see Table 4.2.1). The differences between 35°C and 21°C are discussed in more detail later in this chapter.

Another interesting feature was the appearance of a peak S visible in both slag systems which was not present in either the OPC or the PFA systems. As mentioned previously, this can be attributed to a contribution from the hydration of the slag fraction as in both cases the level of replacement for OPC was significant. Peak S can be seen more clearly on curve A in Figures 4.2.8 (3:1 BFS:OPC) and 4.2.16 (9:1 BFS:OPC).

Cement	**t_m/hrs (35°C)**	**Q_m/ Wkg^{-1}**	**Q_m (normalised)**	**T_m/hrs (21°C)**	**Q_m/ Wkg^{-1}**	**Q_m (normalised)**
OPC	4.80	7.26	-	9.20	3.18	-
3:1 BFS	4.90	2.41	9.64	10.8	1.13	4.52
9:1 BFS	4.00	1.29	11.61	9.00	0.55	4.95
3:1 PFA	10.30	1.48	5.92	17.80	0.76	3.04

Table 4.2.1 Values of t_m & Q_m for the Neat Cement Systems at 21°C and 35°C

After 70 hours hydration a classification of the cement systems (in descending order) with respect to the amount of heat generated can be proposed:

OPC >> 3:1 BFS:OPC > 9:1 BFS:OPC > 3:1 PFA:OPC

This meant that, in terms of the amount of heat generated by each system when metal salts were added, it was necessary to assess each cement system separately. All curves shown for 35°C data were compared to that of the neat cement for each individual system.

4.2.2 100% OPC with Metal Salt Additions

Figures 4.2.4 and 4.2.5 show the rate and total heat output respectively for 100% OPC (neat) and OPC + 0.1% $ZnCl_2$ and 0.1% $Zn(NO_3)_2$. The addition of the $Zn(NO_3)_2$ was undertaken to try to ascertain whether the anion was causing observed effects or if they were predominantly due to the cation. From Figure 4.2.4 it can be clearly seen that both $ZnCl_2$ (B) and $Zn(NO_3)_2$ (C) reduced the rate of heat output and shifted the peak to longer time compared with the neat cement, therefore, displaying classic retardation. The retarding effect shown by the addition of $ZnCl_2$ was greater than that of the $Zn(NO_3)_2$. However, when considering the total heat output (Fig. 4.2.5) it can be seen that the $ZnCl_2$ system eventually reached a similar value to that of the neat OPC, but the $Zn(NO_3)_2$ system fell below both. Therefore, it can be concluded that although the $ZnCl_2$ system took a much longer time to set, overall it generated more heat than the $Zn(NO_3)_2$ system.

Figure 4.2.6 and 4.2.7 show the calorimetric data for neat OPC (A) and OPC + 0.1% $ZnCl_2$ (B) and 1.0% $SnCl_2$ (C). Again, addition of both metal chlorides retarded the set (Fig. 4.2.6), but the $ZnCl_2$ retarded more strongly. Also, the $SnCl_2$ system, although retarded, showed a similar value of Q_m at peak II to that of the neat cement. It also needs to be stated that there was 1.0% $SnCl_2$ added to this system as opposed to only 0.1% $ZnCl_2$. This points to the fact that the zinc caused considerable retardation although the chloride may also have contributed. This was also indicated in the Figures 4.2.4 and 4.2.5 where the nitrate system retarded less than the chloride. Considering the total heat output (Fig. 4.2.7) it can be seen that the $SnCl_2$ eventually liberated more heat than either of the other systems which were similar at 72 hours. All of the total heat results can be seen more clearly in Table 4.2.3. It is immediately apparent that, with the exception of 1% $ZnCl_2$ and 1%

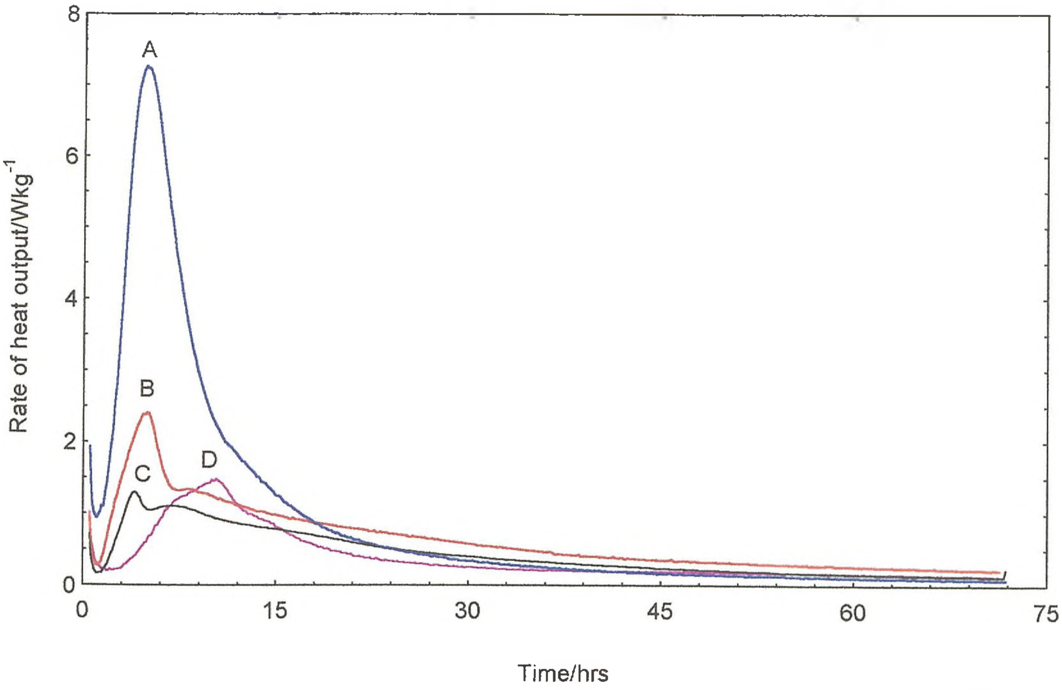

Figure 4.2.2 Rate of heat output for OPC (A), 3:1 BFS:OPC (B), 9:1 BFS:OPC (C) & 3:1 PFA:OPC (D)

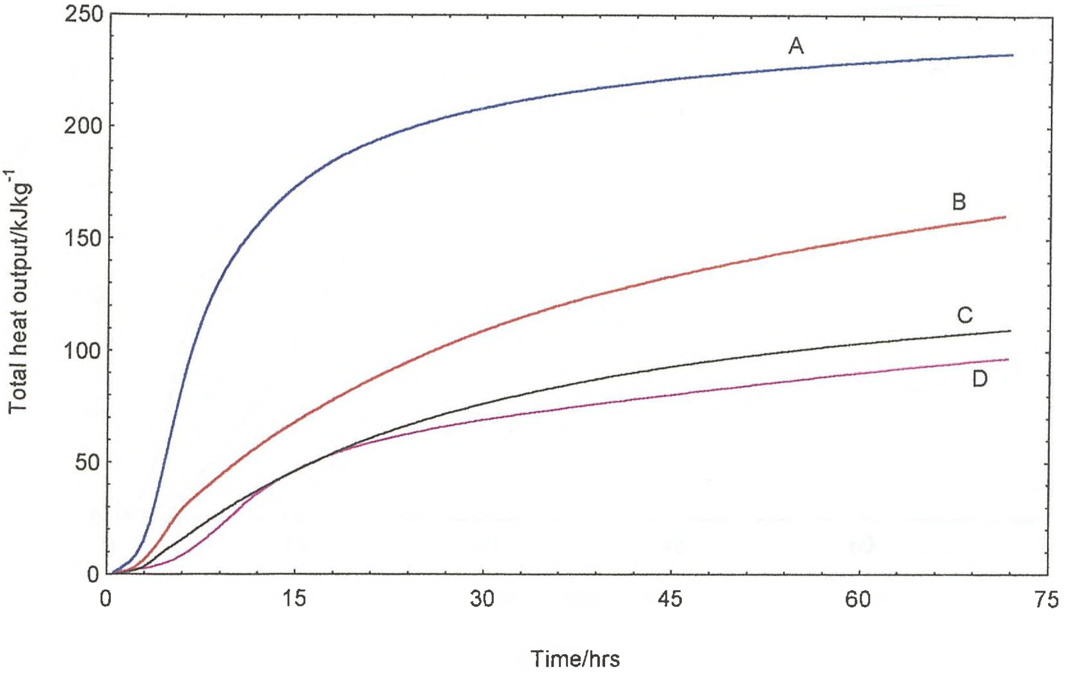

Figure 4.2.3 Total heat output for OPC (A), 3:1 BFS:OPC (B), 9:1 BFS:OPC (C) & 3:1 PFA:OPC (D)

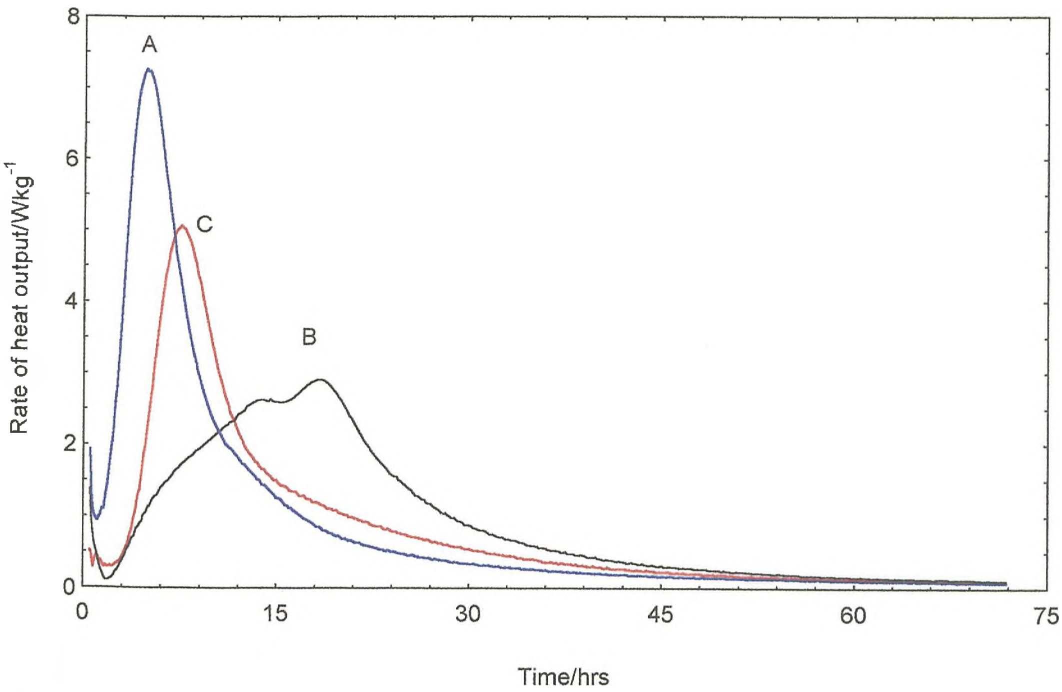

Figure 4.2.4 Rate of heat output for OPC (A), OPC + 0.1% $ZnCl_2$ (B) & OPC + 0.1% $Zn(NO_3)_2$ (C)

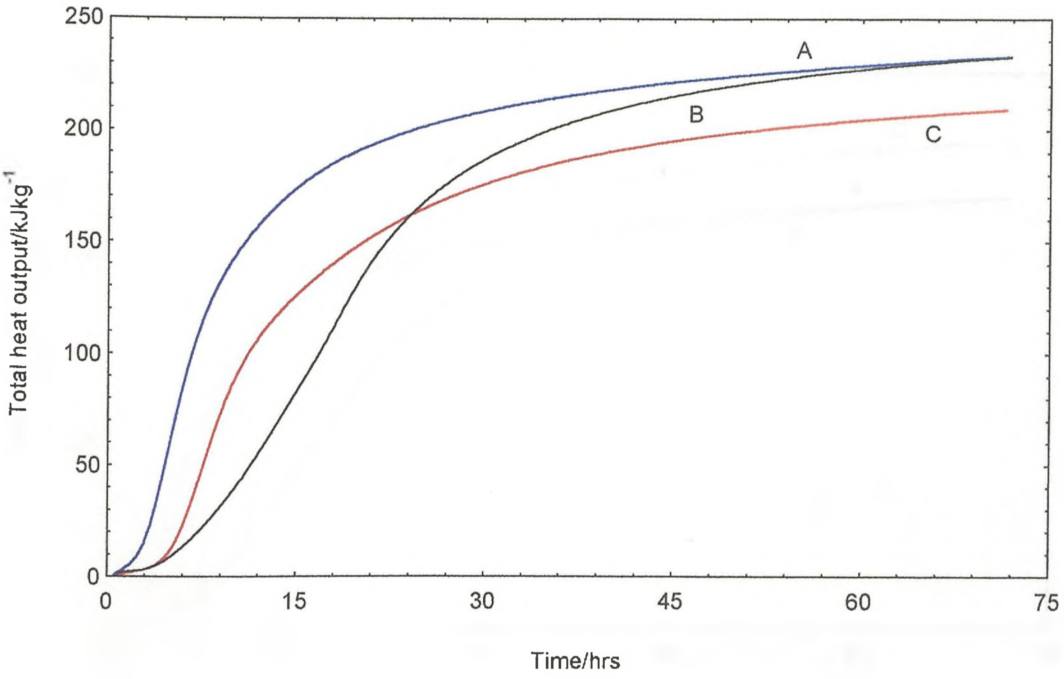

Figure 4.2.5 Total heat output for OPC (A), OPC + 0.1% $ZnCl_2$ (B) & OPC + 0.1% $Zn(NO_3)_2$ (C)

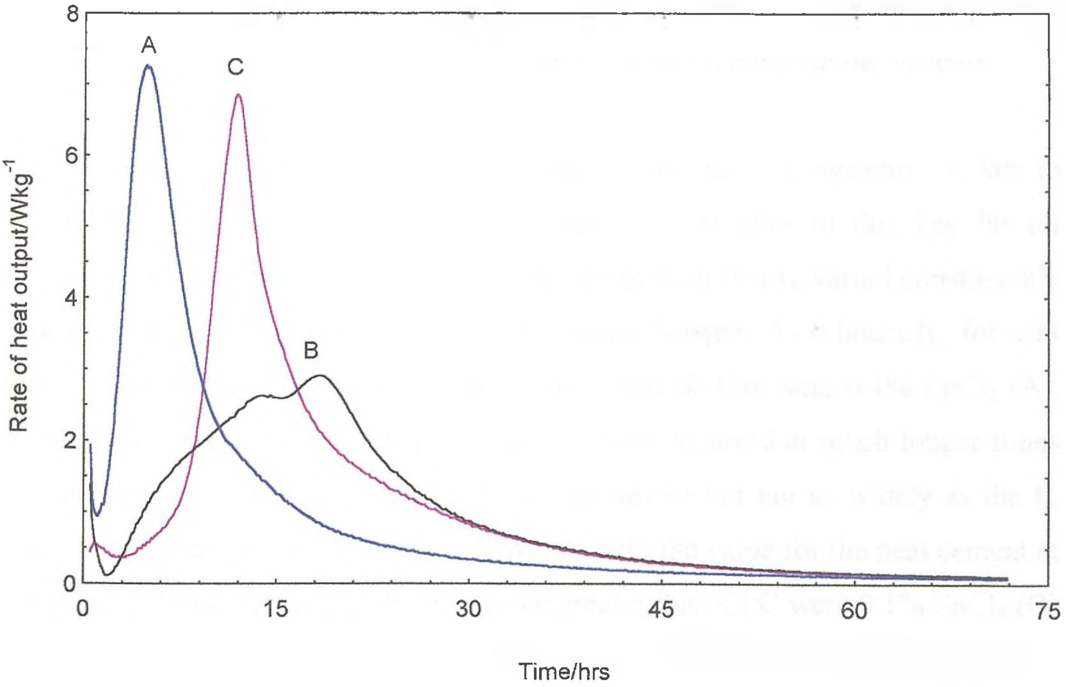

Figure 4.2.6 Rate of heat output for OPC (A), OPC + 0.1% $ZnCl_2$ (B) & OPC + 1.0% $SnCl_2$ (C)

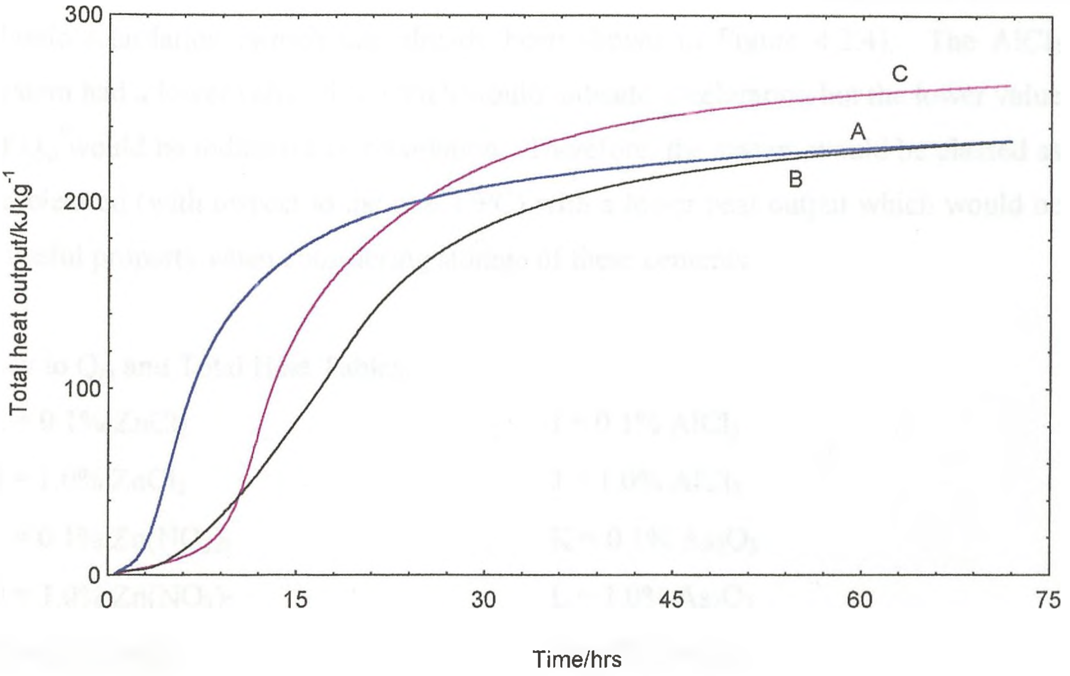

Figure 4.2.7 Total heat output for OPC (A), OPC + 0.1% $ZnCl_2$ (B) & OPC + 1.0% $SnCl_2$ (C)

$Zn(NO_3)_2$ additions, after 70 hours all the systems evolved similar amounts of heat. However, up to 24 hours there was quite a lot of variation between the systems.

Table 4.2.2 shows the values of t_m and Q_m for the OPC systems. A key to these tables is shown below. It will be necessary to refer to this key for all subsequent tables in this section. At 35°C it can be seen that t_m varied considerably although, as a generalisation, it can be said to occur between 3 - 6 hours (t_m for neat cement = 4.8 hours). The systems significantly outside this were 0.1% $ZnCl_2$ (A), 1% $SnCl_2$ (F) and 0.1% $Zn(NO_3)_2$ (C), all of which occurred at much longer times than for the neat OPC. The values of Q_m also varied but not as widely as the t_m values. The variation was between 3 - 9 Wkg^{-1}, with the value for the neat cement at 7.26 Wkg^{-1}. Those systems with a Q_m value greater than OPC were 0.1% $SnCl_4$ (G) and 0.1% $AlCl_3$ (I). They also had values of t_m similar to OPC ($SnCl_4$ > OPC > $AlCl_3$) so it was possible that some slight acceleration ($AlCl_3$) or retardation ($SnCl_4$) of set may have occurred although this would not be significant. Conversely, systems with a lower value of Q_m were 0.1% $ZnCl_2$ (A), 0.1% $Zn(NO_3)_2$ (C) and 1% $AlCl_3$ (J). Both the zinc systems also had a higher value of t_m which would indicate classic retardation (which has already been shown in Figure 4.2.4). The $AlCl_3$ system had a lower value of t_m which would indicate acceleration but the lower value of Q_m would be indicative of retardation. Therefore, the system would be classed as accelerated (with respect to the neat OPC) with a lower heat output which would be a useful property when considering storage of these cements.

Key to Q_m and Total Heat Tables:

A = 0.1% $ZnCl_2$
B = 1.0% $ZnCl_2$
C = 0.1% $Zn(NO_3)_2$
D = 1.0% $Zn(NO_3)_2$
E = 0.1% $SnCl_2$
F = 1% $SnCl_2$
G = 0.1% $SnCl_4$
H = 1.0% $SnCl_4$
I = 0.1% $AlCl_3$
J = 1.0% $AlCl_3$
K = 0.1% As_2O_3
L = 1.0% As_2O_3
M = 5% $ZnCl_2$
N = 5% $SnCl_2$
O = 5% $SnCl_4$

Cement Systems	**t_m/hrs (35°C)**	**Q_m/Wkg^{-1}**	**Q_m (normalised)**
OPC	4.8	7.26	-
A	18.3	2.91	-
B	*	*	-
C	7.5	5.06	-
D	*	*	-
E	5.3	7.86	-
F	11.8	6.86	-
G	5.1	9.15	-
H	3.0	7.93	-
I	4.3	8.82	-
J	3.4	4.38	-
K	5.8	6.85	-
L	4.9	6.55	-

* no values because there was no peak II.

Table 4.2.2 Values of t_m & Q_m for all OPC Systems at 35°C

		Total Heat Evolved/kJkg^{-1} @ 35°C					
Cement System	**Q_m/ Wkg^{-1}**	**@ Q_m**	**3 hrs**	**6 hrs**	**12 hrs**	**24 hrs**	**70 hrs**
OPC	7.26	57.08	16.45	86.06	157.61	199.94	232.71
A	2.91	115.69	3.28	13.35	55.16	161.89	232.31
B	*	*	20.77	31.23	45.56	59.68	82.83
C	5.06	48.38	3.31	23.16	107.29	162.08	208.96
D	*	*	28.52	32.27	34.52	36.35	40.76
E	7.86	59.91	11.09	77.92	155.60	195.66	224.16
F	6.86	73.28	4.13	9.73	77.34	197.18	262.57
G	9.15	7.54	10.43	89.01	165.61	207.01	234.99
H	7.93	36.65	36.65	97.52	150.05	200.83	252.34
I	8.82	61.59	24.06	102.05	163.55	210.47	248.72
J	4.38	34.69	28.18	70.94	120.05	167.46	221.17
K	6.85	61.81	8.22	65.88	150.18	196.99	224.56
L	6.55	60.42	20.52	85.05	154.82	197.25	222.00

* no values because there was no peak II.

Table 4.2.3 Total Heat Values for all OPC Systems at 35°C

4.2.3 3:1 BFS:OPC with Metal Salt Additions

The results for the neat 3:1 BFS:OPC and with additions of 0.1% $ZnCl_2$ and 1.0% $SnCl_2$ can be seen in figures 4.2.8 and 4.2.9. It is clearly illustrated that both additions caused strong retardation of cement hydration. It can be seen from curve B (Fig. 4.2.8 and 4.2.9) that the heat output was eventually starting to rise considerably but only after approximately 48 hours. The run was repeated and left for one week to ascertain if it was the onset of the main peak and the results of this can be seen in figures 4.2.10 and 4.2.11. It can be seen from figure 4.2.10 that the rise in heat output observed in Figs. 4.2.8 and 4.2.9 was the onset of the main peak and, therefore, it can be concluded that the system was highly retarded although it would set within seven days. The $SnCl_2$ system was also strongly retarded and the peak was much broader than that of the neat cement. This was the reason that the total heat outputs of these two systems were very similar after 45 hours. The total heat output for the $ZnCl_2$ system was also similar after 168 hours (Fig. 4.2.11). The $SnCl_2$ appeared to retard the set strongly initially and then possibly accelerate it once heat was being generated. The effects seen were similar to those observed in the OPC system.

Figures 4.2.12 and 4.2.13 show the different effects of adding $SnCl_2$ and $SnCl_4$ to this composite cement. Figure 4.2.12 is shown on a 24 hour scale to highlight the differences more clearly. The $SnCl_2$ retarded slightly and $SnCl_4$ accelerated slightly (i.e. the peak shifted to the left) although the total amount of heat generated was very similar in all three cements systems which is illustrated more clearly in Table 4.2.5 where the total heat values at 70 hours varied between 152 Wkg^{-1} (0.1% $SnCl_4$) and 160 Wkg^{-1} (neat 3:1 BFS:OPC). It is also immediately apparent that the amount of heat generated by any of the systems was significantly less than that of the OPC systems. Also, at all times, there was a lot of variation in the heat output which was dependent on the type and amount of metal salt added. For example, the difference between 0.1% $SnCl_2$ (E) and 1% $SnCl_2$ (F) was quite dramatic. At 3 hours they were very similar but by 6 hours the 0.1% addition level was producing approximately three times that of the 1% level. This continued until 24 hours when they started to become similar again and, by 70 hours, there was very little difference between them.

Figures 4.2.14 and 4.2.15 illustrate the effect of adding 0.1% $AlCl_3$ to the system. Figure 4.2.14 shows that the behaviour was changed with the addition of the metal salt in that the $AlCl_3$ retarded the cement hydration. However, when looking at the total heat evolved (Fig. 4.2.15) there was very little difference, the two lines were similar and crossed each other twice. This means that at certain times one system generated more heat than the other and this behaviour was then reversed.

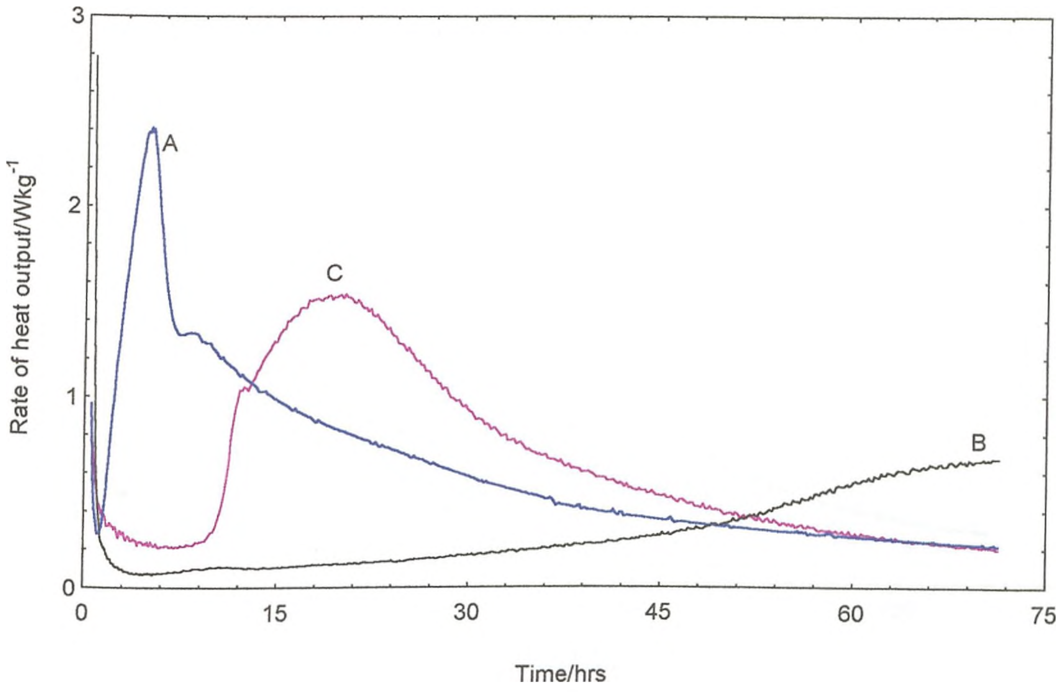

Figure 4.2.8 Rate of heat output for 3:1 BFS:OPC (A), 3:1 BFS:OPC + 0.1% $ZnCl_2$ (B) & 3:1 BFS:OPC + 1.0% $SnCl_2$ (C)

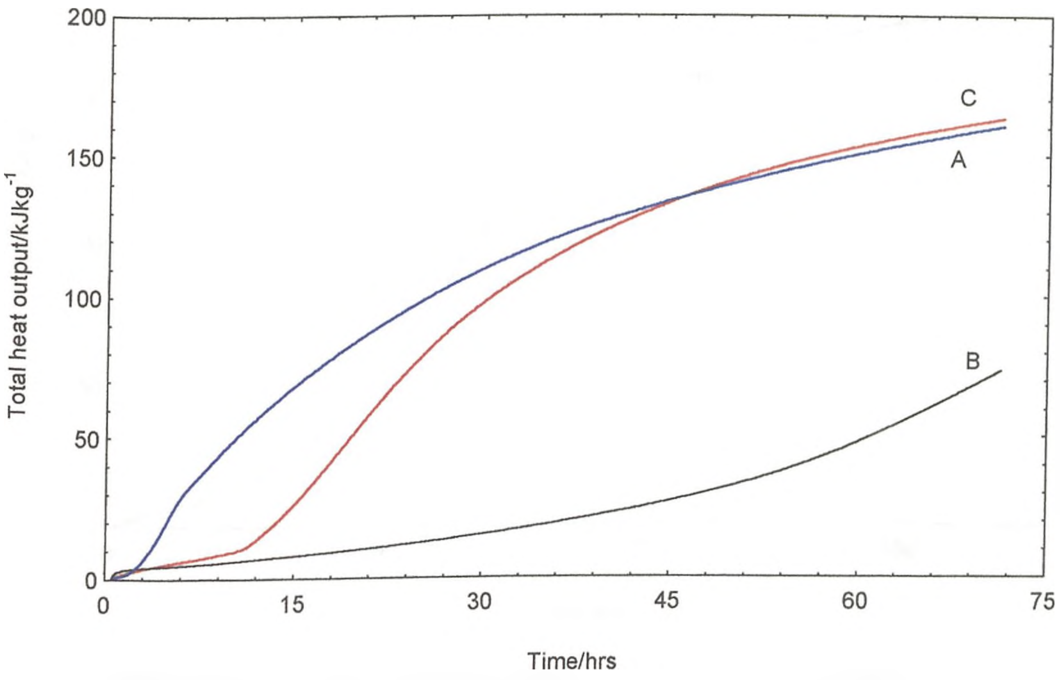

Figure 4.2.9 Total heat output for 3:1 BFS:OPC (A), 3:1 BFS:OPC + 0.1% $ZnCl_2$ (B) & 3:1 BFS:OPC + 1.0% $SnCl_2$ (C)

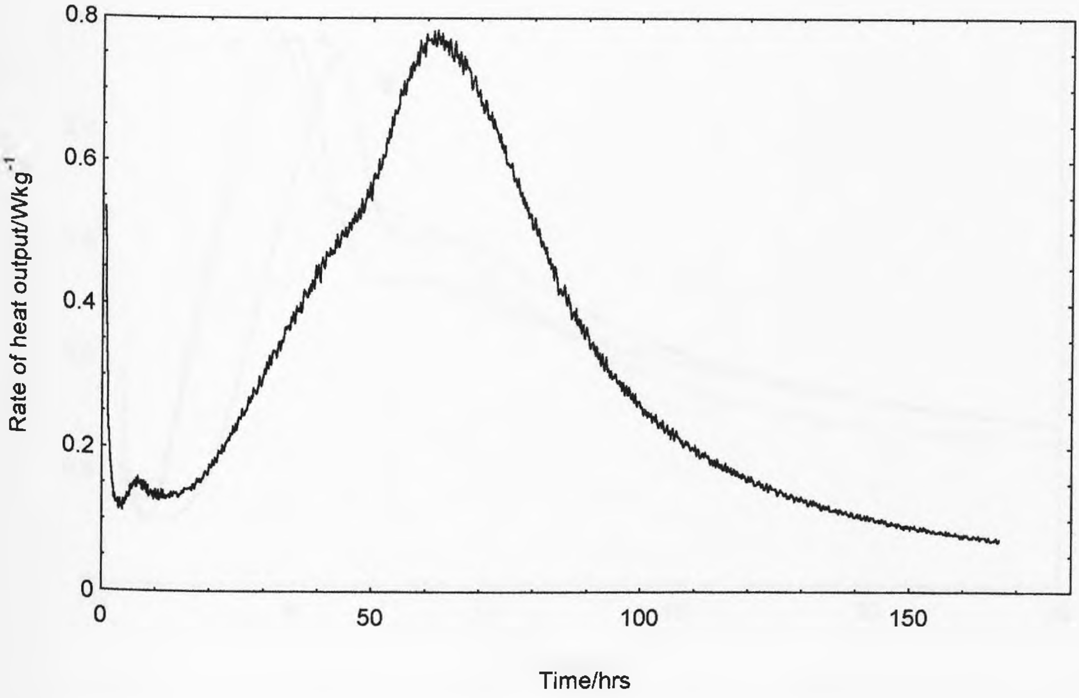

Figure 4.2.10 Rate of heat output for 3:1 BFS:OPC + 0.1% $ZnCl_2$

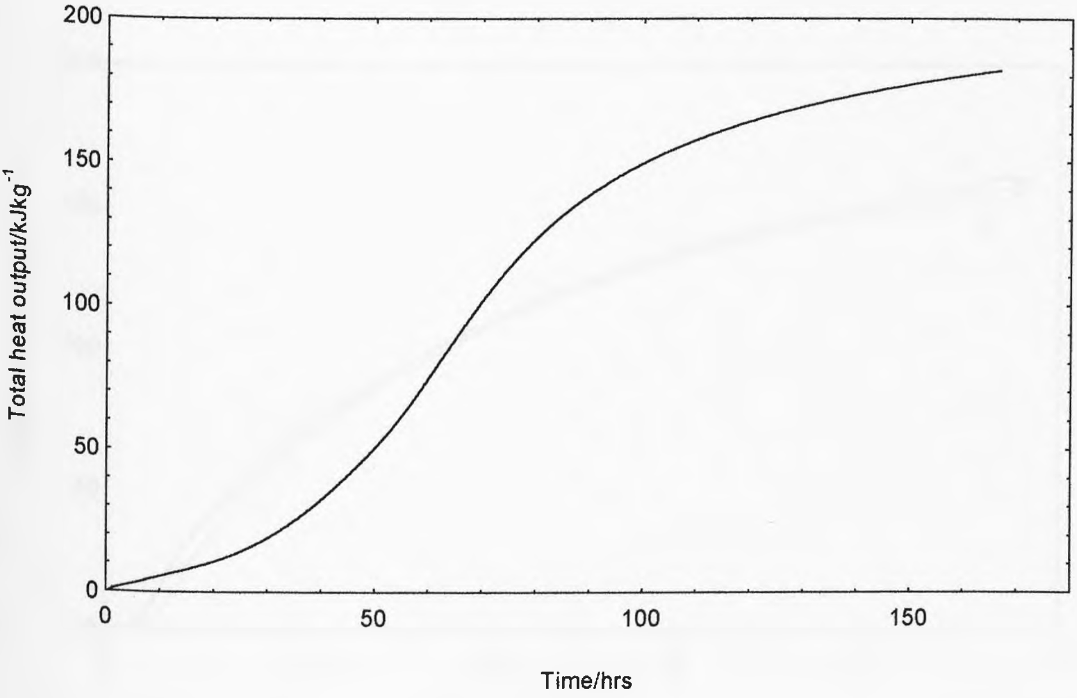

Figure 4.2.11 Total heat output for 3:1 BFS:OPC + 0.1% $ZnCl_2$

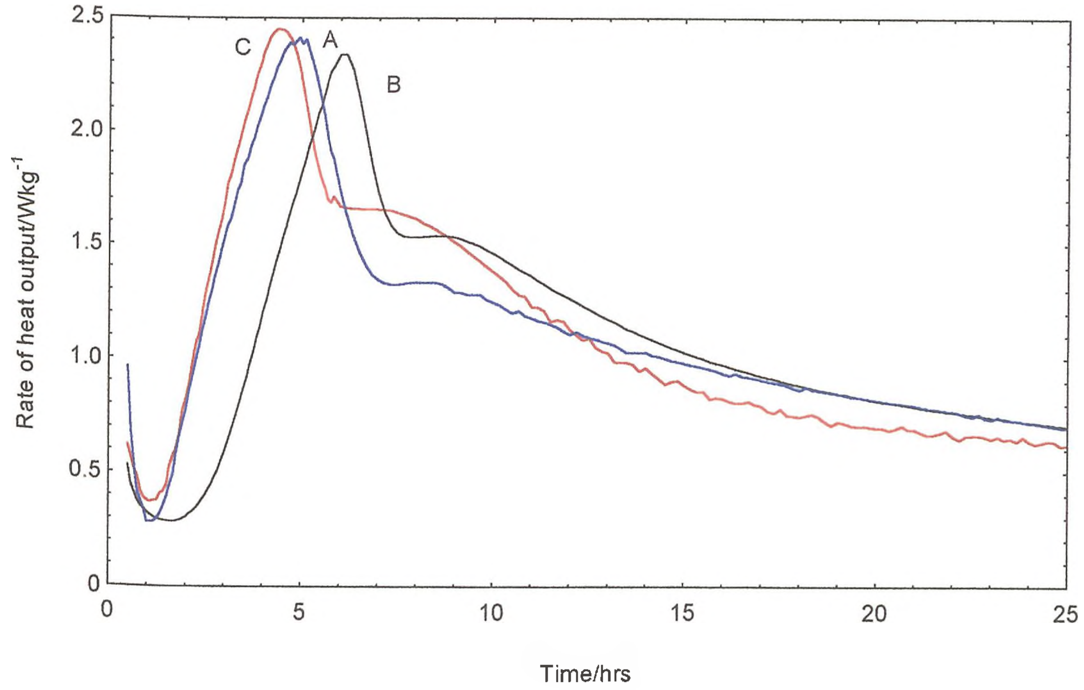

Figure 4.2.12 Rate of heat output for 3:1 BFS:OPC (A), 3:1 BFS:OPC + 0.1% $SnCl_2$ (B) & 3:1 BFS:OPC + 0.1% $SnCl_4$ (C)

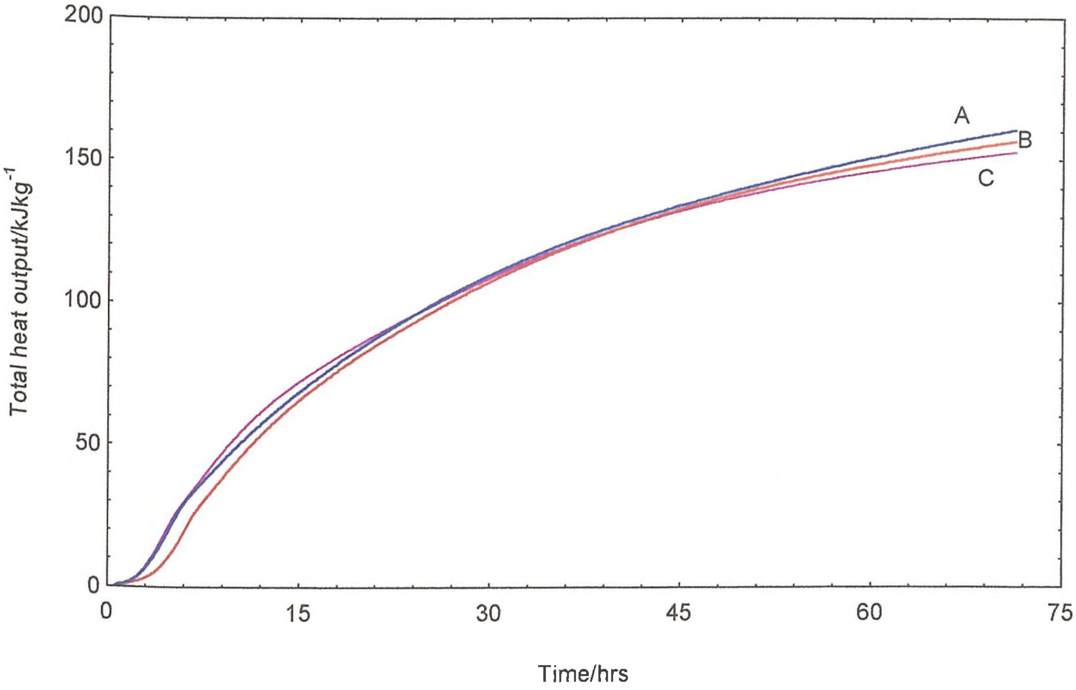

Figure 4.2.13 Total heat output for 3:1 BFS:OPC (A), 3:1 BFS:OPC + 0.1% $SnCl_2$ (B) & 3:1 BFS:OPC + 0.1% $SnCl_4$ (C)

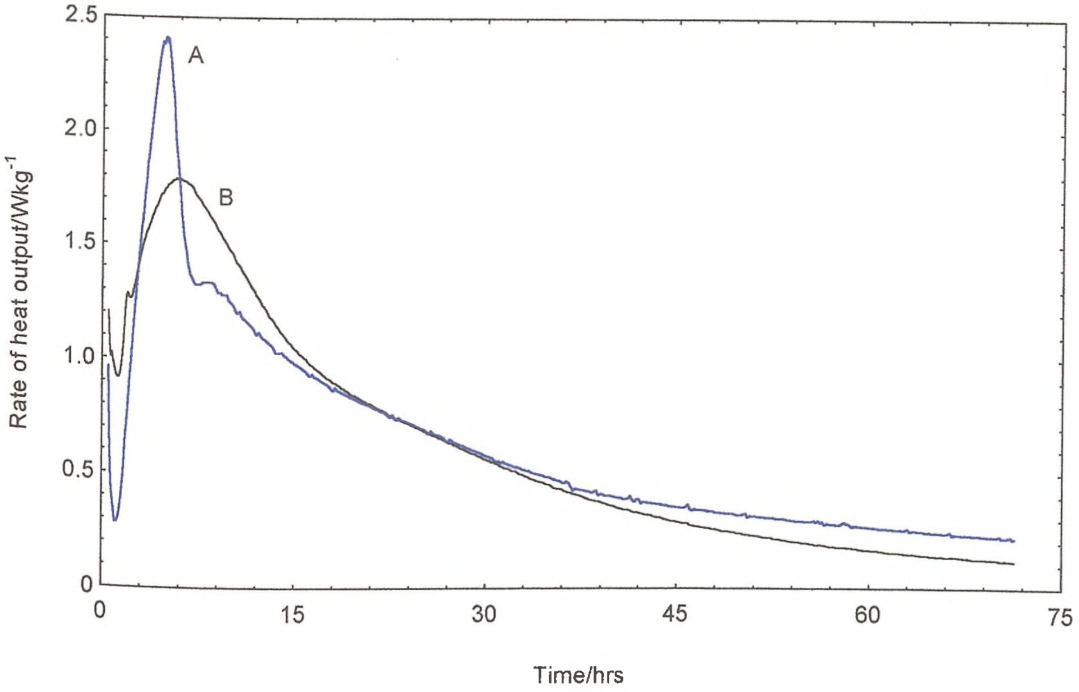

Figure 4.2.14 Rate of heat output for 3:1 BFS:OPC (A) & 3:1 BFS:OPC + 0.1% $AlCl_3$ (B)

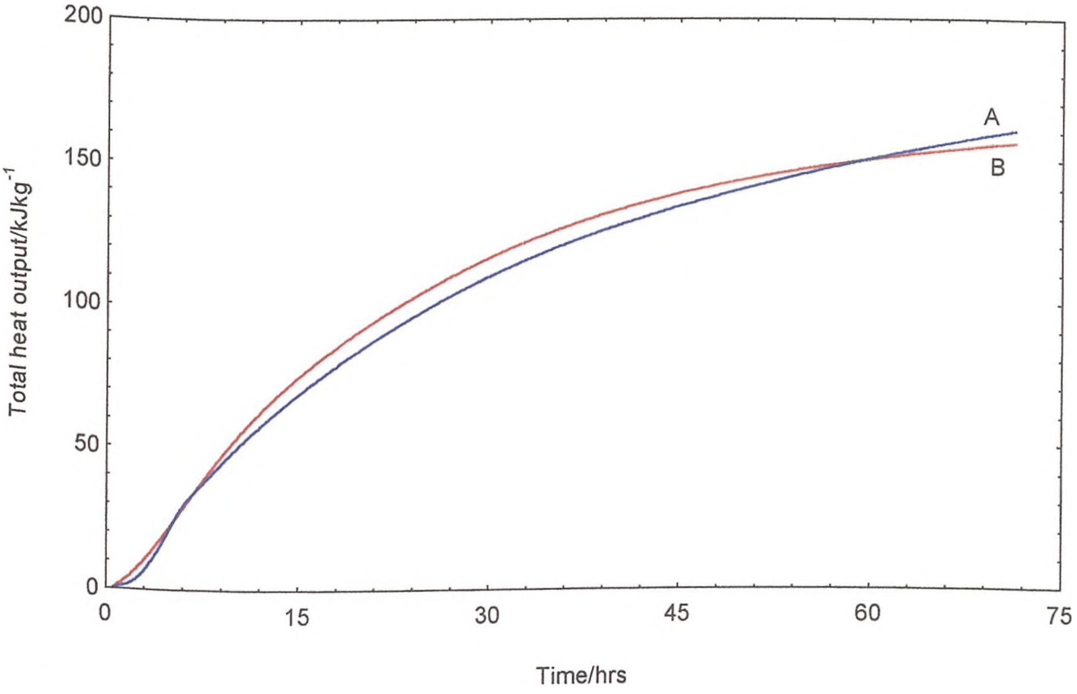

Figure 4.2.15 Total heat output for 3:1 BFS:OPC (A) & 3:1 BFS:OPC + 0.1% $AlCl_3$ (B)

Table 4.2.4 shows the values for t_m and Q_m. At 35°C the values for t_m varied significantly (2.5 - 7 hours with neat cement at 4.9 hours) and the variation was greater than that observed for the OPC system. The systems with similar values to the neat cement were 0.1% $SnCl_4$ (G), 0.1% As_2O_3 (K) and 1% As_2O_3 (L). These systems also had Q_m values similar to the neat cement. Retarded systems were 0.1% $ZnCl_2$ (A), 0.1% $Zn(NO_3)_2$ (C) and 1% $SnCl_2$ (F). This was the same trend as for the OPC system. The addition of 1% $SnCl_4$ (H) reduced the value of t_m quite significantly, although the value of Q_m was similar to that of the neat cement. However, all of the Q_m values were not significantly different to the neat cement - the variation was only 3 Wkg^{-1}. When comparing values of Q_m with those of the OPC systems (Table 4.2.2) it can be seen that the 3:1 BFS:OPC systems have produced a Q_m which was significantly less (this was also the case for 9:1 BFS:OPC (Table 4.2.6) and 3:1 PFA:OPC (Table 4.2.8). This was due to the significant reduction in the amount of OPC present in the composite cements. Therefore, normalised values of Q_m have been supplied in all tables so a more direct comparison can be made. This was achieved by multiplying the absolute value of Q_m by either four (3:1 BFS:OPC and 3:1 PFA:OPC) or ten (9:1 BFS:OPC) to bring the values into line with 100% OPC. For the 3:1 BFS:OPC system, the normalised Qm values did not differ significantly to those of the 100% OPC with the exception of 0.1% $Zn(NO_3)_2$ (C) which was lower and 0.1% $SnCl_2$ (E), 0.1% As_2O_3 (K) and 1% As_2O_3 (L) which were higher.

Cement Systems	**t_m/hrs (35°C)**	**Q_m/ Wkg^{-1}**	**Q_m (normalised)**
3:1 BFS	4.9	2.41	9.64
A	70.8	0.63	2.52
B	*	*	*
C	7.5	0.19	0.76
D	71.3	0.62	2.48
E	6.0	2.34	9.36
F	20.2	1.54	6.16
G	4.4	2.45	9.8
H	2.5	2.22	8.88
I	5.8	1.79	7.16
J	*	*	*
K	4.9	2.39	9.56
L	4.1	2.40	9.60

* no values because there was no peak II.

Table 4.2.4 Values of t_m & Q_m for all 3:1 BFS:OPC Systems and 35°C

		Total Heat Evolved/$kJkg^{-1}$ @ 35°C					
Cement System	**Q_m/ Wkg^{-1}**	**@ Q_m**	**3 hrs**	**6 hrs**	**12 hrs**	**24 hrs**	**70 hrs**
3:1 BFS	2.41	21.06	6.86	29.39	57.44	95.95	159.71
A	0.63	72.56	4.08	4.89	6.97	12.03	70.57
B	*	*	5.67	7.09	8.28	9.30	10.65
C	0.19	2.87	1.74	2.95	6.18	11.77	73.25
D	0.62	≈5.86	4.85	5.75	6.33	6.60	5.86
E	2.34	19.59	3.35	19.59	53.63	93.41	155.91
F	1.54	54.04	3.78	6.35	14.15	73.95	162.52
G	2.45	18.31	7.36	29.97	61.73	96.04	152.27
H	2.22	10.30	14.10	31.02	55.16	84.80	133.45
I	1.79	27.60	10.56	28.68	62.42	102.73	155.85
J	*	*	7.25	11.23	16.64	22.63	31.16
K	2.39	21.49	7.57	30.04	58.99	97.16	159.80
L	2.40	19.49	10.83	33.06	60.17	95.31	152.16

* no values because there was no peak II.

Table 4.2.5 Total Heat Values for all 3:1 BFS:OPC Systems at 35°C

4.2.4 9:1 BFS:OPC (35°C)

Figures 4.2.16 and 4.2.17 show the effects of adding 0.1% $ZnCl_2$ (B) and 0.1% $Zn(NO_3)_2$ (C) to a 9:1 BFS:OPC system. Note the reduced heat output values even compared with the 3:1 BFS:OPC systems. It can be seen that both metal salts had a highly retarding effect on the cement. It is not really possible to say which had the greater effect, although taking into account the total heat output (Fig. 4.2.17), it can be seen the $ZnCl_2$ curve appeared to be rising more quickly.

Figures 4.2.18 - 4.2.21 show the effects of $SnCl_2$ (B) and $SnCl_4$ (C) at both 0.1% (Figs. 4.2.18 and 4.2.19) and 1.0% (Figs. 4.2.20 and 4.2.21) levels. At 0.1% both salts retarded the set slightly. Also, peak II in the $SnCl_4$ system occurred at around the same time as in the neat cement but with a lower heat output. From the values in Table 4.2.7 the total heat evolved for all three systems appeared to be fairly similar which suggests there may not necessarily have been a retardation in set - just a lower value of Q_m. However considering the values of t_m and Q_m at 35°C (Table 4.2.6) it can be seen that both tin systems had t_m values significantly greater than the neat cement and lower Q_m values. Therefore, combining all the data leads to the conclusion there was some retardation of set.

At the 1% level, $SnCl_2$ showed substantial retardation with peak II not occurring until after approximately 45 hours. However, the $SnCl_4$ system did give a small peak at around the same time as in the neat cement but with a much lower heat output. It was not clear from Fig. 4.2.20 alone if this was a 'true' peak which, if it was, would mean that the system was probably retarded but was not exhibiting classic retardation. However, when studying the total heat curves (Fig. 4.2.21) it can be seen that the neat cement (A) and the $SnCl_4$ (C) systems had begun to level off whilst the $SnCl_2$ (B) was still rising. This confirmed the retarded set of the $SnCl_2$ system and showed that the $SnCl_4$ was also retarded but in a different manner to that of the $SnCl_2$ system. Again the data from Tables 4.2.6 and 4.2.7 confirm there was considerable retardation to the set and early hydration of the cement.

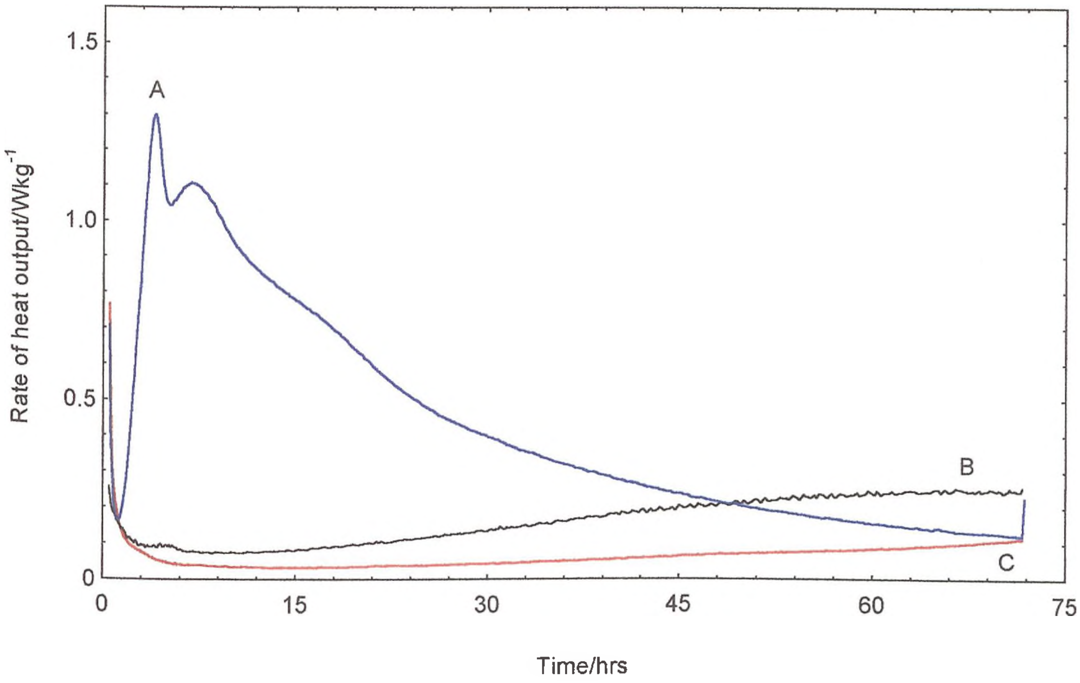

Figure 4.2.16 Rate of heat output for 9:1 BFS:OPC (A), 9:1 BFS:OPC + 0.1% $ZnCl_2$ (B) & 9:1 BFS:OPC + 0.1% $Zn(NO_3)_2$ (C)

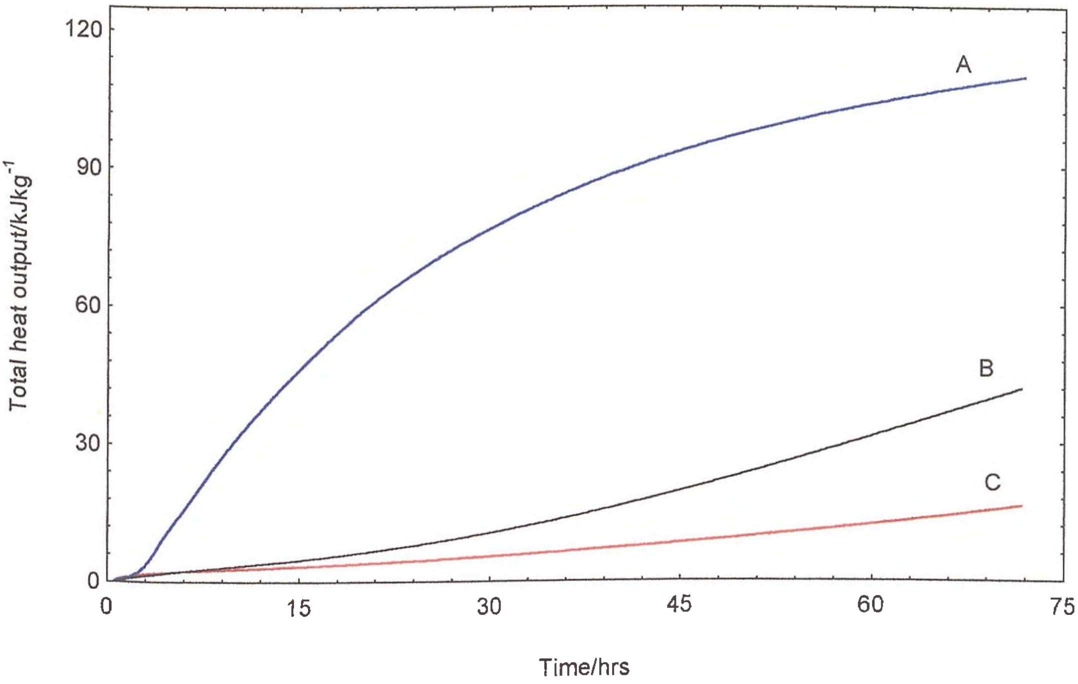

Figure 4.2.17 Total heat output for 9:1 BFS:OPC (A), 9:1 BFS:OPC + 0.1% $ZnCl_2$ (B) & 9:1 BFS:OPC + 0.1% $Zn(NO_3)_2$ (C)

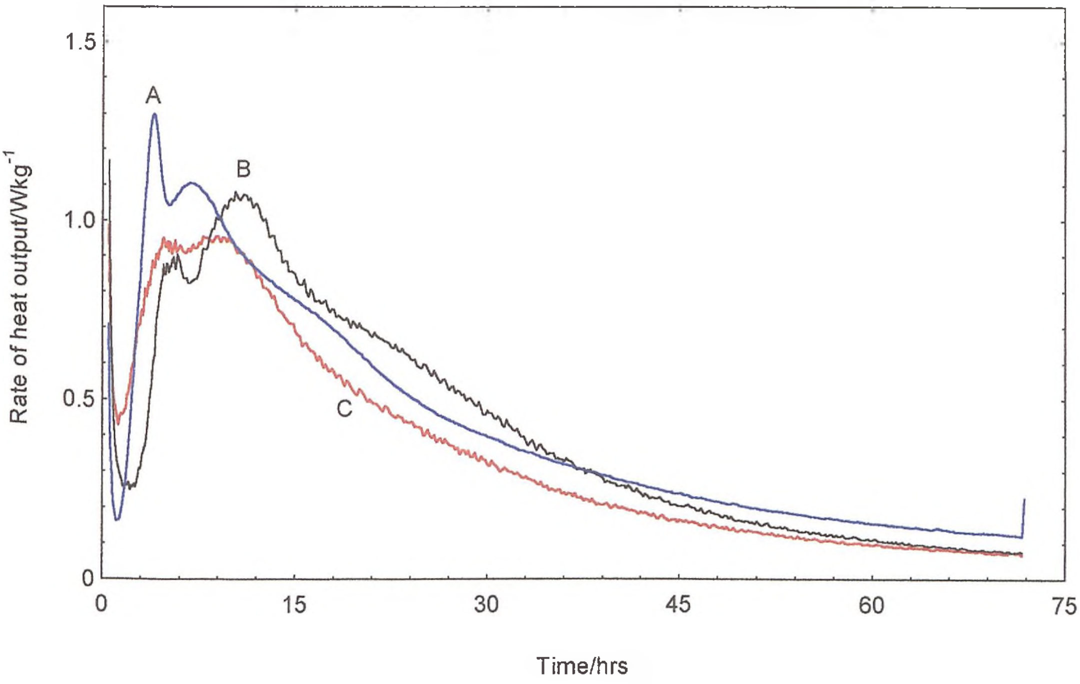

Figure 4.2.18 Rate of heat output for 9:1 BFS:OPC (A), 9:1 BFS:OPC + 0.1% $SnCl_2$ (B) & 9:1 BFS:OPC + 0.1% $SnCl_4$ (C)

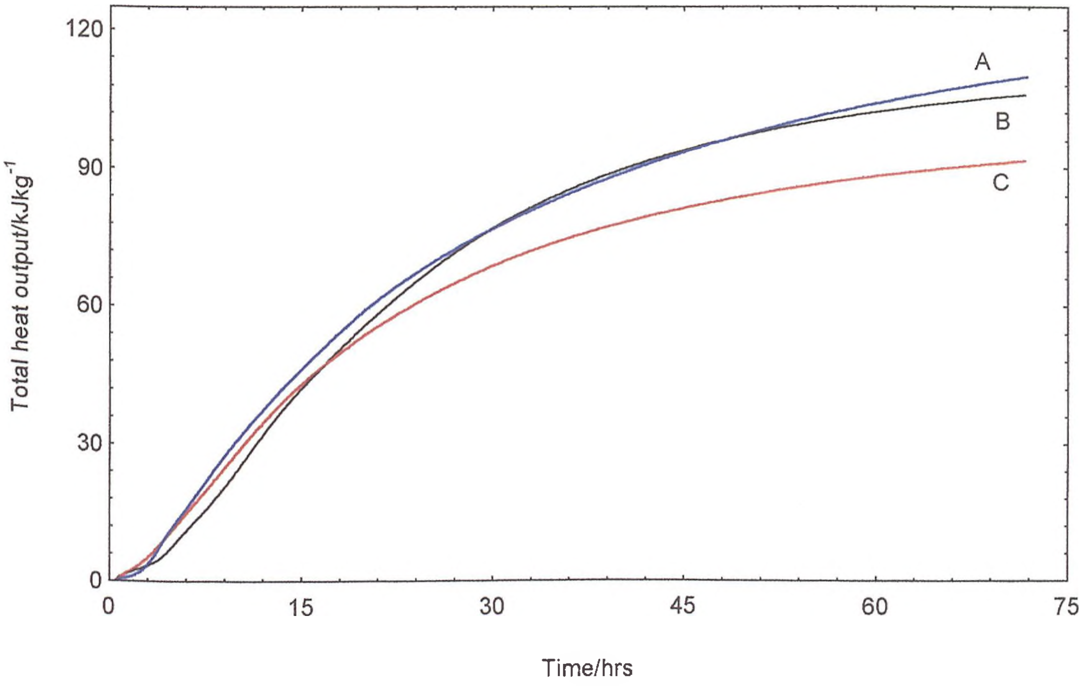

Figure 4.2.19 Total heat output for 9:1 BFS:OPC (A), 9:1 BFS:OPC + 0.1% $SnCl_2$ (B) & 9:1 BFS:OPC + 0.1% $SnCl_4$ (C)

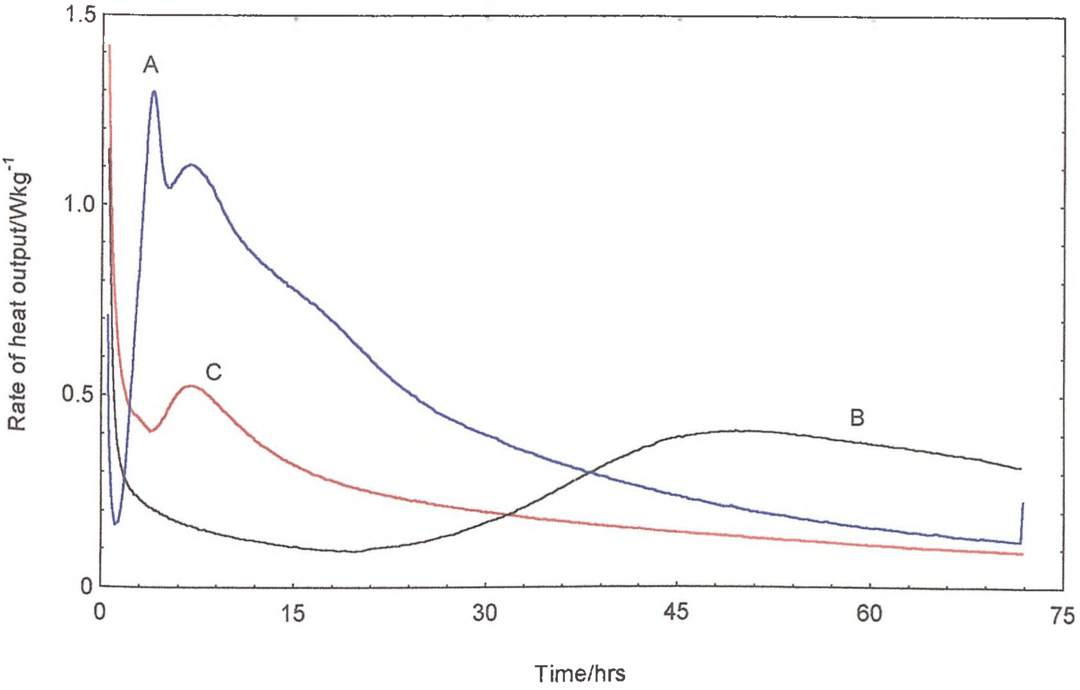

Figure 4.2.20 Rate of heat output for 9:1 BFS:OPC (A), 9:1 BFS:OPC + 1.0% $SnCl_2$ (B) & 9:1 BFS:OPC + 1.0% $SnCl_4$ (C)

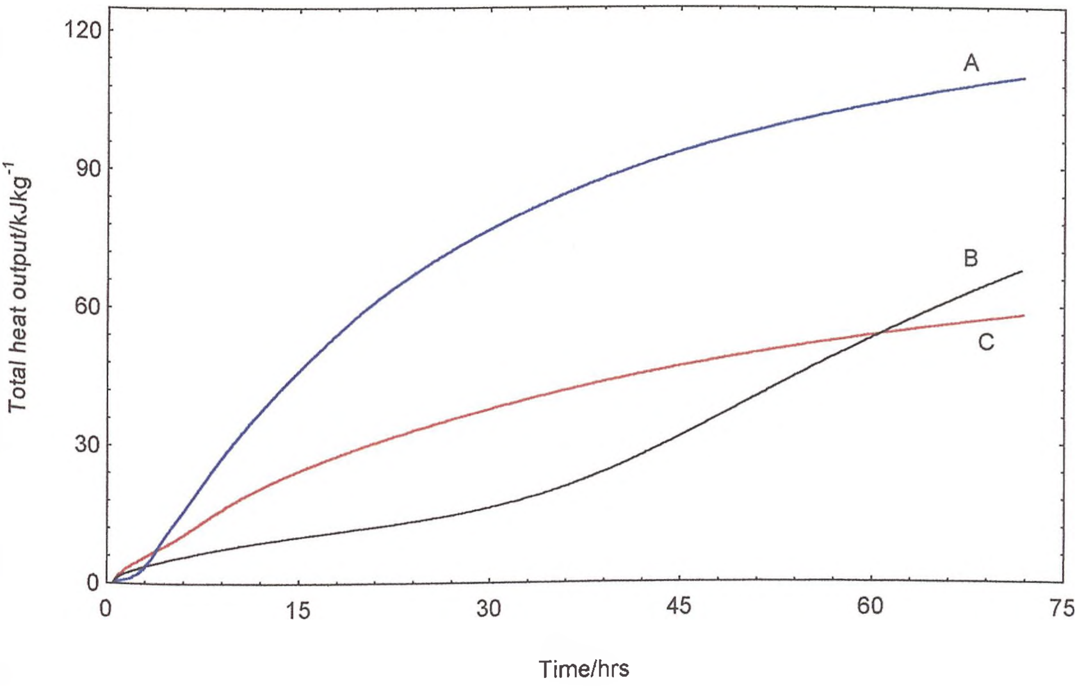

Figure 4.2.21 Total heat output for 9:1 BFS:OPC (A), 9:1 BFS:OPC + 1.0% $SnCl_2$ (B) & 9:1 BFS:OPC + 1.0% $SnCl_4$ (C)

Considering the total heat output of all 9:1 BFS:OPC systems (Table 4.2.7) it can be seen that at all times there was considerable variation in the values (similar to 3:1 BFS:OPC). Also, again similar to 3:1 BFS:OPC systems, the values of t_m varied considerably (4 - 70 hours with the neat cement at 4 hours) (Table 4.2.6). 0.1% As_2O_3 (K) and 1% As_2O_3 (L) showed t_m values similar to the neat cement and also had similar values of Q_m. However, the most obvious difference between the two slag cements was the number of systems which had t_m values significantly less than those of the neat cement. For the 9:1 BFS:OPC cements these were 0.1% $ZnCl_2$ (A), 0.1% $Zn(NO_3)_2$ (C), 0.1% $SnCl_2$ (E), 1% $SnCl_2$ (F), 1% $SnCl_4$ (H), 0.1% $AlCl_3$ (I) and 1% $AlCl_3$ (J). All values of t_m were at least twice that of the neat cement and also the values of Q_m were quite a lot less. That is, most of them were less than 1 Wkg^{-1}. Another difference between these systems and the 3:1 BFS:OPC systems was that the normalised values of Q_m varied a lot and there was no trend with respect to the OPC systems.

Cement Systems	**t_m/hrs (35°C)**	**Q_m/ Wkg^{-1}**	**Q_m (normalised)**
9:1 BFS	4.0	1.29	11.61
A	66.5	0.26	2.34
B	*	*	*
C	71.7	0.11	0.99
D	*	*	*
E	10.3	1.08	9.72
F	49.5	0.41	3.69
G	9.5	0.95	8.55
H	7.2	0.53	4.77
I	13.5	1.14	10.26
J	*	*	*
K	4.0	1.20	10.80
L	3.9	1.10	9.90

* no values because there was no peak II.

Table 4.2.6 Values of t_m & Q_m for all 9:1 BFS:OPC Systems at 35°C

		Total Heat Evolved/$kJkg^{-1}$ @ 35°C					
Cement System	**Q_m/ Wkg^{-1}**	**@ Q_m**	**3 hrs**	**6 hrs**	**12 hrs**	**24 hrs**	**70 hrs**
9:1 BFS	1.29	7.76	3.68	15.79	37.51	67.25	109.08
A	0.26	37.74	1.29	2.27	3.90	7.88	40.47
B	*	*	3.15	3.83	4.00	4.13	3.80
C	0.11	16.46	1.64	2.22	3.02	4.54	15.79
D	*	*	6.84	7.66	7.81	7.34	4.75
E	1.08	25.64	3.40	10.99	32.00	65.35	105.48
F	0.41	38.26	3.69	5.82	8.90	13.42	65.97
G	0.95	26.60	5.24	14.79	34.77	60.63	91.25
H	0.53	12.83	5.85	10.63	20.83	33.31	57.55
I	1.14	28.41	2.91	6.60	22.43	58.86	85.62
J	*	*	4.97	7.28	9.91	12.68	17.24
K	1.20	8.21	4.31	16.14	36.79	64.04	98.34
L	1.10	10.35	7.19	17.93	36.57	59.74	88.90

* no values because there was no peak II.

Table 4.2.7 Total Heat Values for all 9:1 BFS:OPC Systems at 35°C

4.2.5 3:1 PFA:OPC with Metal Salt Additions

It can be seen from figures 4.2.22 and 4.2.23 that $ZnCl_2$ and $Zn(NO_3)_2$ both retarded the set but that, as before, the $ZnCl_2$ retarded more strongly. As with the 3:1 BFS:OPC, the $ZnCl_2$ system was repeated and left to run for one week and, as with the slag cement, this showed that set did eventually occur. The total heat output curves (Fig. 4.2.23) show quite a marked difference between the neat cement (A) and those with metal salts added (curves B & C). The latter started off quite differently but by 72 hours showed a very similar amount of heat generated.

The effects of $SnCl_2$, $SnCl_4$ and $AlCl_3$ at 0.1% and 1% are shown in figures 4.2.24 - 4.2.27. At the 0.1% addition level both $SnCl_4$ (C) and $AlCl_3$ (D) accelerated the set and $SnCl_2$ (B) produced a peak at approximately the same time as that in the neat cement (A) but with a greater heat output. The total heat curves (Fig. 2.2.25) were all very similar and there was considerable overlap during the first 20 hours before they all began to level off. Also, as would be expected from figure 2.2.24, the $SnCl_2$ (B) had the greatest total heat output.

The 1% additions (Fig. 4.2.26) showed quite different results from those for the 0.1% additions. The only system which accelerated here was the $SnCl_4$ (C), whereas both the $SnCl_2$ (B) and $AlCl_3$ (D) retarded significantly. In fact, the $AlCl_3$ appeared to have killed the set of the cement. This is confirmed in Table 4.2.8 as there was no 'real' value of Q_m as t_m occurred at 0.5 hours. The total heat output curves were not as similar to each other as the 0.1% additions either. In these systems the neat cement (A) had the highest output with $AlCl_3$ being the lowest. However, one surprising feature was that the $SnCl_2$ (B), which retarded the system, had a higher total heat than the $SnCl_4$ (C) which accelerated the system. Curve B started off quite slowly but increased rapidly from approximately 15 hours, whereas curve C started off quite rapidly and then slowed down at around the same time that curve B started to increase and the curves intersected after around 30 hours. This can be seen more clearly in Table 4.2.9 where the values were significantly different until approximately 24 hours. These two results are interesting as they help to highlight the differences due to the oxidation state of tin.

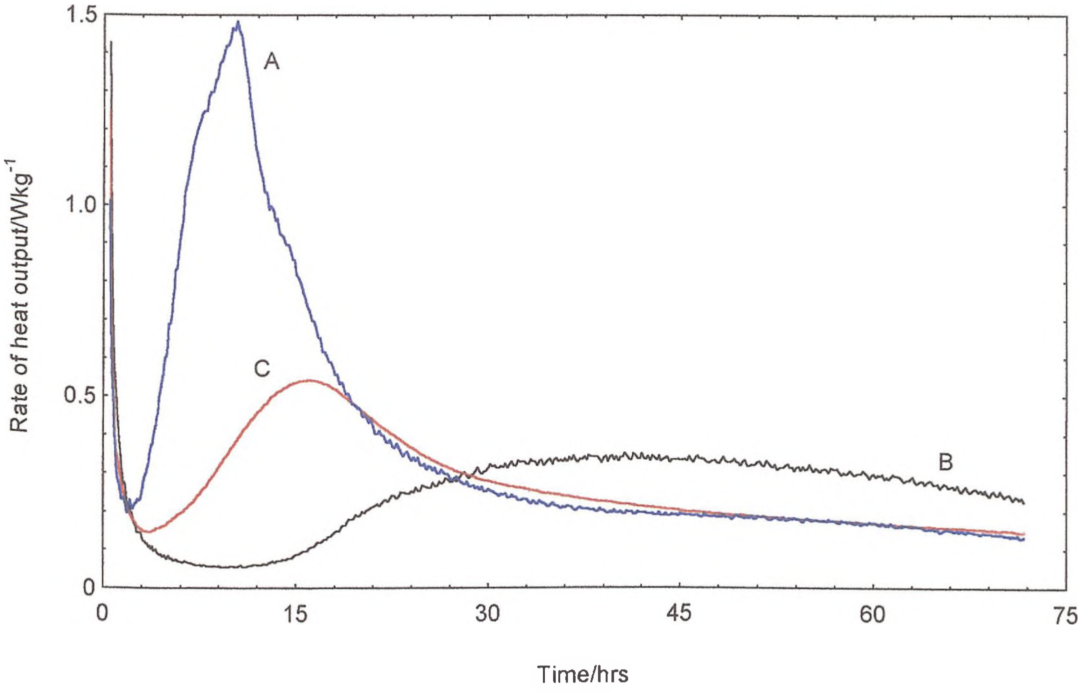

Figure 4.2.22 Rate of heat output of 3:1 PFA:OPC (A), 3:1 PFA:OPC + 0.1% $ZnCl_2$ (B) & 3:1 PFA:OPC + 0.1% $Zn(NO_3)_2$

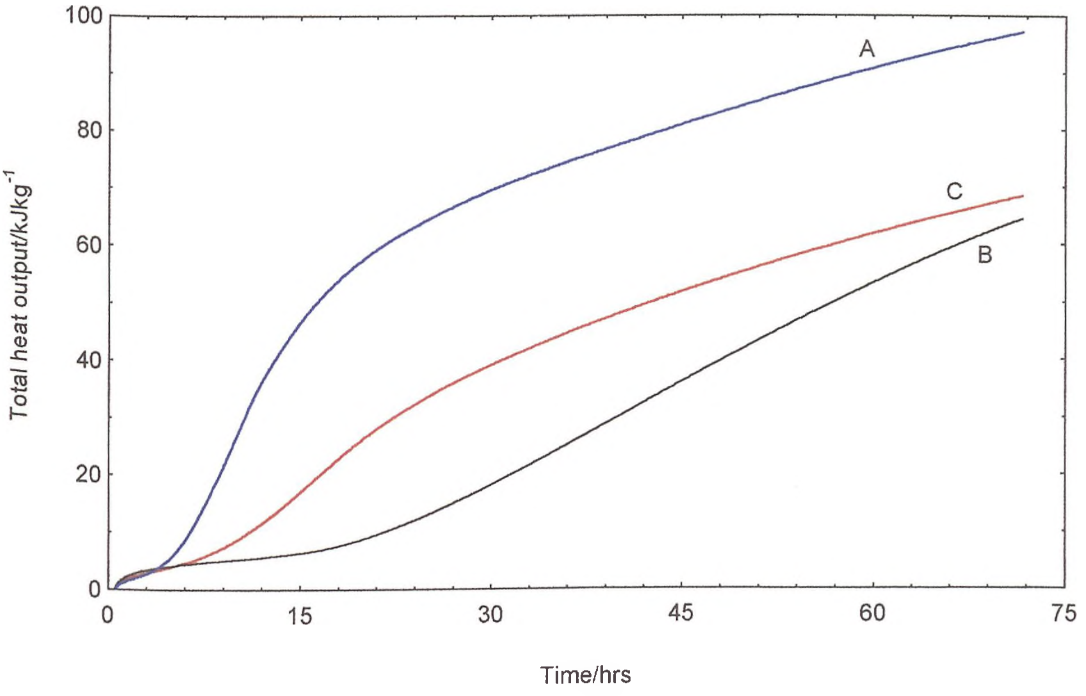

Figure 4.2.23 Total heat output of 3:1 PFA:OPC (A), 3:1 PFA:OPC + 0.1% $ZnCl_2$ (B) & 3:1 PFA:OPC + 0.1% $Zn(NO_3)_2$

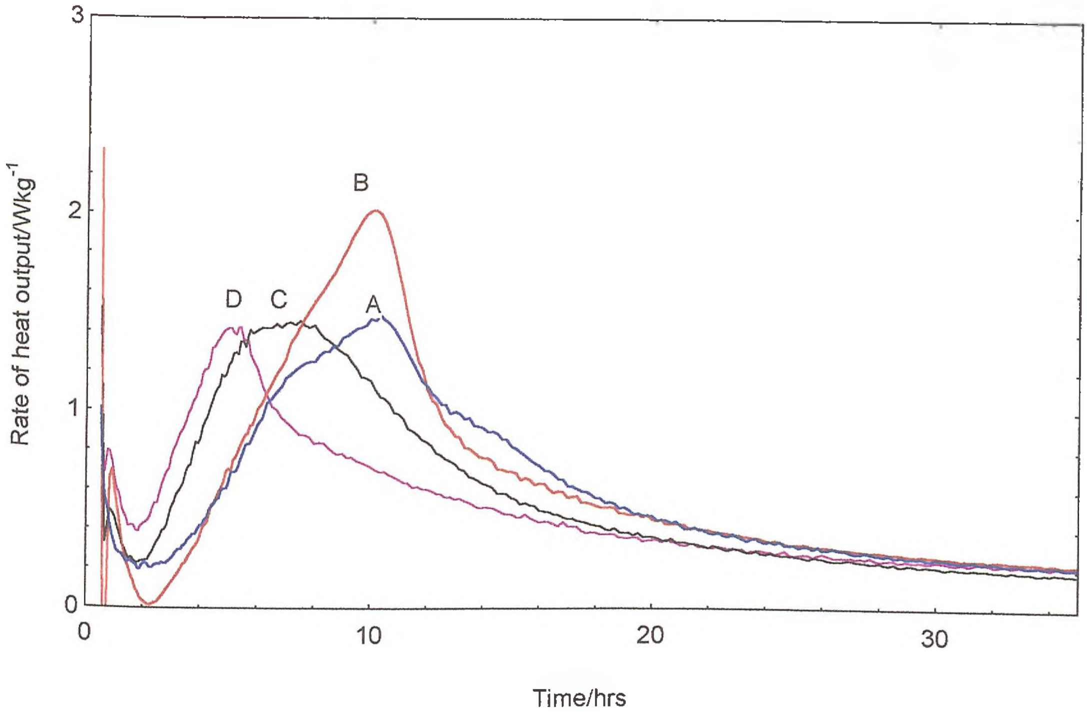

Figure 4.2.24 Rate of heat output of 3:1 PFA:OPC (A), 3:1 PFA:OPC + 0.1% $SnCl_2$ (B), 0.1% $SnCl_4$ (C) & 0.1% $AlCl_3$ (D)

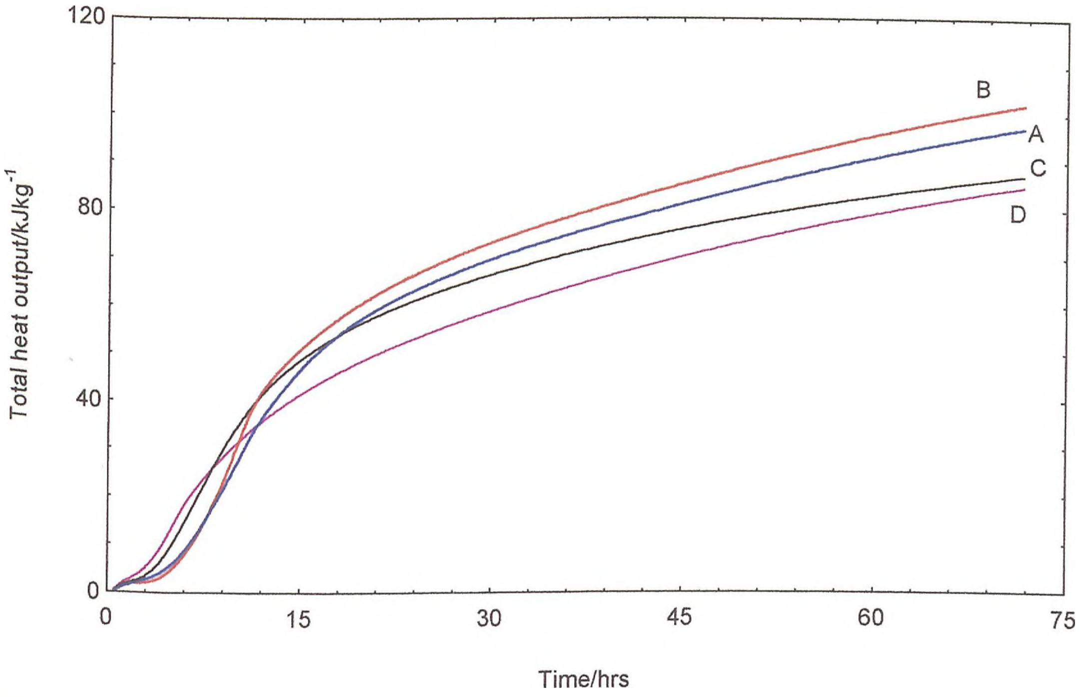

Figure 4.2.25 Total heat output of 3:1 PFA:OPC (A), 3:1 PFA:OPC + 0.1% $SnCl_2$ (B), 0.1% $SnCl_4$ (C) & 0.1% $AlCl_3$ (D)

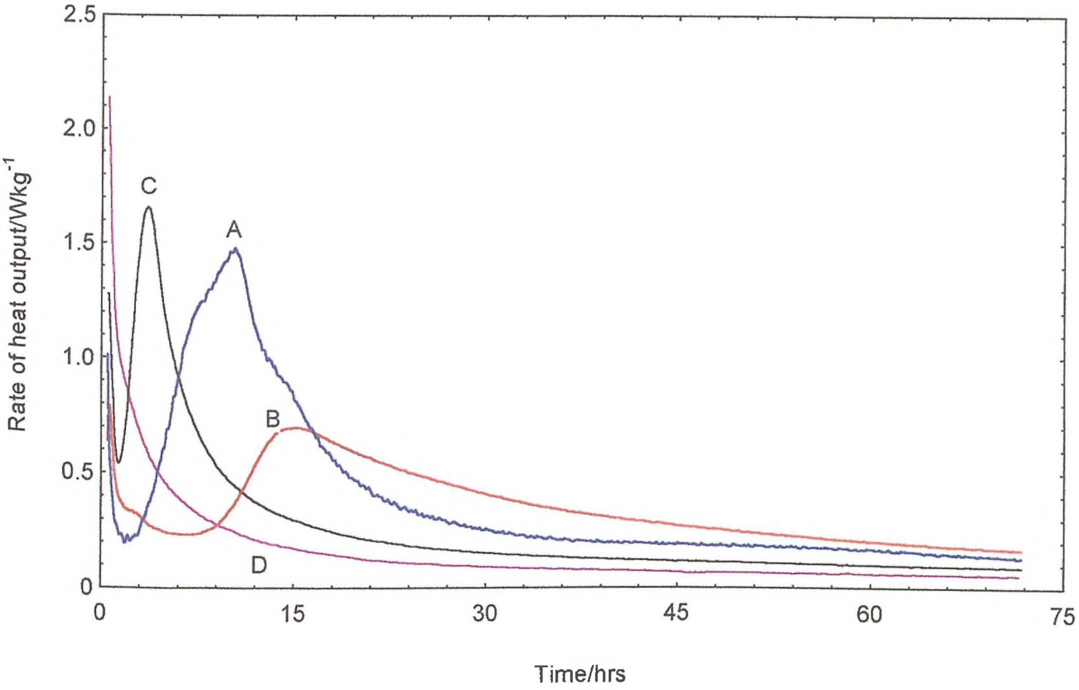

Figure 4.2.26 Rate of heat output of 3:1 PFA:OPC (A), 3:1 PFA:OPC + 1.0% $SnCl_2$ (B), 1.0% $SnCl_4$ (C) & 1.0% $AlCl_3$ (D)

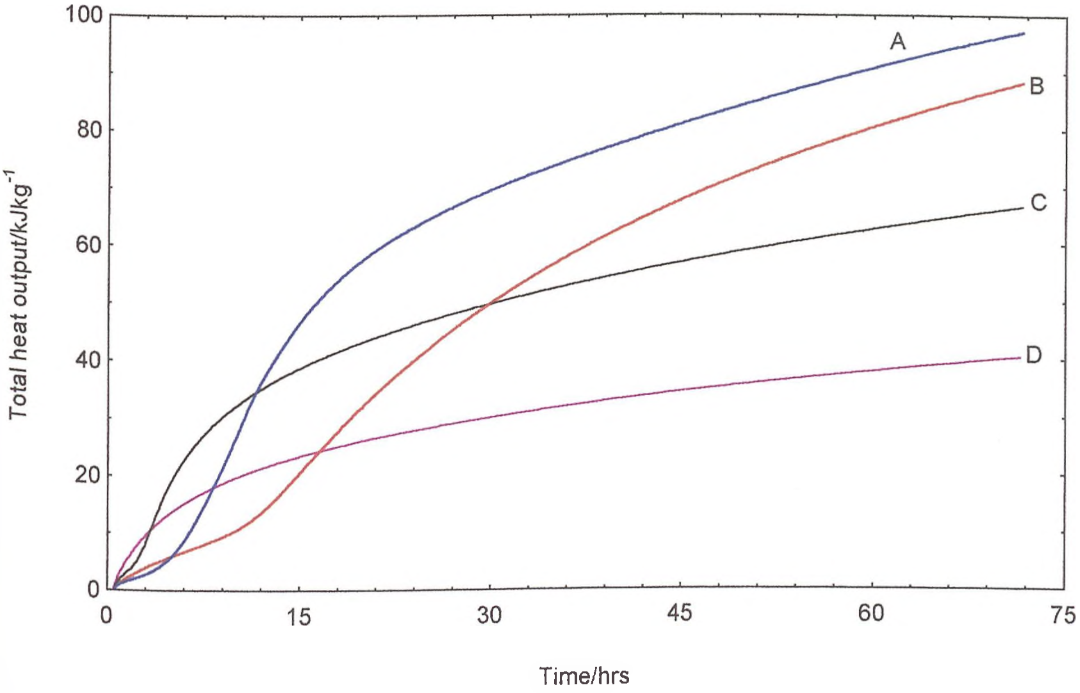

Figure 4.2.27 Total heat output of 3:1 PFA:OPC (A), 3:1 PFA:OPC + 1.0% $SnCl_2$ (B), 1.0% $SnCl_4$ (C) & 1.0% $AlCl_3$ (D)

Table 4.2.9 shows the total heat evolved at 35°C for all systems. Again, as with the two slag cements it can be seen that there was a lot of variation at all the times shown. However, the values of t_m (Table 4.2.8), although varied, showed less variation than the slag cements (4 - 70 hours with the neat cement at 10.3 hours). Systems with t_m values similar to the neat cement were 0.1% $SnCl_2$ (E) which had a value of Q_m greater than the neat cement and 0.1% As_2O_3 (K) whose value of Q_m was similar. The systems which showed retardation were 0.1% $ZnCl_2$ (A), 0.1% $Zn(NO_3)_2$ (C) and 1% $SnCl_2$ (F). These had both a much higher value of t_m and a lower value of Q_m which would, therefore, indicate classic retardation. The systems with a lower value of t_m - 0.1% $SnCl_4$ (G), 1% $SnCl_4$ (H), 0.1% $AlCl_3$ (I) and 1% As_2O_3 (K) - do not necessarily exhibit classic acceleration (Figure 4.2.29) as the values of Q_m were similar to the neat cement but occurred at an earlier time (t_m). The normalised Q_m values were generally similar to or less than the values for 100% OPC.

Cement Systems	**t_m/hrs (35°C)**	**Q_m/ Wkg^{-1}**	**Q_m (normalised)**
3:1 PFA	10.3	1.48	5.92
A	40.7	0.35	1.40
B	*	*	*
C	16.0	0.54	2.16
D	*	*	*
E	10.2	2.02	8.08
F	15.2	0.70	2.8
G	7.5	1.46	5.84
H	3.6	1.66	6.64
I	5.0	1.42	5.68
J	*	*	*
K	9.2	1.20	4.80
L	8.3	1.06	4.24

* no values because there was no peak II.

Table 4.2.8 Values of t_m & Q_m for all 3:1 PFA:OPC Systems at 35°C

		Total Heat Evolved/kJkg^{-1} @ 35°C					
Cement System	**Q_m/ Wkg^{-1}**	**@ Q_m**	**3 hrs**	**6 hrs**	**12 hrs**	**24 hrs**	**70 hrs**
3:1PFA	1.48	28.44	2.78	8.67	36.37	63.39	96.39
A	0.35	30.85	3.39	4.38	5.64	12.07	63.08
B	*	*	5.55	6.71	7.71	8.55	8.99
C	0.54	19.02	2.92	4.68	11.60	32.40	67.66
D	*	*	*	7.14	8.59	10.13	12.88
E	2.02	31.21	2.09	7.91	41.87	66.68	101.24
F	0.70	21.04	3.96	6.76	13.59	40.14	87.36
G	1.46	22.41	3.58	14.69	41.32	61.22	86.56
H	1.66	11.79	8.41	22.88	33.15	46.21	66.22
I	1.42	13.53	5.40	18.39	35.72	53.30	84.15
J	*	*	*	15.21	21.41	37.91	40.20
K	1.20	24.88	3.32	11.80	36.37	60.34	88.03
L	1.06	26.02	7.52	17.31	38.67	59.09	88.48

* no values because there was no peak II.

Table 4.2.9 Total Heat Values for all 3:1 PFA:OPC Systems at 35°C

4.2.6 Comparison of 35°C and 21°C Data

4.2.6.1 100% OPC Systems

Figures 4.2.32 and 4.2.33 show 100 % OPC at 35°C (A) and 21°C (B). As expected, it can be seen that at 21°C the set of the cement was retarded in comparison to that at 35°C. The rate of heat output at 21°C was approximately half that of 35°C and Q_m was shifted to longer times. However, when considering the total heat output (Fig. 4.2.33) the two results were fairly similar after 72 hours. This was due to the 21°C peak being much broader than that at 35°C. These results are illustrated more clearly in Tables 4.2.10 and 4.2.11. From Table 4.2.10 it can be seen that Q_m at 21°C was approximately half the value at 35°C and occurred at approximately double the time. From the total heat tables (4.2.2 (35°C)and 4.2.11 (21°C)) the amount of heat evolved after 12 hours at 35°C was still double that at 21°C and it wasn't until 24 hours that the value at 21°C started to rise significantly.

Figure 4.2.34 shows OPC with 0.1% $SnCl_2$ at 35°C (A) and 21°C (B) and also 5% $SnCl_2$ at 21°C (C). It can be seen that the 0.1% $SnCl_2$ at 35°C gave a very similar result to the neat OPC (Fig. 4.2.32) at the same temperature. Also, the effect of lowering the temperature had a similar effect on these systems as with the neat OPC. That is, at 21°C the rate of heat output was approximately half that of the 35°C sample and peak II was displaced and broadened, i.e. retardation occurred. Again, the total heat results mirrored those of the neat cements. It was not clear if the addition of 5% $SnCl_2$ at 21°C (curve C) caused retardation of set or whether it killed the set completely. There appeared to be some evidence for a peak II (Fig. 4.2.34) but this was not conclusive. However, from Table 4.2.10 it can be seen that there was a value for Q_m which occurred at 20 hours which correlates with the possible peak II observed in Figure 4.2.34. It could, therefore, be concluded that the $SnCl_2$ did not kill the set but merely caused a classic retardation which would also account for the decrease in total heat output. The total heat result (Fig. 4.2.35 and Table 4.2.11) indicated a much reduced output overall and, also, a more steady increase as opposed to the sharp rise observed in curves A and B which was indicative of the occurrence of peak II.

The results for the addition of 0.1% $SnCl_4$ (Figs. 4.2.36 and 4.2.37) mirrored the effects caused by the addition of 0.1% $SnCl_2$. The rate of heat output of peak II at 35°C (A) was slightly higher than that observed for 0.1% $SnCl_2$ although not substantially different.

Cement Systems	**t_m/hrs (35°C)**	**Q_m/ Wkg^{-1}**	**Q_m (normalised)**	**t_m/hrs (21°C)**	**Q_m/ Wkg^{-1}**	**Q_m (normalised)**
OPC	4.8	7.26	-	9.2	3.18	-
E	5.3	7.86	-	10.3	3.64	-
G	5.1	9.15	-	7.8	3.95	-
M	-	-	-	0.9	1.85	-
N	-	-	-	20	1.12	-
O	-	-	-	3.0	4.20	-

Table 4.2.10 Values of t_m and Q_m for Selected OPC Systems at 21°C & 35°C

		Total Heat Evolved/$kJkg^{-1}$ @ 21°C					
Cement System	**Q_m/ Wkg^{-1}**	**@ Q_m**	**3 hrs**	**6 hrs**	**12 hrs**	**24 hrs**	**70 hrs**
OPC	3.15	47.76	3.70	16.09	78.97	150.66	217.03
E	3.64	58.82	3.45	12.43	80.12	157.71	222.52
G	3.95	49.40	4.90	25.10	102.42	166.60	221.94
M	1.85	7.97	18.44	26.89	36.55	47.02	63.72
N	1.12	61.42	11.36	19.42	33.29	77.33	169.12
O	4.20	30.66	30.66	64.77	95.93	124.08	162.21

Table 4.2.11 Total Heat Values for Selected OPC Systems at 21°C

4.2.6.2 3:1 BFS:OPC Systems

The effect of a reduction in temperature causing a retardation of set as seen in the OPC system (section 4.2.6.1) was again apparent for the neat 3:1 BFS:OPC system (Figs. 4.2.38 and 4.2.39). Both the rate and total heat outputs were reduced substantially at 21°C. However, the occurrence of a peak S, seen clearly in curve A, did not happen at 21°C (B). This was another indication of the retardation of set as, it could be concluded that, the slag fraction had not started to hydrate significantly at 21°C.

Figures 4.2.40 and 4.2.41 show the effect of the addition of 0.1% $SnCl_2$ at 35°C (A) and 21°C (B) and 5% $SnCl_2$ at 21°C (C). Again it is immediately apparent that there was a retardation of set at the 0.1% addition level. This was clear from both the rate and total heat output data. However, when considering the 5% addition it was not clear if the peak was a peak II or if it was a peak I although the shape of the overall curve was similar to that of A (0.1% $SnCl_2$ at 35°C) with a definite peak S. When considering the values of t_m and Q_m (Table 4.2.12) and the total heat values (Table 4.2.13) it would appear that there was a peak II with a peak S and it could, therefore, be concluded that the system was accelerated. The value of Q_m was approximately the same as the neat cement but it occurred at a much earlier time. Another interesting feature was the definite split into two peaks observed at 21°C with the addition of 0.1% $SnCl_2$. The effect of temperature on the 0.1% $SnCl_4$ addition (Figures 4.2.42 and 4.2.43) mirrored that of the neat cement. That is, classic retardation and a less obvious peak S at 21°C (B).

Cement Systems	t_m/hrs (35°C)	Q_m/ Wkg^{-1}	Q_m (normalised)	t_m/hrs (21°C)	Q_m/ Wkg^{-1}	Q_m (normalised)
3:1 BFS	4.9	2.41	9.64	10.8	1.13	4.52
E	6.0	2.34	9.36	10.2	0.94	3.76
G	4.4	2.45	9.8	8.8	1.23	4.92
M	-	-	-	3.4	0.48	1.92
N	-	-	-	1.1	1.10	4.40
O	-	-	-	1.1	0.99	3.96

Table 4.2.12 Values of t_m and Q_m for Selected 3:1 BFS:OPC Systems at 21°C & 35°C

		Total Heat Evolved/$kJkg^{-1}$ @ 21°C					
Cement System	Q_m/ Wkg^{-1}	@ Q_m	**3 hrs**	**6 hrs**	**12 hrs**	**24 hrs**	**70 hrs**
3:1BFS	1.13	24.50	1.21	7.41	29.00	54.75	101.67
E	0.94	14.69	1.01	4.35	19.13	45.69	86.23
G	1.23	21.22	2.28	9.82	32.55	59.72	105.87
M	0.48	8.34	7.66	12.26	18.40	24.14	13.40
N	1.10	1.57	7.87	15.78	26.60	37.72	64.91
O	0.99	7.97	13.20	17.85	24.18	32.22	48.10

Table 4.2.13 Total Heat Values for Selected 3:1 BFS:OPC Systems at 21°C

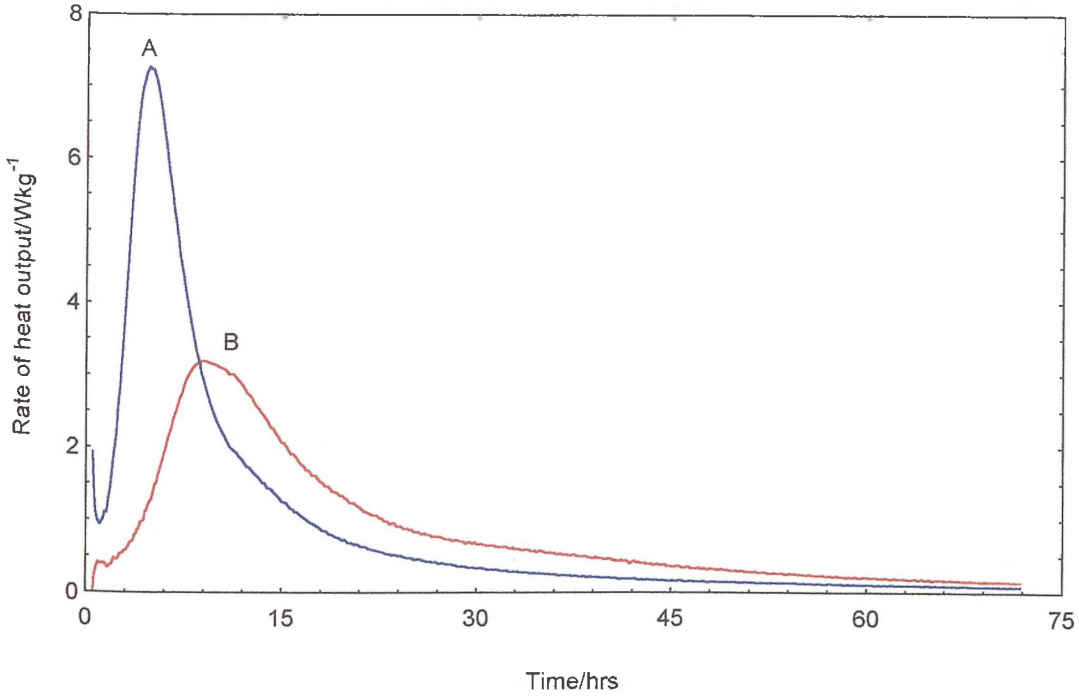

Figure 4.2.32 Rate of heat output for OPC at 35°C (A) & 21°C (B)

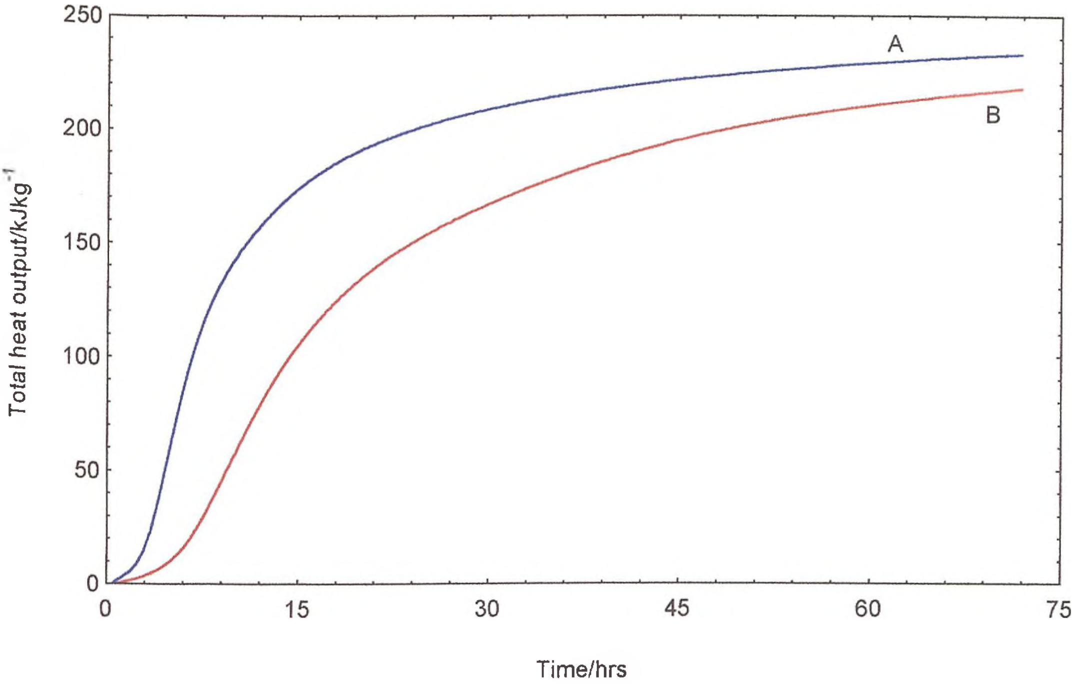

Figure 4.2.33 Total heat output for OPC at 35°C (A) & 21°C (B)

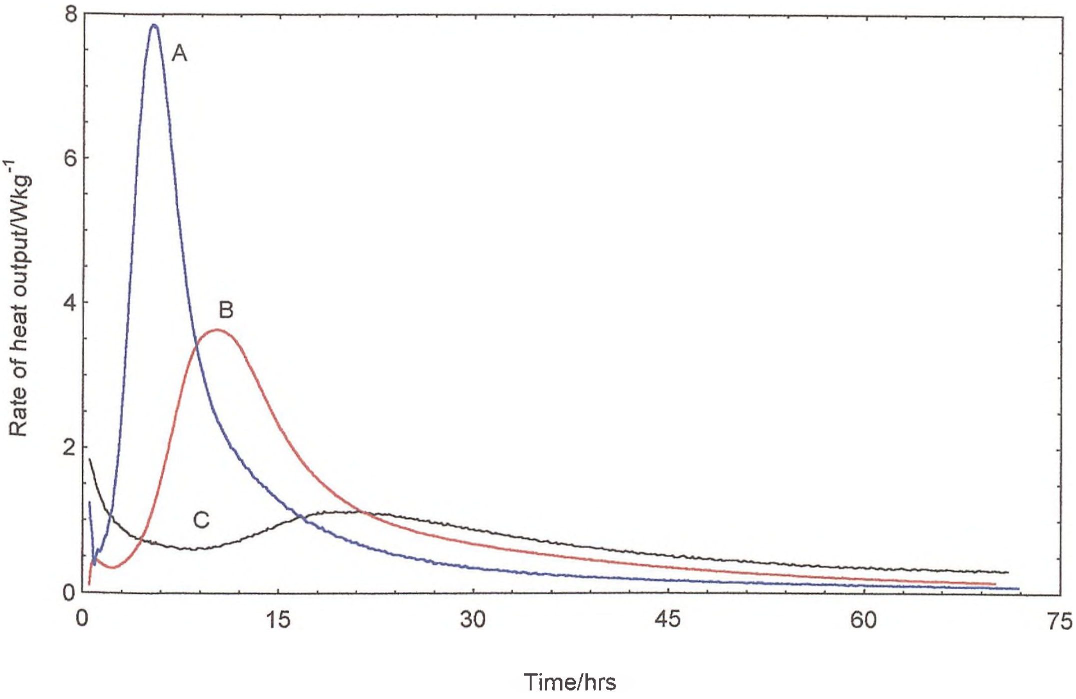

Figure 4.2.34 Rate of heat output for OPC + 0.1% $SnCl_2$ at 35°C (A) and 21C (B) & + 5% $SnCl_2$ at 21°C (C)

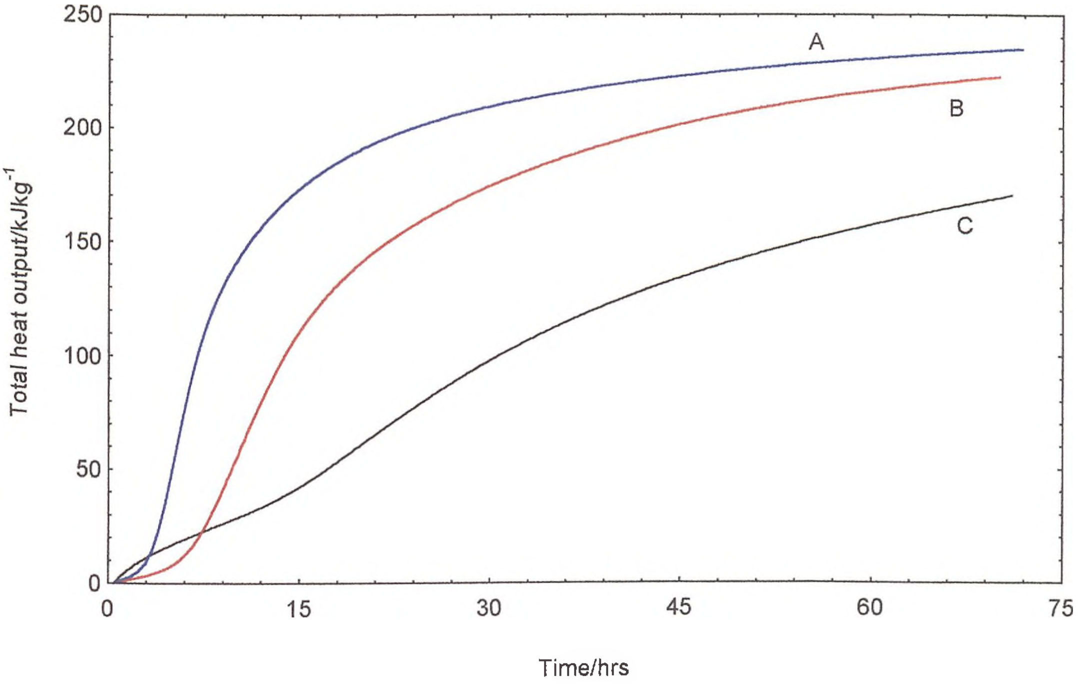

Figure 4.2.35 Total heat output for OPC + 0.1% $SnCl_2$ at 35°C (A) and 21C (B) & + 5% $SnCl_2$ at 21°C (C)

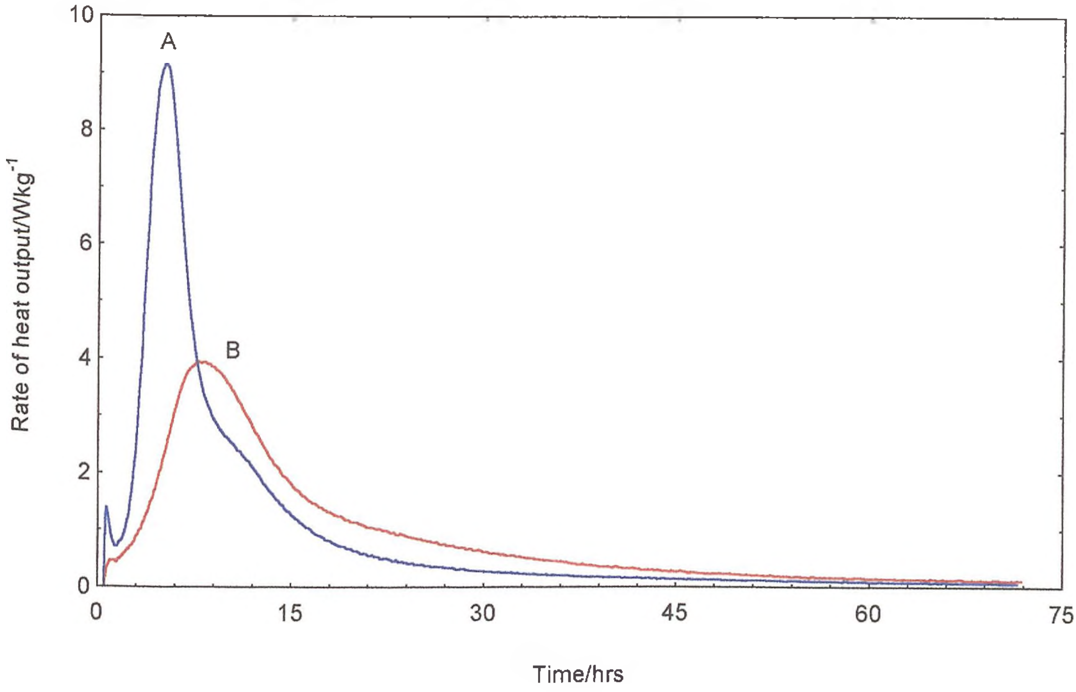

Figure 4.2.36 Rate of heat output for OPC + 0.1% $SnCl_4$ at 35°C (A) & 21°C (B)

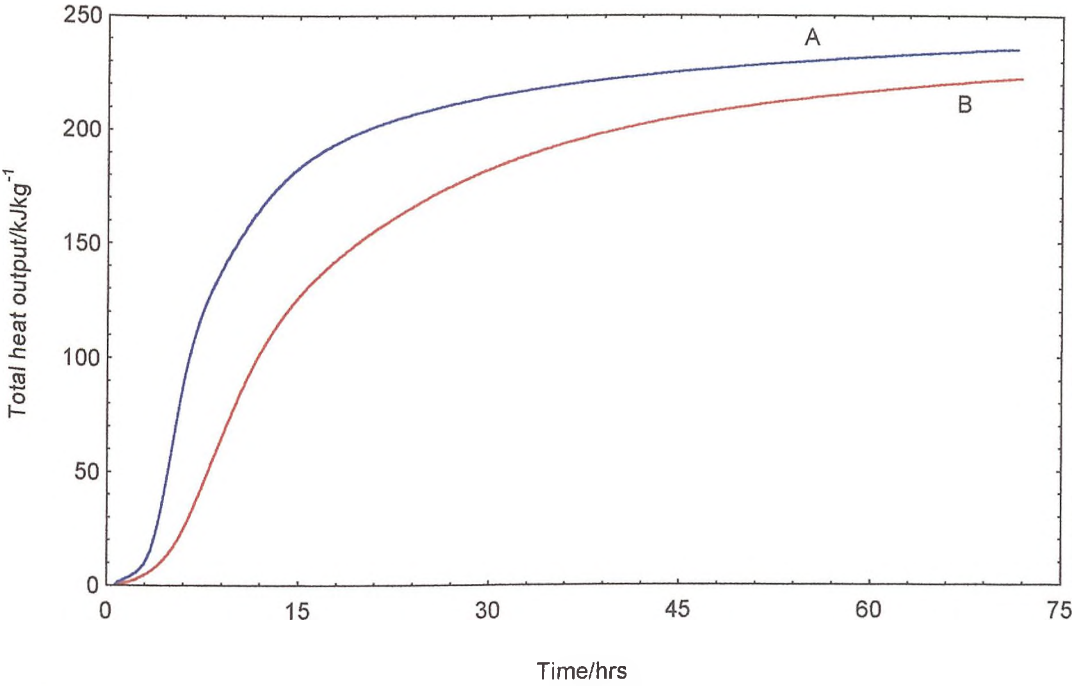

Figure 4.2.37 Total heat output for OPC + 0.1% $SnCl_4$ at 35°C (A) & 21°C (B)

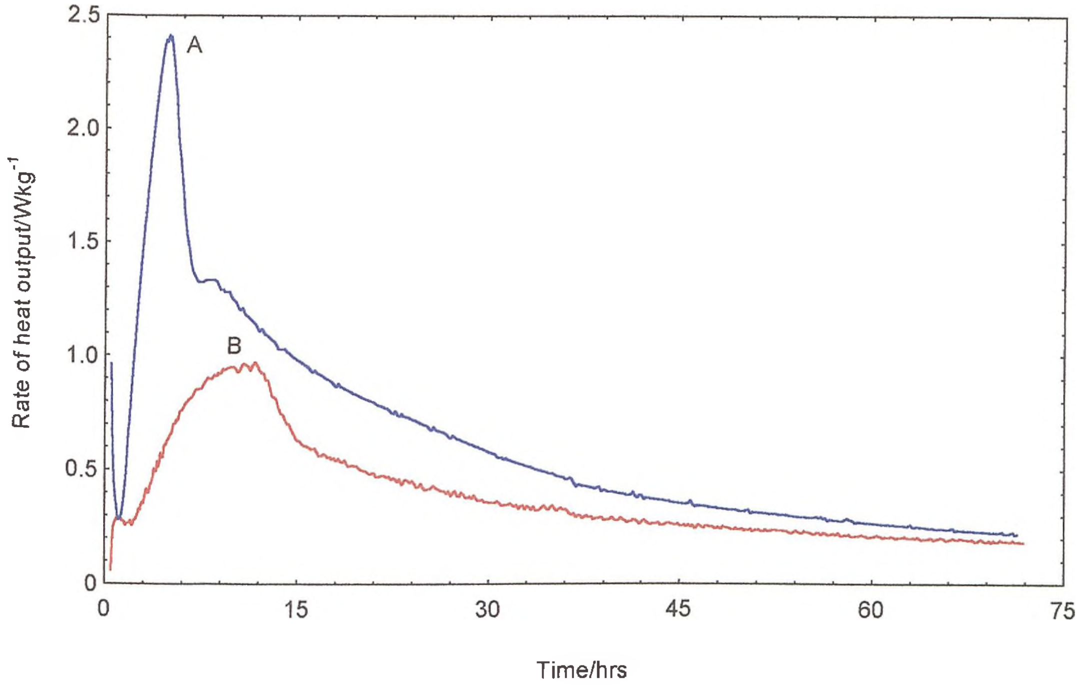

Figure 4.2.38 Rate of heat output for 3:1 BFS:OPC at 35°C (A) & 21°C (B)

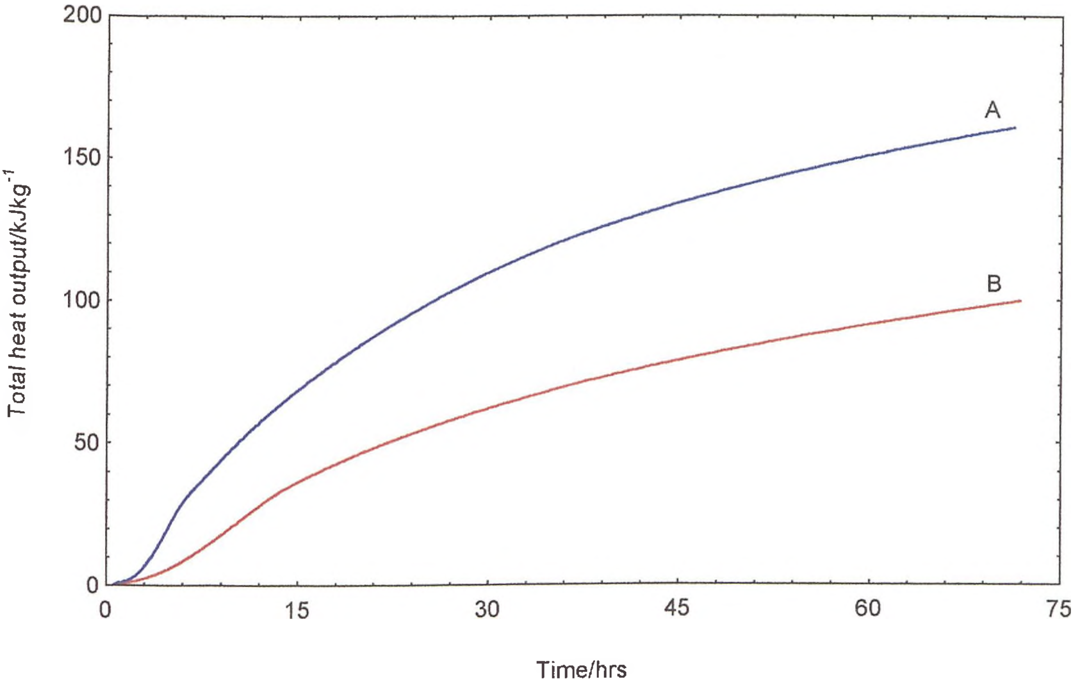

Figure 4.2.39 Total heat output for 3:1 BFS:OPC at 35°C (A) & 21°C (B)

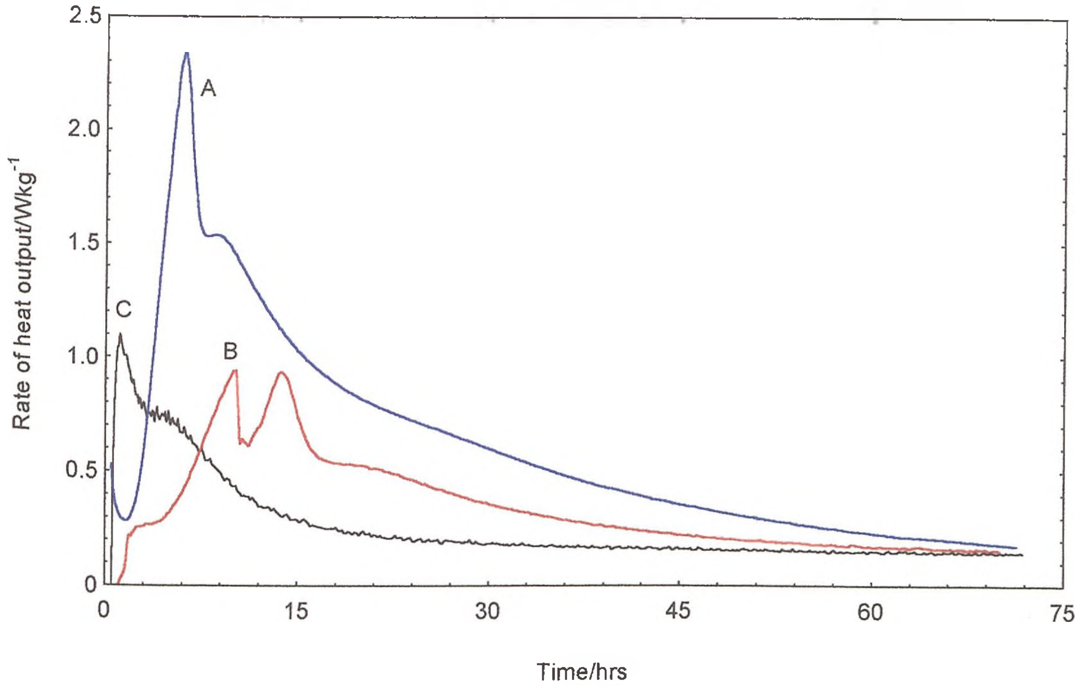

Figure 4.2.40 Rate of heat output for 3:1 BFS:OPC + 0.1% $SnCl_2$ at 35°C (A) and 21°C (B) & + 5% $SnCl_2$ at 21°C (C)

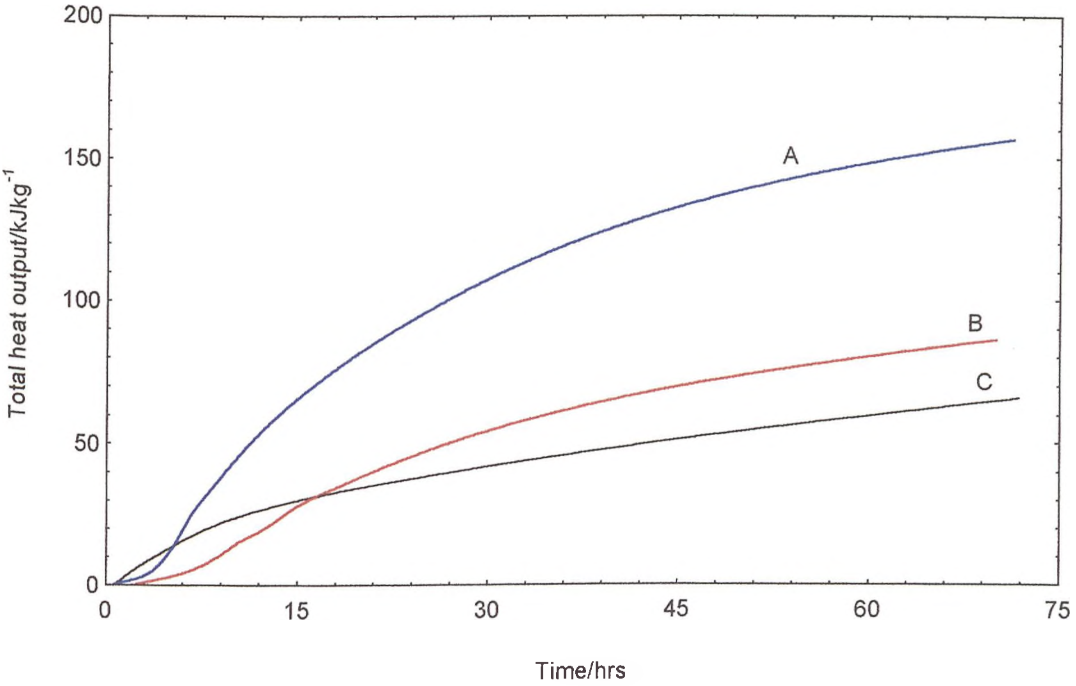

Figure 4.2.41 Total heat output for 3:1 BFS:OPC + 0.1% $SnCl_2$ at 35°C (A) and 21°C (B) & + 5% $SnCl_2$ at 21°C (C)

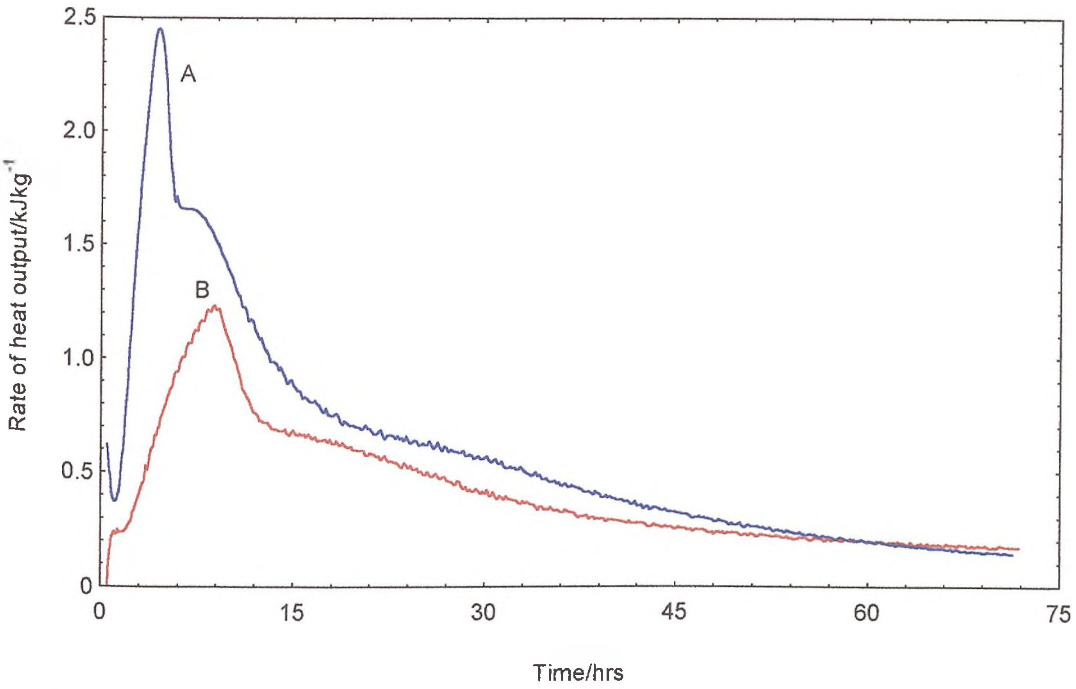

Figure 4.2.42 Rate of heat output for 3:1 BFS:OPC + 0.1% $SnCl_4$ at 35°C (A) & 21°C (B)

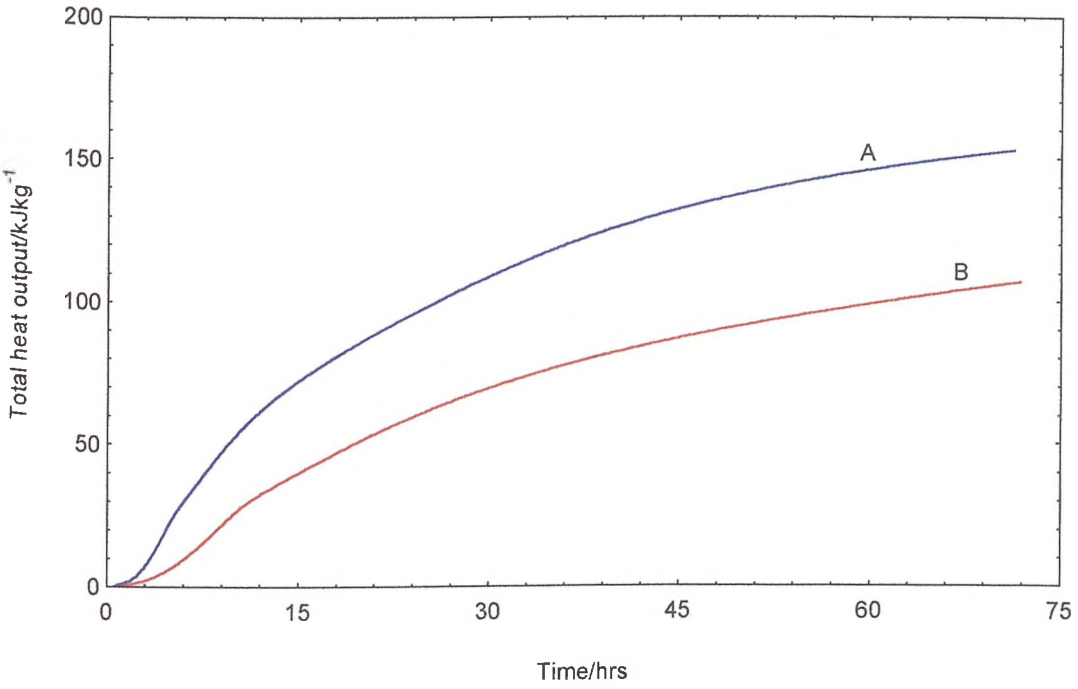

Figure 4.2.43 Total heat output for 3:1 BFS:OPC + 0.1% $SnCl_4$ at 35°C (A) & 21°C (B)

4.2.6.3 9:1 BFS:OPC Systems

Both the neat cement system (Figs. 4.2.44 and 4.2.45) and the 0.1% $SnCl_2$ system (Figs. 4.2.46 and 4.2.47) show classic retardation of set and, as with the 3:1 BFS:OPC system, a less obvious peak S at 21°C. The tin system was interesting in that at 35°C peak S was greater the peak II. This was then reversed at 21°C although peak S was quite broad. The total heat values at 21°C were significantly less than at 35°C (Tables 4.2.14 and 4.2.15). However, there was no particular trend, such as the one observed in the 100% OPC system, between the temperatures for the t_m and Q_m values.

Cement Systems	**t_m/hrs (35°C)**	**Q_m/ Wkg^{-1}**	**Q_m (normalised)**	**t_m/hrs (21°C)**	**Q_m/ Wkg^{-1}**	**Q_m (normalised)**
9:1 BFS	4.0	1.29	11.61	9.0	0.55	4.95
E	10.3	1.08	9.72	12.2	0.54	4.86
G	9.5	0.95	8.55	6.5	0.51	4.59
M	-	-	-	0.7	3.80	34.20
N	-	-	-	-	-	-
O	-	-	-	1.2	1.10	9.90

Table 4.2.14 Values of t_m and Q_m for Selected 9:1 BFS:OPC Systems at 21°C & 35°C

		Total Heat Evolved/kJkg^{-1} @ 21°C					
Cement System	**Q_m/ Wkg^{-1}**	**@ Q_m**	**3 hrs**	**6 hrs**	**12 hrs**	**24 hrs**	**70 hrs**
9:1 BFS	0.55	9.20	1.29	4.23	14.71	31.48	66.86
E	0.54	11.76	1.66	3.58	11.44	31.74	78.38
G	0.51	6.54	1.86	5.63	13.94	29.23	81.04
M	3.80	2.68	18.93	22.77	24.36	26.23	28.28
N	-	-	-	-	-	-	-
O	1.10	7.79	13.45	19.23	26.15	33.86	47.26

Table 4.2.15 Total Heat Values for Selected 9:1 BFS:OPC Systems at 21°C

4.2.6.4 3:1 PFA:OPC Systems

Again, as with the previous systems, the effect of lowering temperature was to decrease the heat output (both rate and total) and also to broaden peak II at 21°C, i.e. retardation of set (Figures 4.2.48 and 4.2.49). The addition of 0.1% $SnCl_2$ to the system at 21°C appeared to have little effect with respect to the neat cement at the same temperature. The value of Q_m was very similar for both the neat cement and the 0.1% $SnCl_2$ system (E) although t_m was reduced slightly for the tin system (Table 4.2.16). The total heat evolved for the two systems was also very similar from 3 hours to 70 hours (Table 4.2.17). Again, as for 9:1 BFS:OPC, there was no trend in the values of t_m and Q_m between the two temperatures.

Cement Systems	t_m/hrs (35°C)	Q_m/ Wkg^{-1}	Q_m (normalised)	t_m/hrs (21°C)	Q_m/ Wkg^{-1}	Q_m (normalised)
3:1 PFA	10.3	1.48	5.92	17.8	0.76	3.04
E	10.2	2.02	8.08	12.3	0.82	3.28
G	7.5	1.46	5.84	15.5	0.93	3.72
M	-	-	-	1.0	0.76	3.04
N	-	-	-	0.9	1.09	4.36
O	-	-	-	1.3	1.20	4.80

Table 4.2.16 Values of t_m and Q_m for Selected 3:1 PFA:OPC Systems at 21°C & 35°C

		Total Heat Evolved/$kJkg^{-1}$ @ 21°C					
Cement System	Q_m/ Wkg^{-1}	@ Q_m	3 hrs	6 hrs	12 hrs	24 hrs	70 hrs
3:1PFA	0.76	30.82	2.19	4.54	15.80	45.29	72.67
E	0.82	19.33	1.93	4.51	18.35	46.46	72.28
G	0.93	30.77	1.83	4.91	19.65	48.85	75.45
M	0.76	0.54	4.14	6.81	9.77	12.63	16.71
N	1.09	0.96	6.35	10.47	15.81	22.33	38.73
O	1.20	9.57	14.89	20.44	26.43	30.18	22.29

Table 4.2.17 Total Heat Values for Selected 3:1 PFA:OPC Systems at 21°C

In all systems it appears that reducing the temperature increased the time it took for the cement to set and also reduced the amount of heat produced. However, in the examples chosen, the effect of temperature alone was not sufficient to retard the set sufficiently to reach a point where it would be impractical to use.

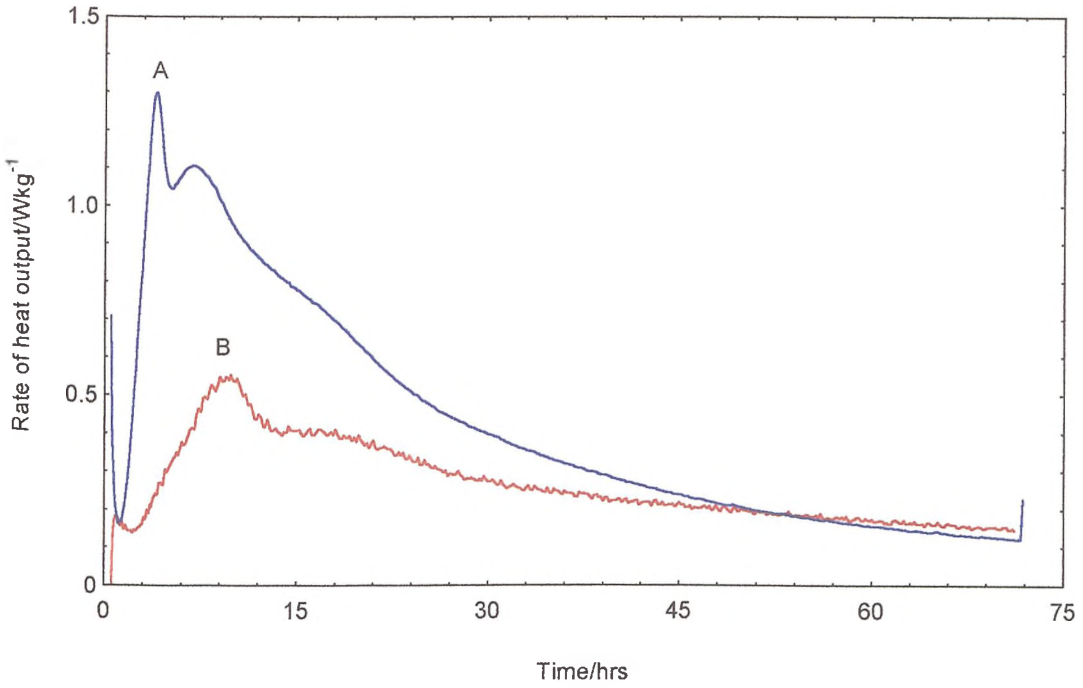

Figure 4.2.44 Rate of heat output for 9:1 BFS:OPC at 35°C (A) & 21°C (B)

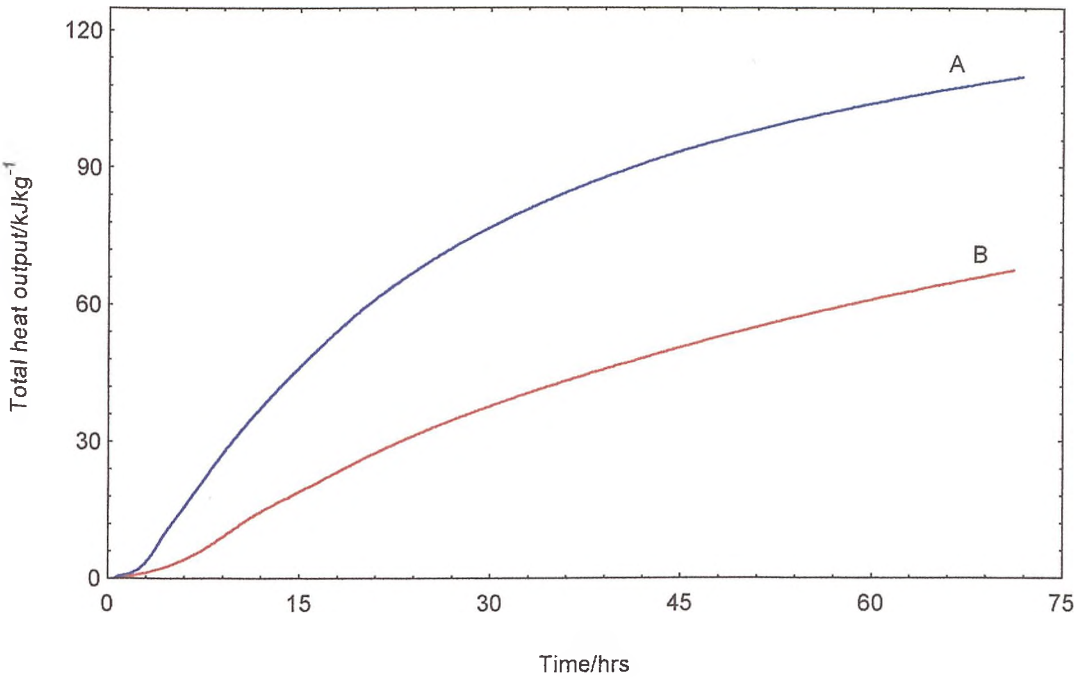

Figure 4.2.45 Total heat output for 9:1 BFS:OPC at 35°C (A) & 21°C (B)

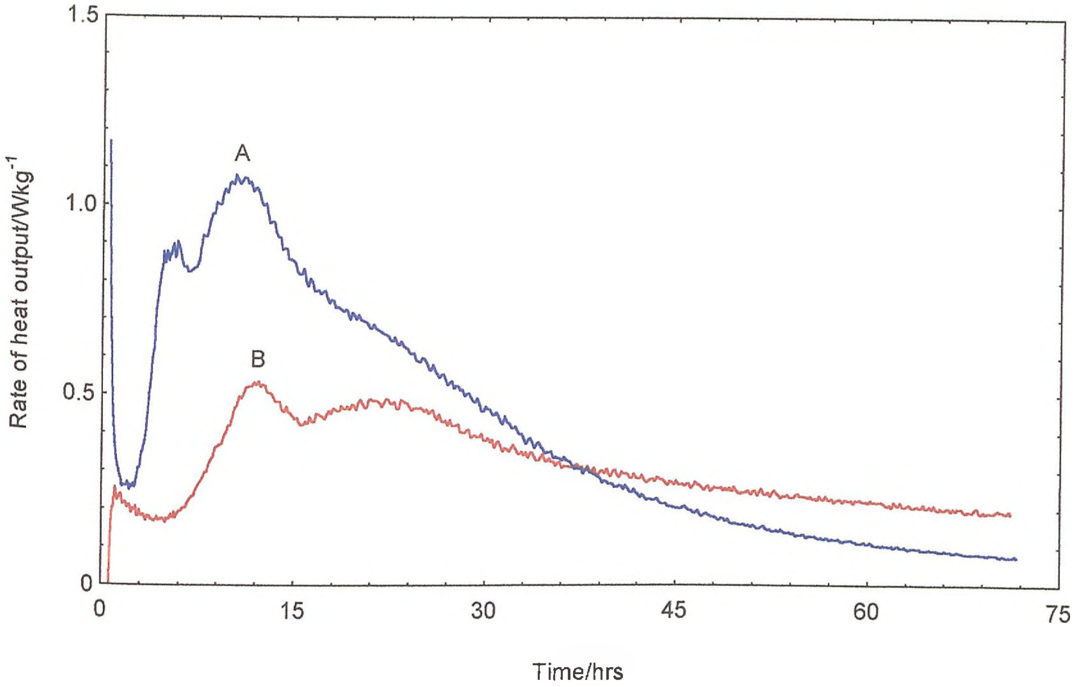

Figure 4.2.46 Rate of heat output for 9:1 BFS:OPC + 0.1% $SnCl_2$ at 35°C (A) & 21°C (B)

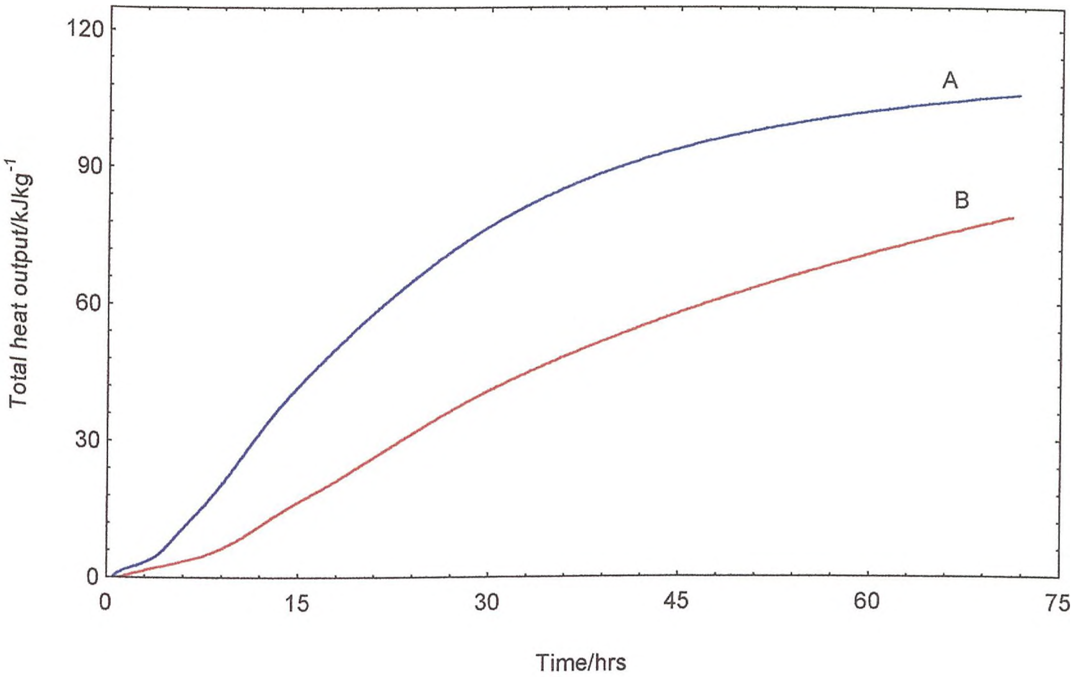

Figure 4.2.47 Total heat output for 9:1 BFS:OPC + 0.1% $SnCl_2$ at 35°C (A) & 21°C (B)

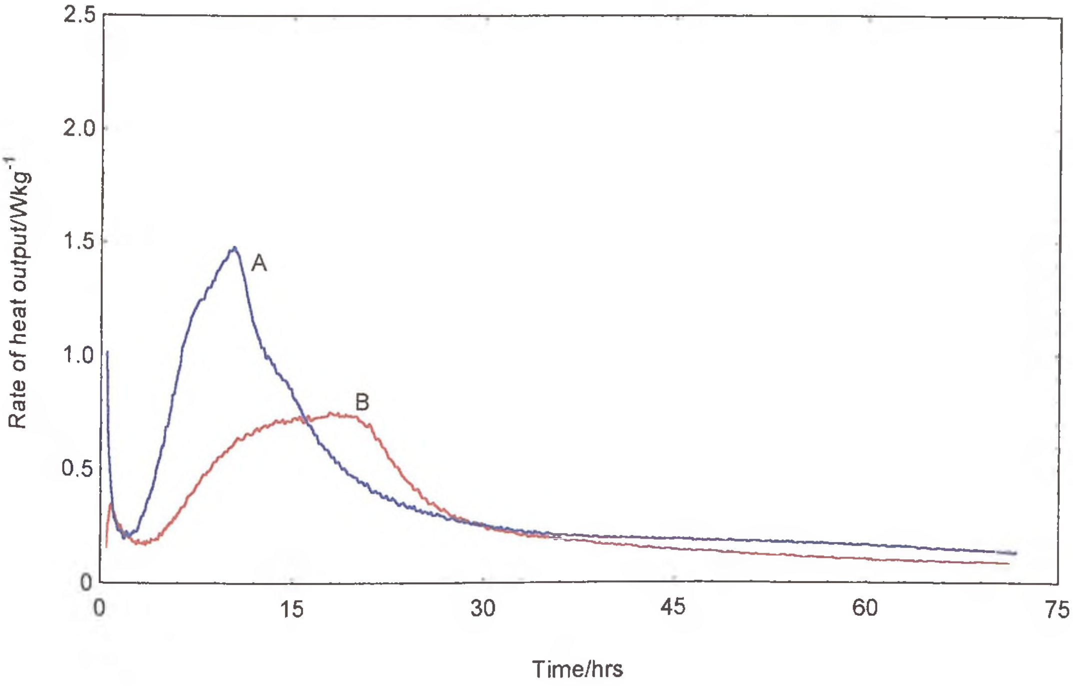

Figure 4.2.48 Rate of heat output for 3:1 PFA:OPC at 35°C (A) & 21°C (B)

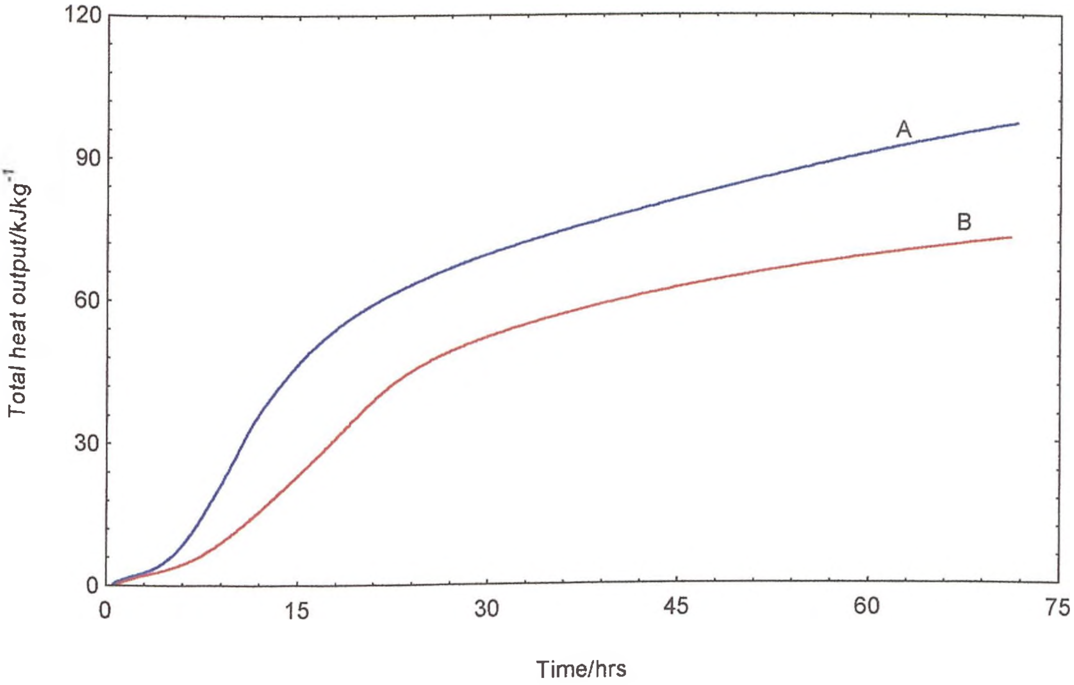

Figure 4.2.49 Total heat output for 3:1 PFA:OPC at 35°C (A) & 21°C (B)

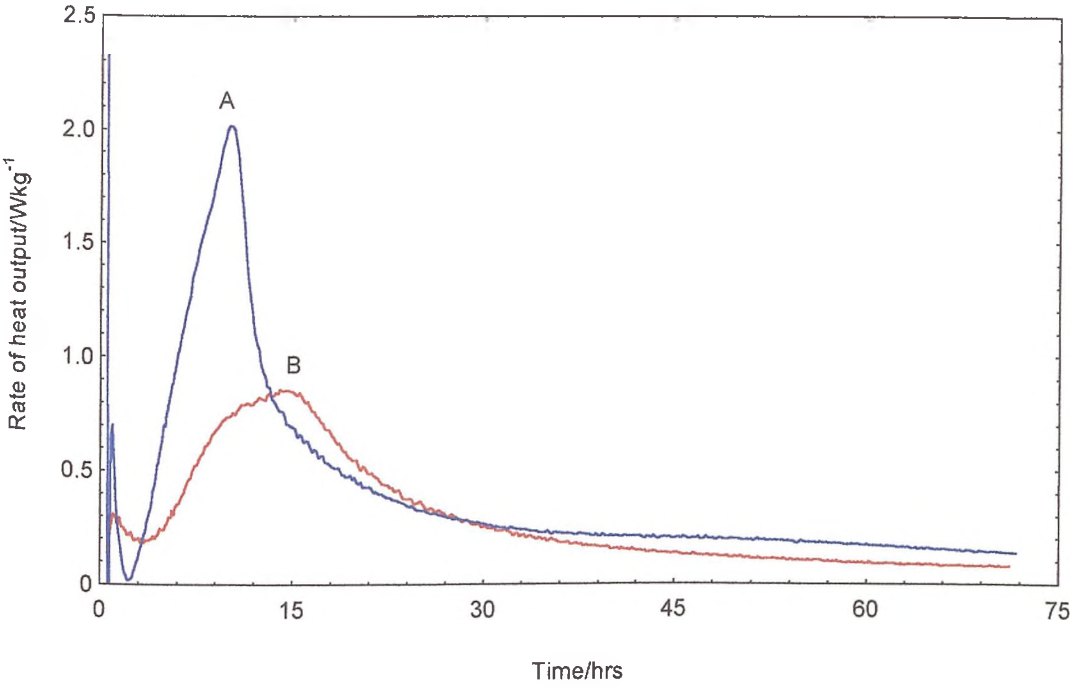

Figure 4.2.50 Rate of heat output for 3:1 PFA:OPC + 0.1% SnCl$_2$ at 35°C (A) & 21°C (B)

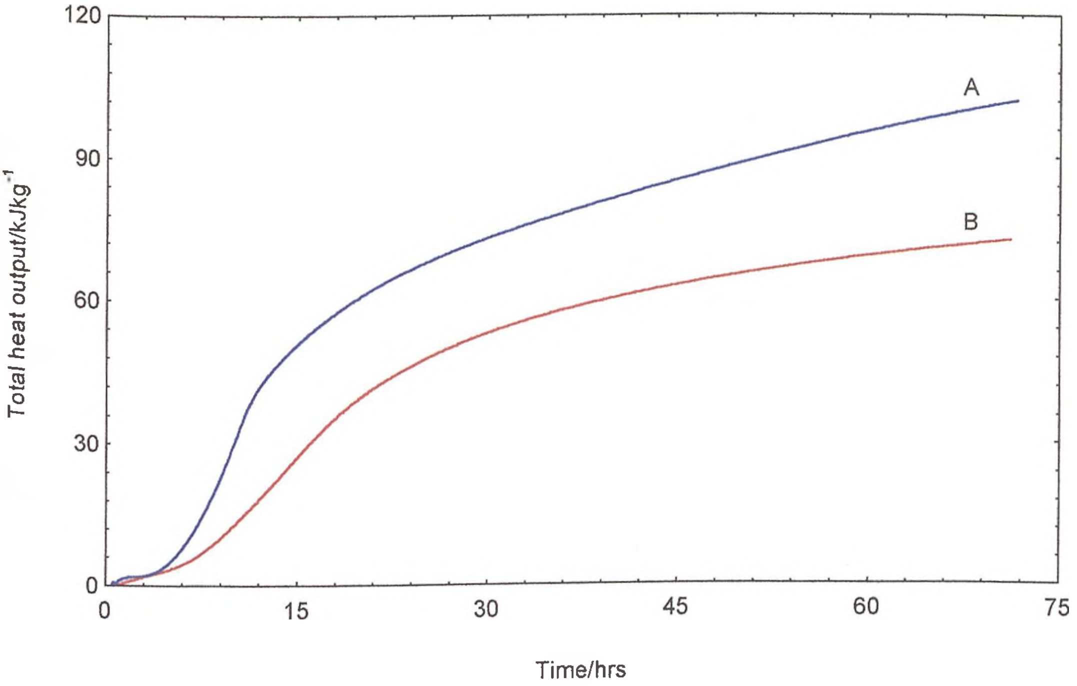

Figure 4.2.51 Total heat output for 3:1 PFA:OPC + 0.1% SnCl$_2$ at 35°C (A) & 21°C (B)

4.3 X-RAY DIFFRACTION

X-ray diffraction has been used to study the effects of the addition of inorganic metal salts on the hydration phases formed. The sample preparation was described in section 3.3.2 and the main aim of this study was to attempt to identify both the standard and non-standard hydration products formed.

X-ray diffraction is a very useful tool for the investigation of the crystal structure of materials. The technique began with the discovery by von Laue in 1912 that crystals diffract x-rays with the manner of diffraction revealing the structure of the crystal.[56] The technique is now not only used for structure determination, but also for chemical analysis, stress measurement and the orientation of one crystal or the ensemble of orientations in a polycrystalline material.

There are various methods which can be utilised, but the one used for this project was powder x-ray diffraction in which the sample was ground to a very fine powder (<75μm) and placed in a beam of x-rays from a copper source. The computer then plots intensity of the diffracted beam against the angle between the transmitted and diffracted beam (2θ). The d-spacings are calculated to allow identification of the phases and this is done by utilising Bragg's Law which is:

$$\lambda = 2d \sin\theta \qquad \text{Equation 4.1}$$

Where: λ = wavelength of copper (1.541838Å)

d = d-spacing

θ = diffraction angle.

Abbreviations have been used to label the x-ray diffraction traces and the following key gives an explanation of those abbreviations.

Key To XRD Traces:

CH = Calcium hydroxide ($Ca(OH)_2$)
CC = Calcium carbonate ($CaCO_3$)
E = Ettringite ($Ca_6Al_2(OH)_{12}(SO_4)_3.26H_2O$)
G = Gehlenite ($Ca_2Al(Al,Si)_2O_7$)
Q = Quartz (SiO_2)
M = Mullite ($3Al_2O_3.2SiO_2$)
C_3S = Tricalcium silicate (Ca_3SiO_5)
FS = Friedel's salt ($Ca_3Al_2O_6.CaCl_2.10H_2O$)
X = Calcium hydroxo stannate ($CaSn(OH)_6$)
Z = Calcium zincate ($CaZn_2(OH)_6.2H_2O$)

The tables of d-spacings included in this section show the d-spacing from the JCPDS card system (under the column headed JCPDS), the experimental d-spacing as measured from x-ray diffraction (d) (both of which are measured in angstroms (Å)) and the raw intensity of the peaks measured from the x-ray diffraction traces (I). The 100% peak has also been indicated on these tables to illustrate where a phase of particular interest was the strongest peak measured. If there are no peaks indicated for a particular trace, this was because a different phase to those of interest was the largest peak. Some of the d-spacings quoted for the different phases overlap with each other. For example, the third strongest calcium hydroxide peak at around 1.93Å overlaps with the second strongest gehlenite peak at around 1.92Å. The outcome of this is that on occasion the intensity of a peak may appear to increase even thought there is no evidence for it on the XRD trace due to there being increased amounts of the other phase present. The y-axes on the figures in this section vary depending on the systems being illustrated. However, all traces which are compared to each other have the same y-axis. That is, each set of four figures will be compared and, therefore, have the same axes.

4.3.1 Neat Cement Systems

Figures 4.3.1 - 4.3.4 show the neat cement systems after 3, 28, 90 and 180 days hydration with the exception of the 9:1 BFS:OPC system which has 7 day data instead of 3 day. These illustrate the standard hydration products expected from the different cement systems across the age range. Figures 4.3.1 and 4.3.2 show 100% OPC and 3:1 PFA:OPC, respectively. It can be seen that there is a marked difference in the hydration products of the two cement systems. In the OPC system the standard hydration products were: calcium hydroxide (CH), calcium carbonate (CC) and ettringite (E), whereas for the 3:1 PFA:OPC system they were: calcium carbonate (CC), quartz (Q) and mullite (M). Table 4.3.1 shows the d-spacings and the angles of the most frequently occurring hydration phases for all cement systems for ease of reference. The strongest three peaks were referenced and the angles were calculated using Bragg's Law (Equation 4.1). Figure 4.3.1 shows how the hydration products of neat OPC changed with time. It can be seen that, as expected, there was a decrease of calcium hydroxide with time whilst the calcium carbonate increased up to 28 days hydration and then decreased to a steady level after 90 days hydration (Table 4.3.2). This was because of the carbonation of the calcium hydroxide which occurred due to the samples being cured in air. In addition to this the amount of tricalcium silicate (C_3S) decreased over time (again as expected). There was still some ettringite in evidence after 180 days hydration which was not necessarily expected.

Figure 4.3.2 shows the development of the 3:1 PFA:OPC systems with time and, as with the OPC system, the differences in the hydration products can be clearly seen. The main change was in the amount of calcium carbonate produced as there was a substantial increase between 3 and 180 days indicative of a relatively high carbonation process. It can also be seen that the amount of quartz and mullite decreased over the same time period. The decrease in the amount of quartz present is clearly illustrated in table 4.3.3. The occurrence of the quartz peak with the two mullite peaks at around $25°2\theta$ was a classic product of the PFA and both phases were present in the original PFA.

Phase	**d-spacing/Å**[1]	**Angle/°2θ**
CH	2.63	34.09
	4.90	18.10
	1.93	47.09
CC	3.04	29.38
	2.29	39.35
	2.10	43.07
E	9.73	9.09
	5.61	15.80
	3.88	22.92
G	2.86	31.28
	1.93	47.09
	1.82	50.12
Q	3.34	26.69
	4.26	20.85
	1.82	50.12

Table 4.3.1 Expected d-Spacings and Angles of Common Hydration Phases

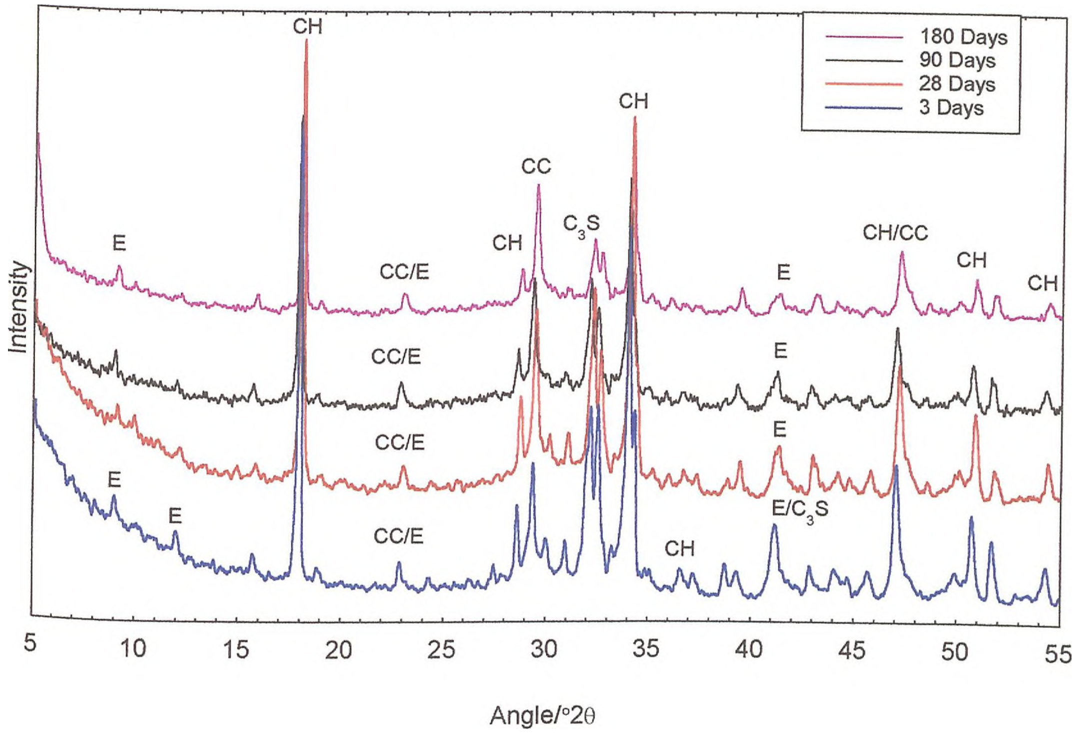

Figure 4.3.1 100% OPC

Days		**3**		**28**		**90**		**180**	
	JCPDS	**d**	**I**	**d**	**I**	**d**	**I**	**d**	**I**
CH	2.63	2.64	810	2.62	835	2.64	509	2.62	391
	4.90	4.94	1022*	4.91	999*	4.94	636*	4.90	427*
	1.93	1.93	325	1.93	329	1.93	206	1.93	164
CC	3.04	3.04	325	3.03	441	3.04	303	3.03	296
	2.29	2.29	103	2.28	129	2.29	86	2.28	84
	2.10	2.11	115	2.10	126	2.11	87	2.10	71
E	9.73	9.81	255	9.69	240	9.81	151	9.69	125
	5.61	5.63	139	5.60	123	5.63	86	5.60	67
	3.88	3.89	123	3.86	121	3.89	90	3.87	72

* = 100% peak A = absent

Table 4.3.2 d-Spacings and Raw Intensities for Neat OPC

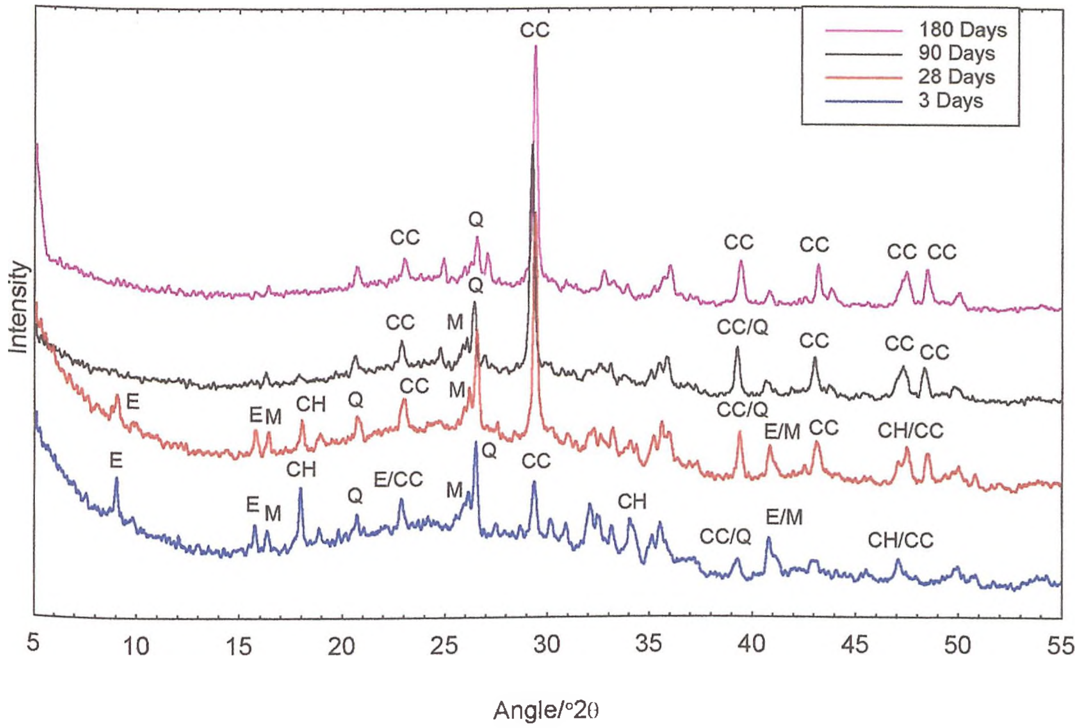

Figure 4.3.2 3:1 PFA:OPC

Days		**3**		**28**		**90**		**180**	
	JCPDS	**d**	**I**	**d**	**I**	**d**	**I**	**d**	**I**
CH	2.63	2.63	199	2.63	160	A	A	A	A
	4.90	4.93	267	4.92	206	A	A	A	A
	1.93	1.93	118	1.93	119	A	A	A	A
CC	3.04	3.04	277	3.04	630*	3.05	568*	3.04	585*
	2.29	2.29	117	2.29	178	2.29	151	2.29	129
	2.10	2.10	114	2.10	158	2.10	131	2.10	122
E	9.73	9.77	287	9.75	258	A	A	A	A
	5.61	5.63	179	5.63	186	A	A	A	A
	3.88	3.88	244	3.87	252	3.88	169	3.86	138
Q	3.34	3.36	359	3.35	390	3.37	247	3.35	180
	4.26	4.28	212	4.28	214	4.30	138	4.27	122
	1.82	1.82	105	1.82	110	A	A	1.82	68

* = 100% peak A = absent

Table 4.3.3 d-Spacings and Raw Intensities for Neat 3:1 PFA:OPC

Figures 4.3.3 and 4.3.4 show the x-ray traces for the two slag cements (3:1 and 9:1 BFS:OPC respectively). Note that there is no 3 day data for the 9:1 BFS:OPC system but 7 day data are provided instead. This was done for consistency as systems with metal salt additions have no 3 day data due to the cements being so retarded that it was not possible to grind the samples for investigation before 7 days hydration. The two systems had very similar hydration products, as would be expected. The main phases were: gehlenite (G), calcium carbonate (CC), calcium hydroxide (CH) and ettringite (E). Gehlenite is associated with the anhydrous slag, therefore, it would be expected that there would be more in the 9:1 BFS:OPC than the 3:1 BFS:OPC and that, in both systems, the amount present would remain constant or decrease as hydration proceeded. It can be seen to have decreased in both systems although in the 9:1 BFS:OPC system the gehlenite did not decrease substantially with time which could be due to less hydration having occurred in comparison to the 3:1 BFS:OPC system. This is confirmed in tables 4.3.4 (3:1 BFS:OPC) and 4.3.5 (9:1 BFS:OPC). It can clearly be seen that the gehlenite content of the 9:1 BFS:OPC system remained relatively constant in the two weaker peaks but decreased quite substantially between 7 and 180 days hydration in the strongest peak. However, in the 3:1 BFS:OPC system, all peaks decreased over time. The amount of calcium hydroxide present and the differences between the two slag systems with respect to this phase are also clearly illustrated and help to clarify the results shown in figures 4.3.3 and 4.3.4.

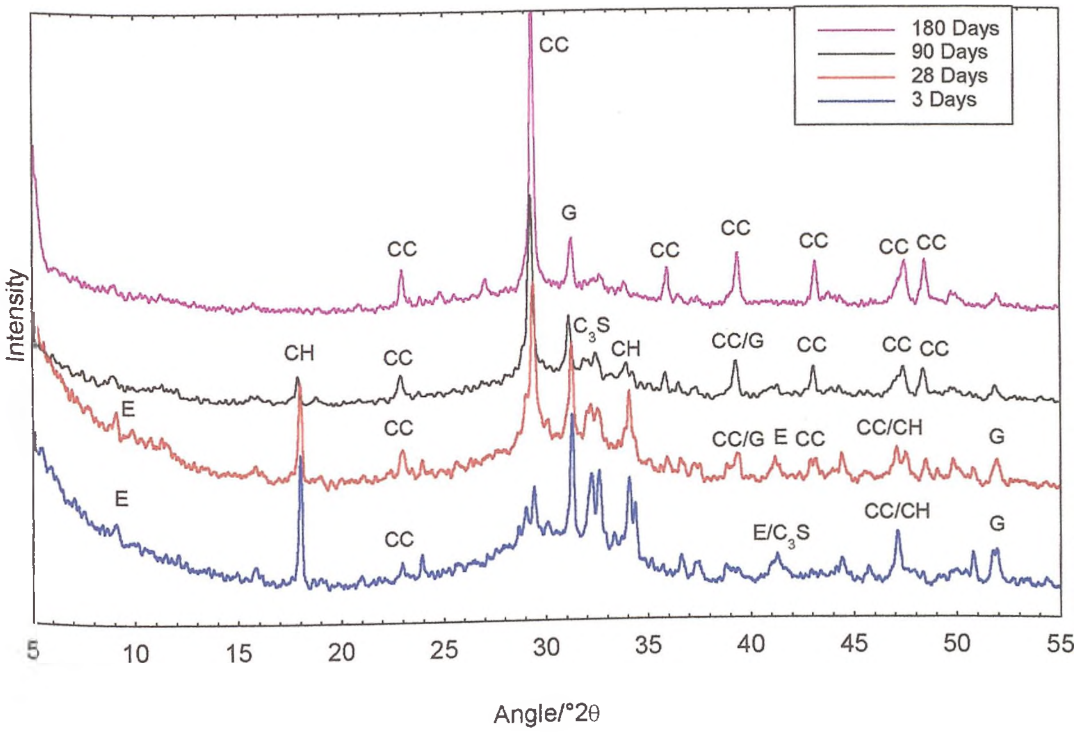

Figure 4.3.3 3:1 BFS:OPC

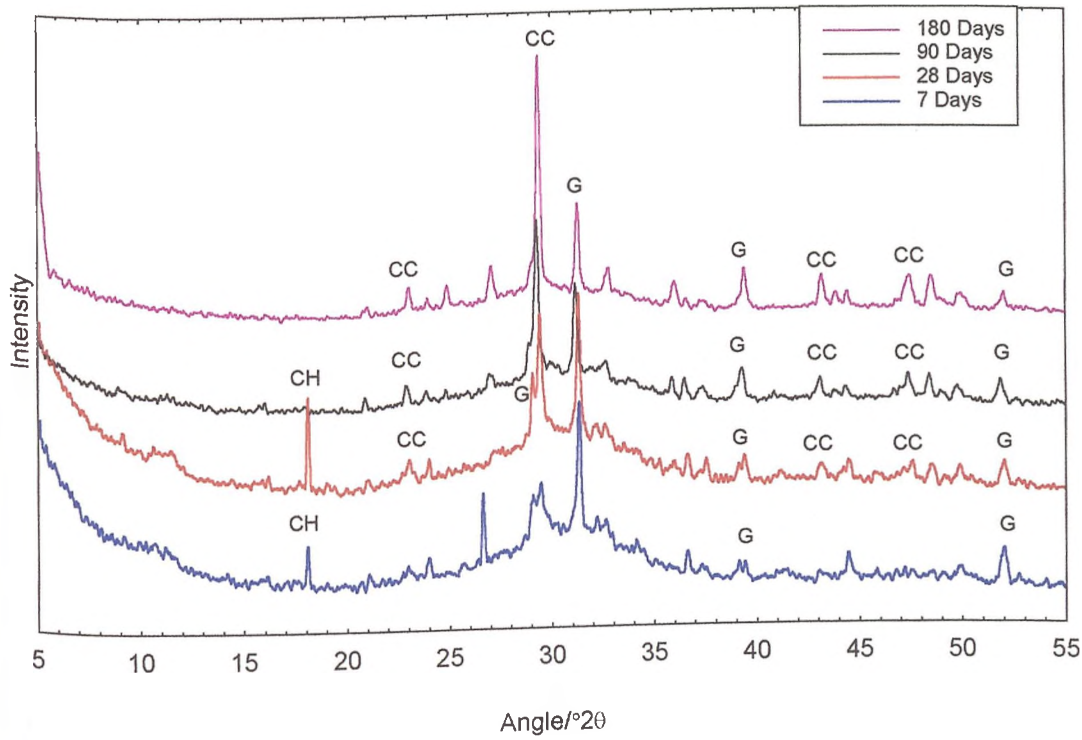

Figure 4.3.4 9:1 BFS:OPC

Days		**3**		**28**		**90**		**180**	
	JCPDS	**d**	**I**	**d**	**I**	**d**	**I**	**d**	**I**
CH	2.63	2.62	269	2.63	267	2.62	105	A	A
	4.90	4.90	382	4.92	294	4.96	107	A	A
	1.93	1.93	165	1.93	148	1.92	112	A	A
CC	3.04	3.03	308	3.03	493*	3.05	472*	3.04	686*
	2.29	2.30	115	2.29	136	2.29	125	2.29	183
	2.10	2.10	110	2.11	122	2.10	113	2.10	130
E	9.73	9.67	219	9.71	237	A	A	A	A
	5.61	5.57	113	5.58	126	A	A	A	A
	3.88	3.87	119	3.86	154	3.88	106	3.87	123
G	2.86	2.86	383	2.86	368	2.87	222	2.86	183
	1.93	1.93	165	1.93	148	1.92	112	1.91	131
	3.72	3.71	128	3.71	133	A	A	A	A

* = 100% peak A = absent

Table 4.3.4 d-Spacings and Raw Intensities for Neat 3:1 BFS:OPC

Days		**7**		**28**		**90**		**180**	
	JCPDS	**d**	**I**	**d**	**I**	**d**	**I**	**d**	**I**
CH	2.63	2.63	174	A	A	A	A	A	A
	4.90	4.91	178	4.90	280	A	A	A	A
	1.93	1.93	110	A	A	A	A	A	A
CC	3.04	3.03	295	3.03	439	3.05	428*	3.04	576*
	2.29	2.28	125	2.29	143	2.29	119	2.28	126
	2.10	2.10	104	2.09	124	2.10	99	2.10	110
E	9.73	A	A	9.71	211	A	A	A	A
	5.61	A	A	A	A	A	A	A	A
	3.88	3.87	133	3.86	149	3.88	100	A	A
G	2.86	2.85	458*	2.86	478*	2.87	297	2.86	266
	1.93	1.93	110	1.91	128	1.92	107	1.91	107
	3.72	3.71	148	3.70	150	A	A	A	A

* = 100% peak A = absent

Table 4.3.5 d-Spacings and Raw Intensities for Neat 9:1 BFS:OPC

The following four figures (4.3.5 - 4.3.8) show all four cement systems at the same age on the same axes. These data are the same as those shown in the previous four figures, but presented in this format they illustrate more clearly the differences between the cement systems as opposed to the dependence of these systems with time. Figure 4.3.5 shows the four cement systems after only 3 days hydration. The main difference was in the amount of calcium hydroxide present. Not surprisingly, the OPC system had significantly more than any other system due to there being substantially more Portland cement in this system compared to the composite cements and the 9:1 BFS:OPC system had virtually none at all as there was only 10% OPC present in this system and, therefore, it would be unlikely that there would be significant calcium hydroxide formation. It is also easy to see the different product phases for the different cements as mentioned earlier. For example, the mullite/quartz peak in the 3:1 PFA:OPC at approximately 25°2θ and the gehlenite peak at 31°2θ in the slag cements were clearly not present in the other systems.

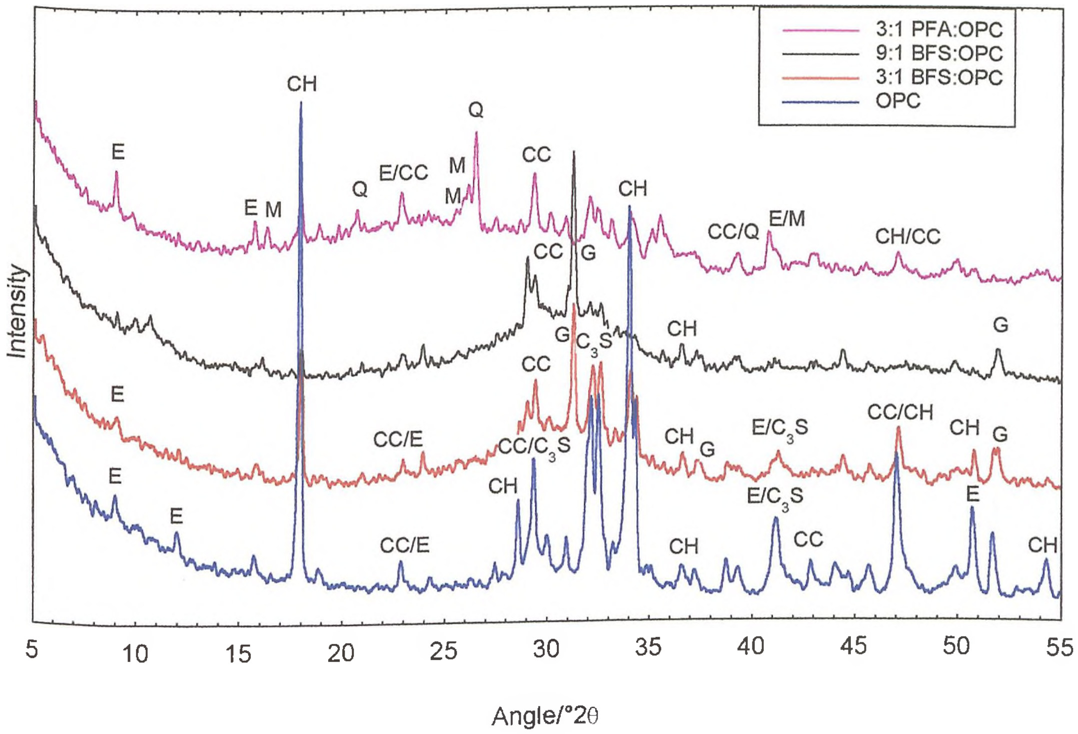

Figure 4.3.5 Neat Cements after 3 Days Hydration

After 28 days hydration (Fig 4.3.6) the systems were similar to those after 3 days with the exception of the calcium carbonate formation which had increased significantly, especially in the 3:1 PFA:OPC system. By 90 days (Fig 4.3.7) there was quite a significant change in most of the cement systems. There was no longer any evidence of calcium hydroxide in the 3:1 PFA:OPC system, very little in the 3:1 BFS:OPC cement and the amount present in the OPC system had declined considerably. Also, the calcium carbonate was still increasing and this was still most significant in the 3:1 PFA:OPC cement.

Figure 4.3.8 shows the four cements after 180 days hydration. The main phase was now calcium carbonate although there were still some remnants of gehlenite and quartz from the original anhydrous composite materials. Also, the calcium hydroxide has disappeared in all systems except 100% OPC and the amount here had decreased substantially compared with earlier ages. In all cases of the neat cements the hydration phases produced and the trends observed were what would have been expected for these types of cement. However, it was necessary to identify

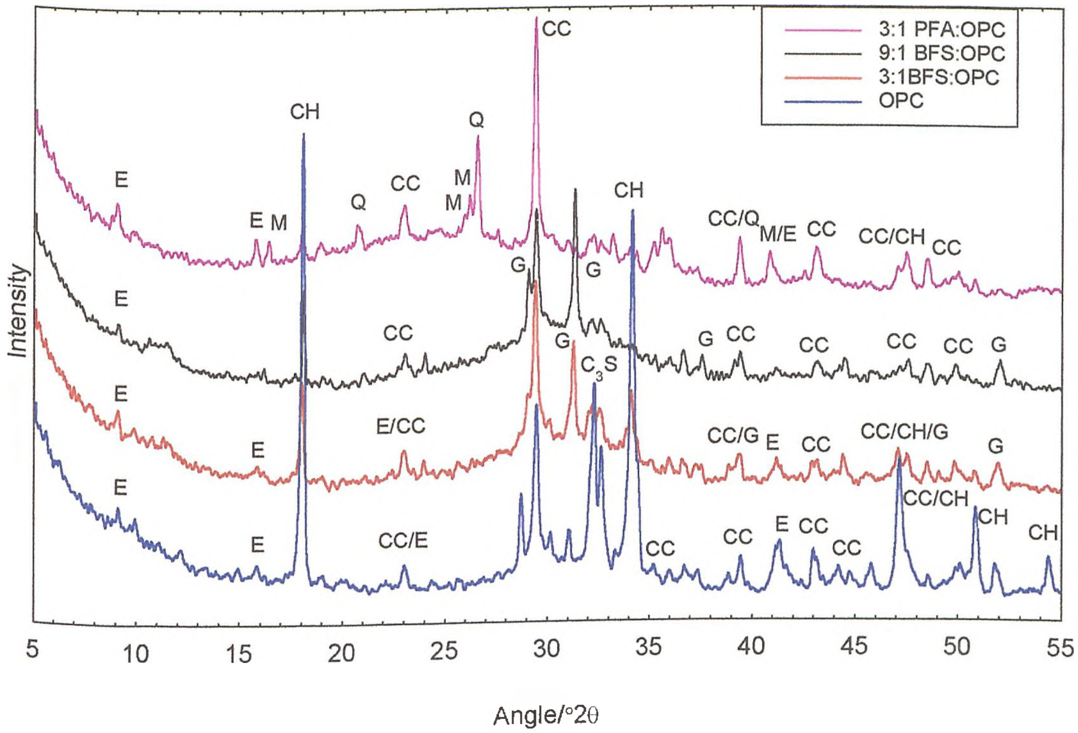

Figure 4.3.6 Neat Cements after 28 Days Hydration

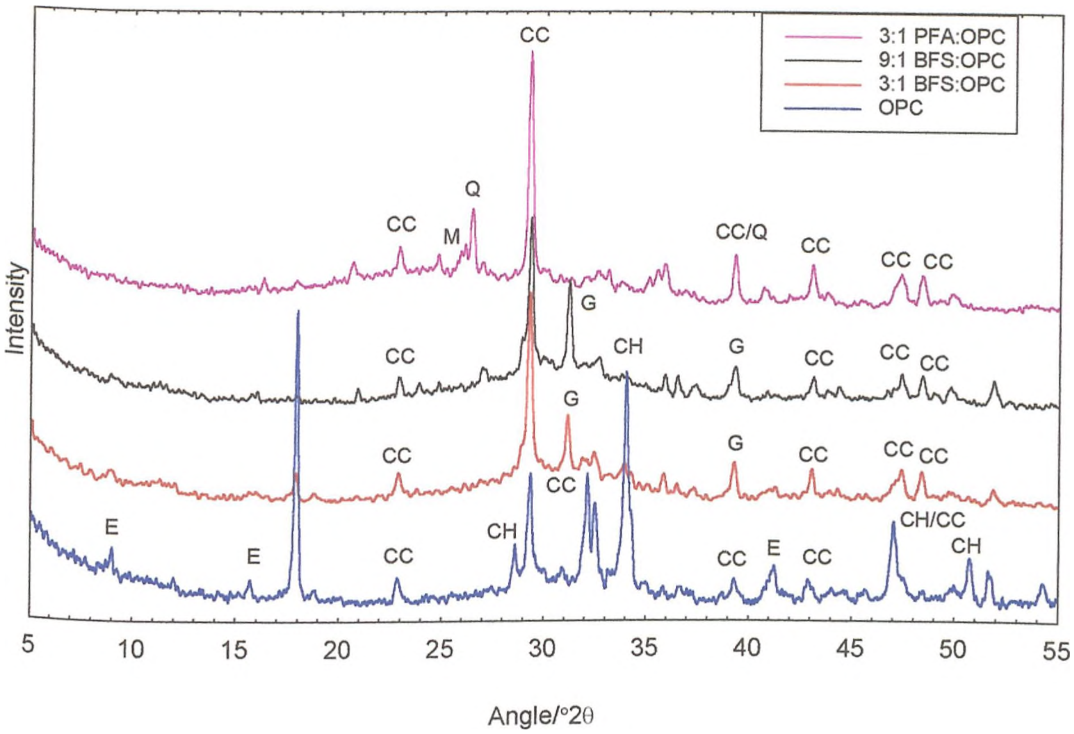

Figure 4.3.7 Neat cements after 90 Days Hydration

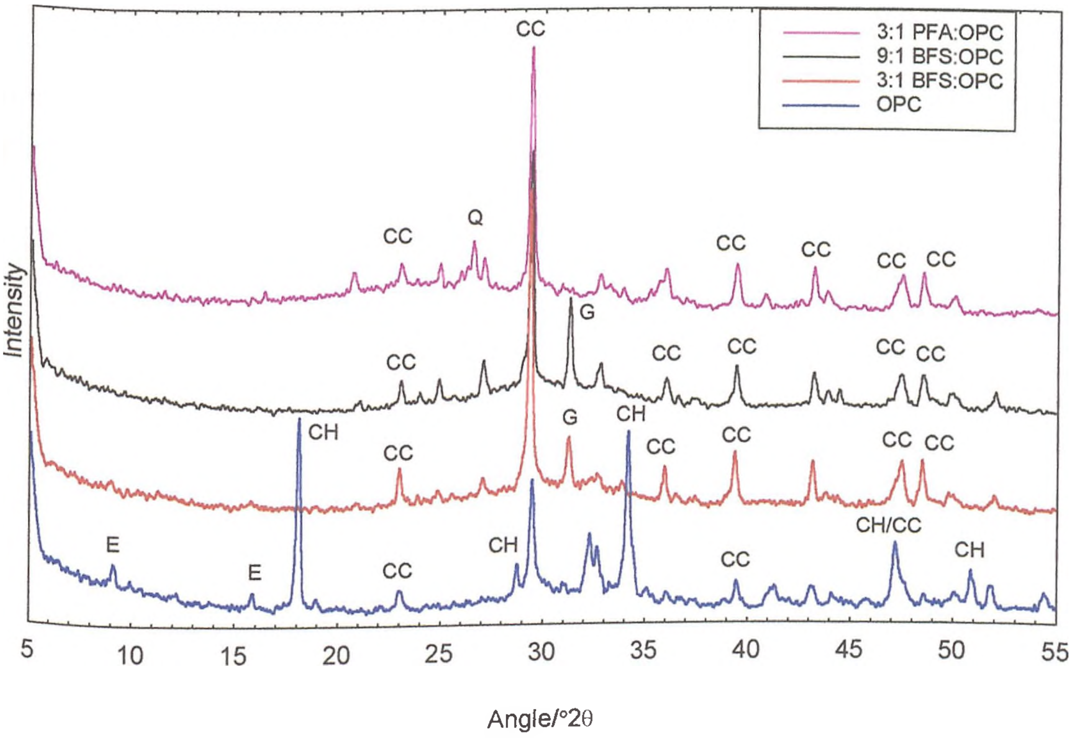

Figure 4.3.8 Neat cements after 180 Days Hydration

this so that comparisons could be made with the cements with the metal salt additions to identify any non-standard hydration phases.

4.3.2 $SnCl_2$ Systems (5% Addition)

Figure 4.3.9 shows 100% OPC and 100% OPC + 5% $SnCl_2$ having been hydrated for 3 days. The trace labelled 13 is that of the neat OPC which has been shown previously to contain the standard hydration phases, calcium hydroxide, ettringite and calcium carbonate. With the 5% $SnCl_2$ addition (trace 13B1 - this numbering system has been identified in Chapter 3) the standard hydration phases were also identified, although the amount of calcium hydroxide was drastically reduced compared with the neat cement. This is most clearly illustrated with the main two peaks at approximately 18°2θ and 34°2θ. However, there were also some extra peaks in addition to those found with the neat cement. One of these was identified as Friedel's salt (FS) and the other, labelled X, was found to be $CaSn(OH)_6$. It was immediately apparent that these phases were not present in the neat cement and it was of interest to follow their progress as the cement paste matured.

Table 4.3.6 shows the expected d-spacings and angles for the non-standard hydration phases identified in this section. The d-spacings were taken from the JCPDS card system and the angle calculated using Bragg's Law (Eqn. 4.1).

Phase	d-spacing/Å	Angle/°2θ
X	4.06	21.89
	4.69	18.92
	2.87	31.16
	1.81	50.42
	2.34	38.47
	2.57	34.91
	2.45	36.68
	2.03	44.64
	2.17	41.62
FS	2.88	31.05
	7.92	11.17
	2.45	36.68
	3.86	23.04
	2.34	38.47
	3.04	29.38
	2.03	44.64
	2.28	39.53
	2.17	41.62

Card numbers: X = 9-30; FS = 28-207

Table 4.3.6 d-Spacings and Angles for the Non-Standard Hydration Phases

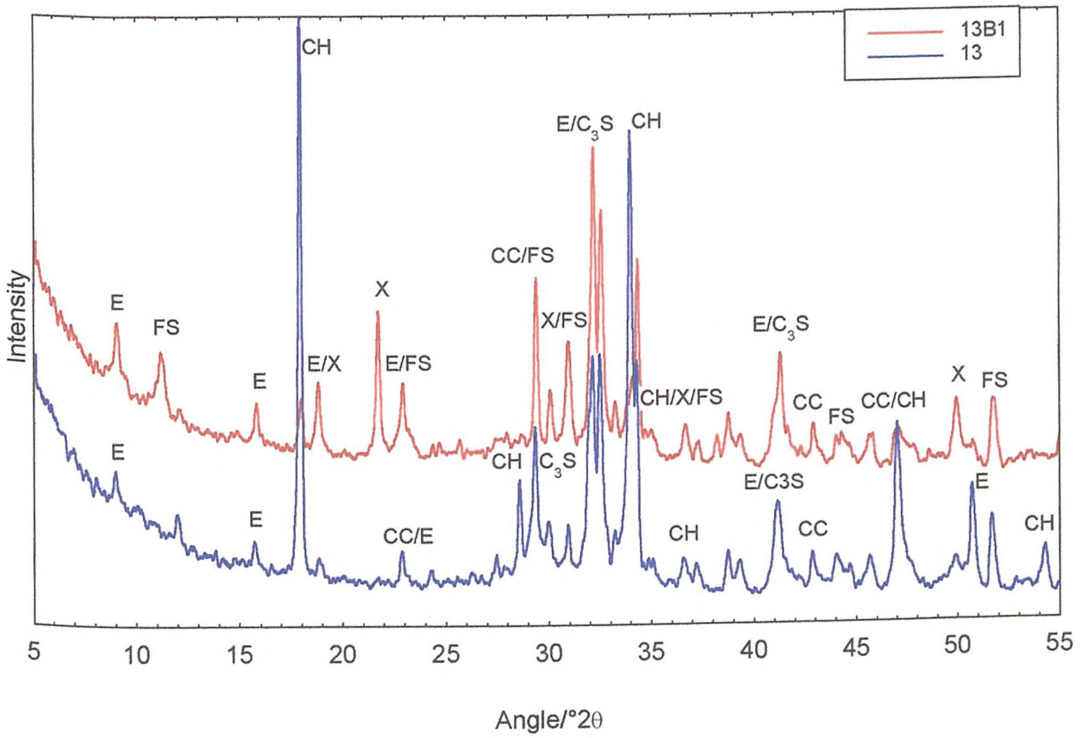

Figure 4.3.9 OPC (13) & OPC + 5% $SnCl_2$ (13B1) Hydrated for 3 Days

After 28 days hydration (Fig 4.2.10) there were increasing amounts of Friedel's salt and phase X (with respect to those present after 3 days hydration). Otherwise, there was not much difference between the two ages. The amount of calcium hydroxide present in the system with the $SnCl_2$ addition was still much less than in the corresponding neat cement although, as would be expected, it had increased in relation to that present after 3 days hydration in the same system. Overall, there was not much difference between the cements at 3 and 28 days hydration. However, after 90 days (Fig. 4.3.11) there was a marked difference. The amount of calcium hydroxide in the neat cement had decreased substantially as had the ettringite content. In the tin containing cement (190B1), the amount of Friedel's salt and phase X continued to increase as did the calcium hydroxide (see also Table 4.3.7), although not to the levels contained in the neat cement. As the calcium hydroxide in the neat cement had decreased substantially and was increasing in the tin containing system, it could be said that the tin had caused some retardation of the cement hydration. The calorimetry data in section 4.2 confirmed this observation up to 72 hours (Table 4.2.10). The time it took to reach a maximum value (t_m) at 21°C for the neat cement was 9.2 hours whereas for the tin system it was 20 hours. The maximum values (Q_m) for the two systems were also significantly different - 31.8 Wkg^{-1} for the neat cement and 1.12 Wkg^{-1} for the tin containing cement.

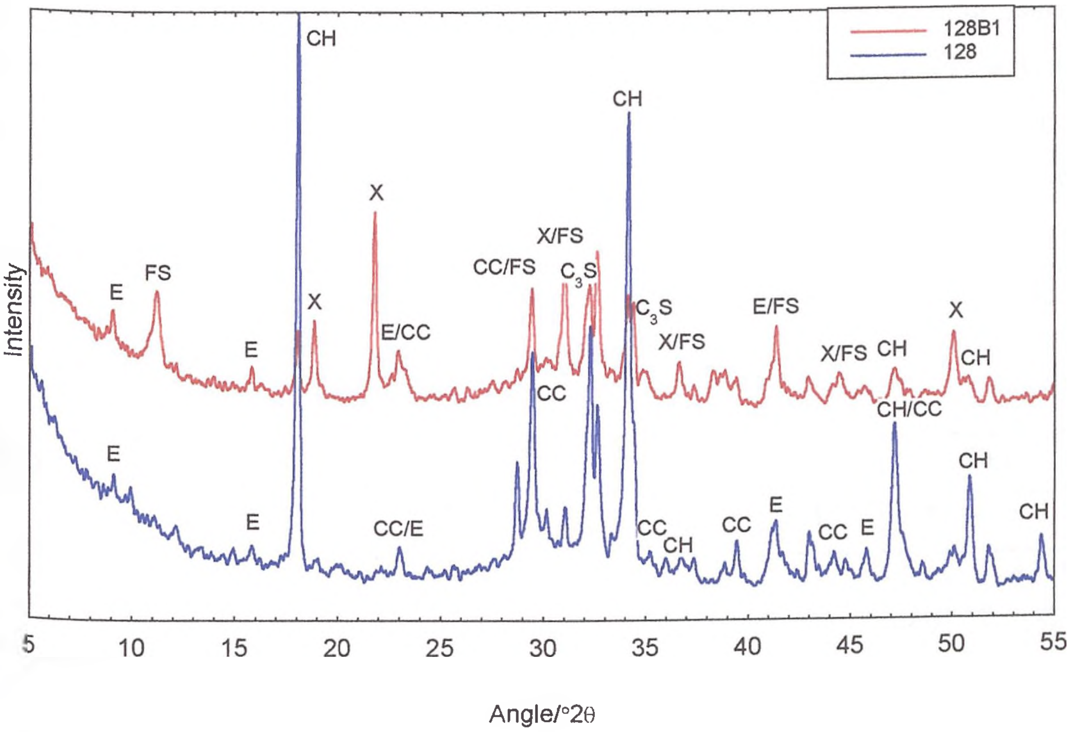

Figure 4.3.10 OPC (128) & OPC + 5% $SnCl_2$ (128B1) Hydrated for 28 Days

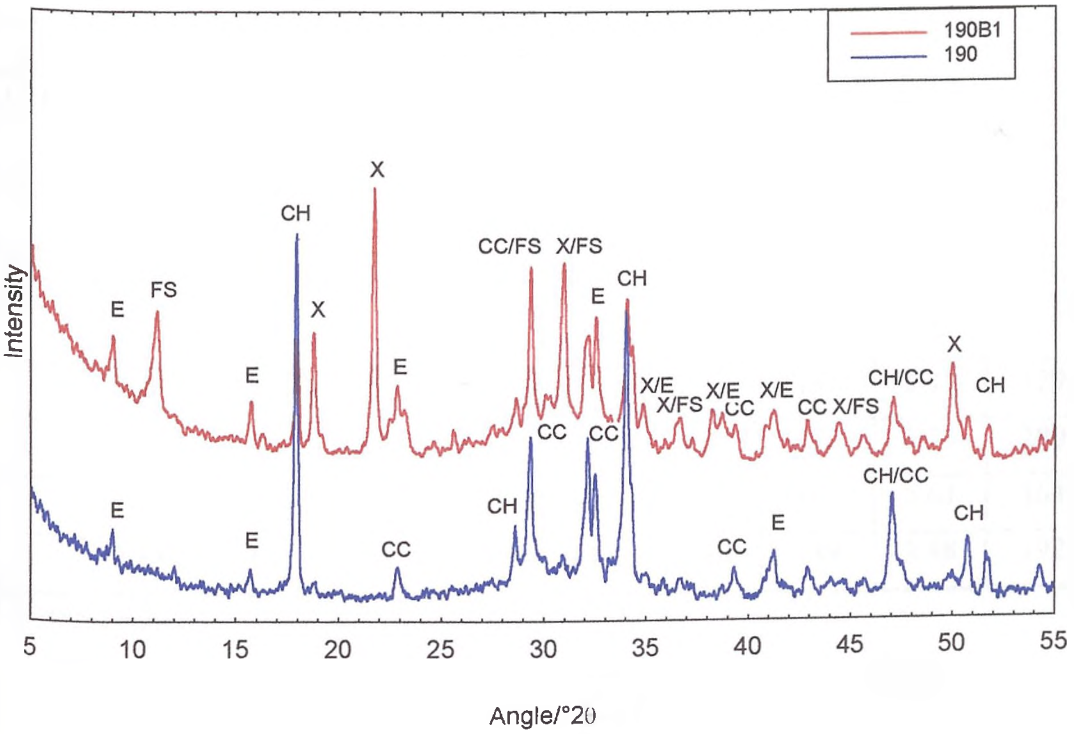

Figure 4.3.11 OPC (190) & OPC + 5% $SnCl_2$ (190B1) Hydrated for 90 Days

Figure 4.3.12 shows the cements after 180 days hydration. The main difference between this and 90 days hydration was that the amount of calcium hydroxide in the tin-containing cement had started to decrease. The amount of phase X and Friedel's salt were approximately the same as were other standard hydration phases. In the neat cement the calcium hydroxide continued to decrease as seen previously. As with the 3 and 28 day data, there was no significant difference between the 90 and 180 day results apart from the decrease in calcium hydroxide in the tin-containing system although this was not significant, as can be seen in Table 4.3.7.

Days		**3**		**28**		**90**		**180**	
	JCPDS	**d**	**I**	**d**	**I**	**d**	**I**	**d**	**I**
X	4.06	4.08	316	4.07	371*	4.08	512*	4.07	484*
	4.69	4.71	200	4.71	192	4.72	275	4.71	270
	2.87	2.88	365	2.88	291	2.88	390	2.88	412
FS	2.88	2.88	265	2.88	291	2.88	390	2.88	412
	7.92	7.88	247	7.88	240	7.91	310	7.87	309
	2.45	2.45	126	2.45	124	2.45	137	2.45	135
CH	2.63	2.63	204	2.62	233	2.63	329	2.63	307
	4.90	4.92	173	4.91	176	4.92	264	4.91	272
	1.93	1.94	110	1.93	110	1.93	164	1.93	184
CC	3.04	3.04	370	3.02	245	3.04	382	3.04	410
	2.29	2.29	109	2.29	97	2.29	129	2.29	129
	2.10	2.10	125	2.11	97	2.11	131	2.11	129
E	9.73	9.75	298	9.75	209	9.77	270	9.75	280
	5.61	5.59	166	5.60	117	5.63	163	5.61	164
	3.88	3.87	197	3.87	144	3.88	189	3.88	192

* = 100% peak A = absent

Table 4.3.7 d-Spacings and Raw Intensities for OPC + 5% $SnCl_2$

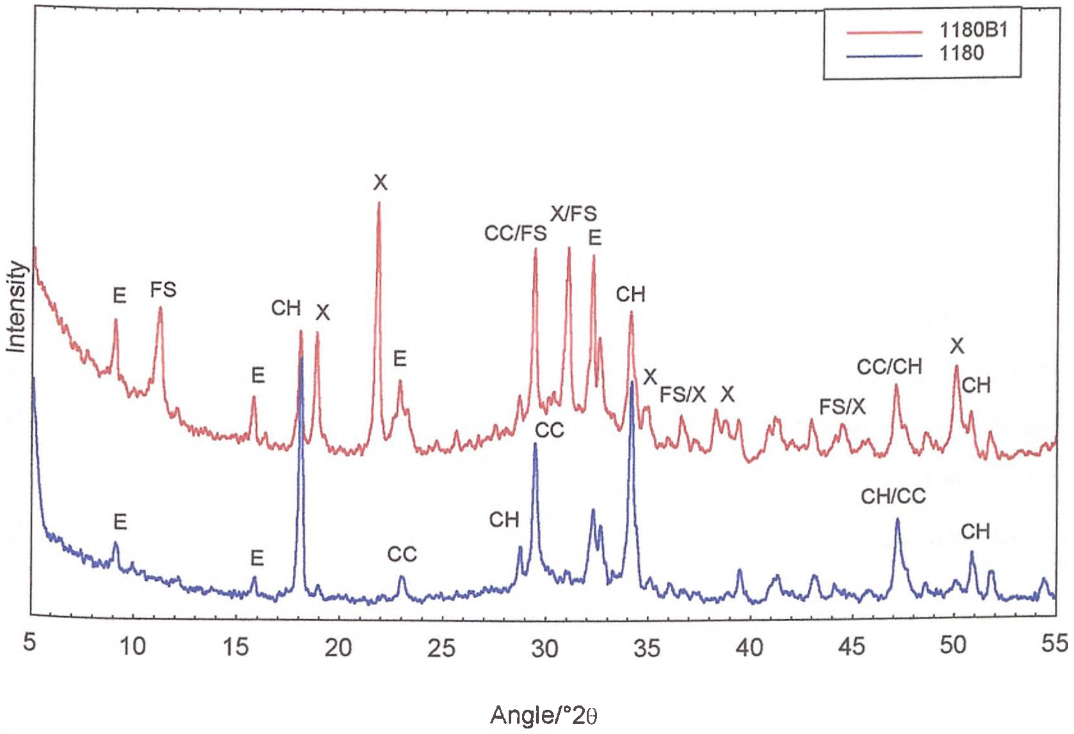

Figure 4.3.12 OPC (1180) & OPC + 5% $SnCl_2$ (1180B1) Hydrated for 180 Days

As mentioned previously, the phase labelled X was found to be $CaSn(OH)_6$. From this formula it can be seen that the oxidation state of the tin is +4 whereas the oxidation state of the tin when added as the chloride was +2. Therefore, it was apparent that the tin had oxidised at some point in the process. It is well documented that tin will oxidise in the presence of atmospheric oxygen. When $SnCl_2.2H_2O$ is dissolved in water an acid solution is formed and, unless metallic tin is added, $SnCl_4$ (stannic chloride) and stannous oxychloride are formed. Equation 4.2 shows this oxidation:[57]

$$6SnCl_2 + 2H_2O + O_2 = 2SnCl_4 + 4Sn(OH)Cl \qquad \text{Equation 4.2}$$

It seems that this occurred when the tin salt was dissolved in the water used for mixing the cement. With this information a proposal for the formation of Friedel's salt and $CaSn(OH)_6$ is given in equation 4.3:

$$SnCl_4 + 2Ca_3Al_2O_6 + 3Ca(OH)_2 + 20\ H_2O \downarrow 2Ca_3Al_2O_6.CaCl_2.10\ H_2O + CaSn(OH)_6$$

Equation 4.3

(Friedel's Salt) (Phase X)

It can be seen that the products are formed from the tricalcium aluminate and calcium hydroxide phases of the cement. Hence, the formation of Friedel's salt and calcium hydroxo stannate ($CaSn(OH)_6$) consumes the calcium leaving less available for the formation of calcium hydroxide. This explains the much reduced amount of calcium hydroxide present in the cements containing the tin salt, as well as the evidence for the formation of Friedel's salt and $CaSn(OH)_6$.

In a similar way to the OPC systems, the composite cement systems didn't show significant differences between 3 & 28 and 90 & 180 days hydration. Therefore, not all data will be presented, only those which show the greatest differences. However, Tables 4.3.8 - 4.3.10 summarise all the data obtained for the composite cement systems with the addition of 5% $SnCl_2$. Figure 4.3.13 shows 3:1 BFS:OPC (23) and 3:1 BFS:OPC + 5% $SnCl_2$ (23B1) hydrated for 3 days. It can be seen that the neat cement shows the standard phases expected for a slag cement, as seen previously (Fig. 4.3.3). The main difference in the tin containing system was the absence of any calcium hydroxide. There were some peaks evident (Table 4.3.8) but these were not sufficient to state that there was significant calcium hydroxide present. There was some evidence for the existence of phase X and Friedel's salt although this was by no means as obvious as in the OPC system at the same age. As there was much less OPC (25%) in this composite cement, the reduced formation of these particular hydration phases (Eqn. 4.3) was to be expected. As hydration proceeded the amount of phase X and Friedel's salt increased although there was still no evidence for the presence of any calcium hydroxide. After 180 days hydration (Fig. 4.3.14) there were significant differences in both systems compared to 3 days hydration. The neat cement showed an absence of calcium hydroxide and only a small amount of gehlenite was present, although there was a significant increase in the amount of calcium carbonate produced. The tin containing system showed a significant increase in the formation of ettringite, Friedel's salt and phase X and a lot less calcium carbonate than in the neat cement. However, there was more gehlenite present and this appeared not to differ significantly in amount from that present after 3 days hydration. This all suggests that, as with the OPC system the tin caused some retardation with respect to the neat cement. This cannot be confirmed or denied by the calorimetry data as at 3 days the 5% $SnCl_2$ system showed acceleration of set when compared with the neat cement (Table 4.2.12). The values of Q_m (at 21°C) for both systems were fairly similar at approximately 1.1 Wkg^{-1} but the time it took to reach this maximum (t_m) was significantly different - 10.8 hours for the neat cement as opposed to 1.1 hours for the tin containing system. However, after three days hydration (Fig 4.3.13) the differences in the hydration phases between the two systems were not as great as those at later ages. Therefore, it would be dangerous to comment much further without calorimetry studies which continued to much longer times.

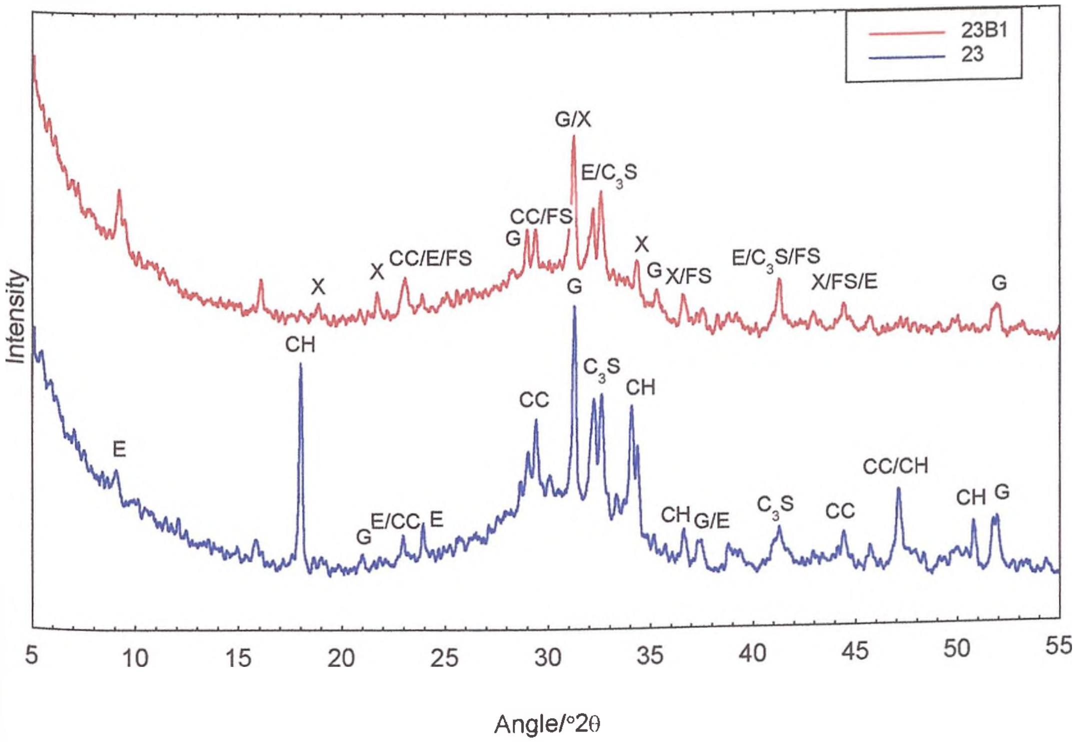

Figure 4.3.13 3:1 BFS:OPC (23) & 3:1 BFS:OPC + 5% $SnCl_2$ (23B1) Hydrated for 3 Days

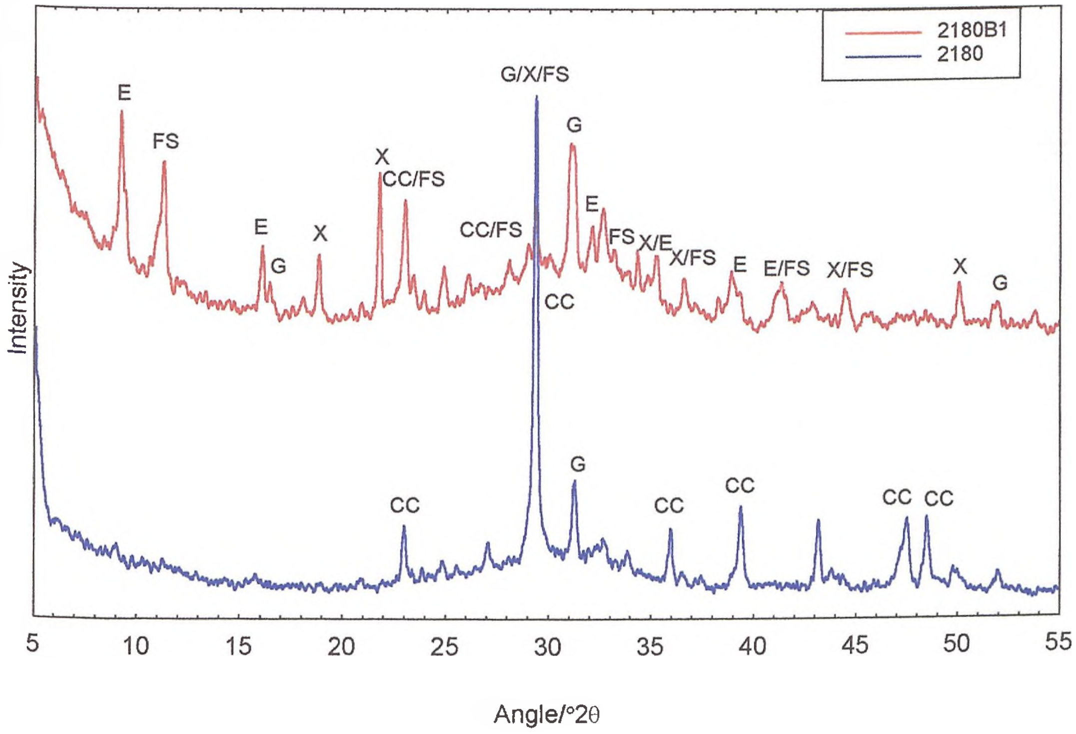

Figure 4.3.14 3:1 BFS:OPC (2180) & 3:1 BFS:OPC + 5% $SnCl_2$ (2180B1) Hydrated for 180 Days

Days		**3**		**28**		**90**		**180**	
	JCPDS	**d**	**I**	**d**	**I**	**d**	**I**	**d**	**I**
X	4.06	4.08	138	4.07	239	4.10	331	4.08	285
	4.69	4.70	123	4.71	145	4.75	192	4.71	178
	2.87	2.86	342	2.88	256	2.88	387	2.87	321
FS	2.88	2.86	342	2.88	256	2.88	387	2.88	324
	7.92	A	A	A	A	7.92	262	A	A
	2.45	2.46	133	2.46	124	2.46	157	2.46	146
CH	2.63	2.61	178	A	A	2.63	175	A	A
	4.90	A	A	A	A	A	A	4.91	121
	1.93	1.92	98	A	A	A	A	A	A
CC	3.04	3.03	221	3.04	216	3.05	273	3.04	242
	2.29	A	A	2.29	103	2.3	133	2.29	127
	2.10	A	A	A	A	2.11	131	A	A
E	9.73	A	A	A	A	9.73	294	9.58	365
	5.61	A	A	A	A	5.56	182	A	A
	3.88	A	A	A	A	3.88	263	3.86	250
G	2.86	2.86	342	2.86	272	2.88	387	2.88	324
	1.93	1.92	98	A	A	A	A	A	A
	3.72	A	A	3.72	124	A	A	3.72	130

* = 100% peak A = absent

Table 4.3.8 d-Spacings and Raw Intensities for 3:1 BFS:OPC + 5% $SnCl_2$

There were no 3 day data available for the 9:1 BFS:OPC system containing $SnCl_2$ due to the cement taking longer to set than the 3:1 BFS:OPC system. Therefore, it can be assumed that the hydration process was retarded in comparison. After 28 days hydration (Fig. 4.3.15) it can be seen that there was definite evidence for the formation of phase X although not much Friedel's salt was apparent. The peak at around 11°2θ was not in evidence at all and that which was identified occurred alongside other phases such as gehlenite and calcium carbonate which would be expected to occur. This could be due to there being even less cement present than in the 3:1 BFS:OPC system, i.e. only 10% and, therefore, insufficient tricalcium aluminate to enable significant formation of the phase. Also, as there was distinct evidence for phase X it would appear that the limited amount of calcium which would be present (due to the lack of cement) was being preferentially taken up for the formation of $CaSn(OH)_6$ (phase X). This was also the most likely reason for the complete lack of calcium hydroxide present in the system. There was evidence for only small amounts of ettringite being formed.

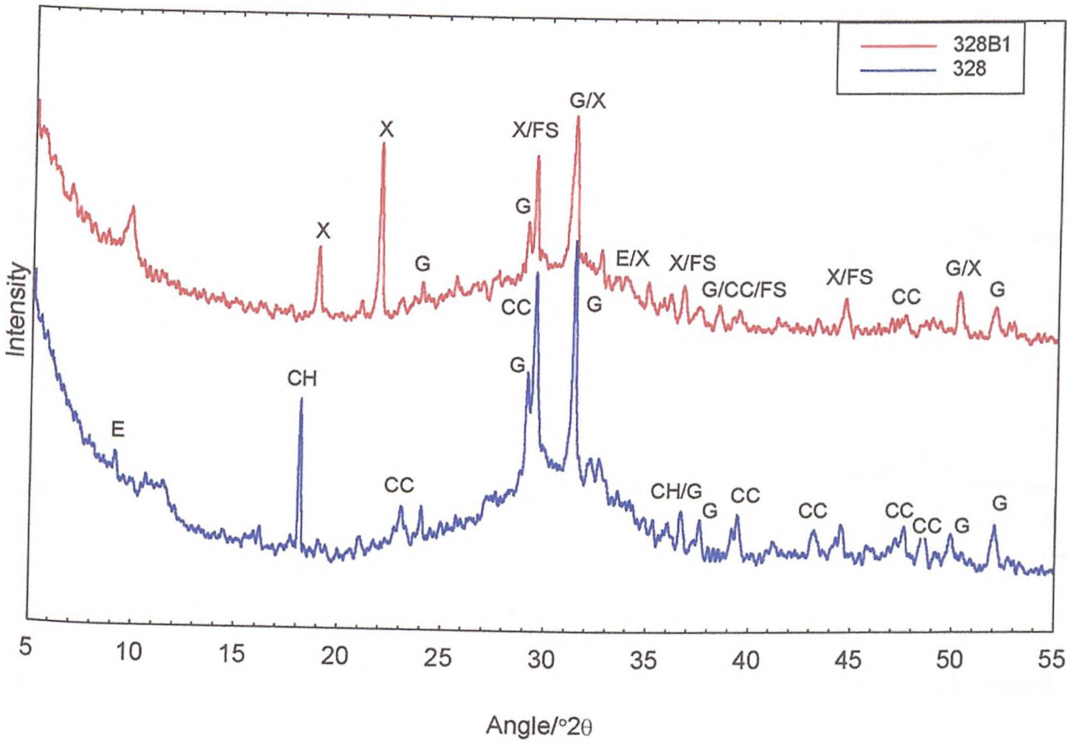

Figure 4.3.15 9:1 BFS:OPC (328) & 9:1 BFS:OPC + 5% $SnCl_2$ (328B1) Hydrated for 28 Days

After 90 days hydration (Fig. 4.3.16) it can be seen that the neat cement (390) consisted mainly of calcium carbonate with some gehlenite present and no calcium hydroxide (which was evident at 28 days). In contrast, the tin containing system (390B1) still showed clear evidence for the presence of gehlenite and phase X, which was prominent although it did not appear to have increased at all from 28 days. There was still no evidence for any Friedel's salt or calcium hydroxide which continued to be the case after 180 days hydration, making the earlier explanation that the lack of availability of C_3A is the reason for the absence of Friedel's salt seem to be more reasonable. Table 4.3.9 shows some evidence for Friedel's salt and calcium hydroxide. However, the Friedel's salt peak at approximately 31°2θ corresponds with phase X and gehlenite peaks and the calcium hydroxide peak which, from the table, appears to be present also overlaps with a gehlenite peak at the same d-spacing (approximately 1.93Å). Therefore, as there was very little evidence for either phase on its own, it would be safe to say that there was very little present.

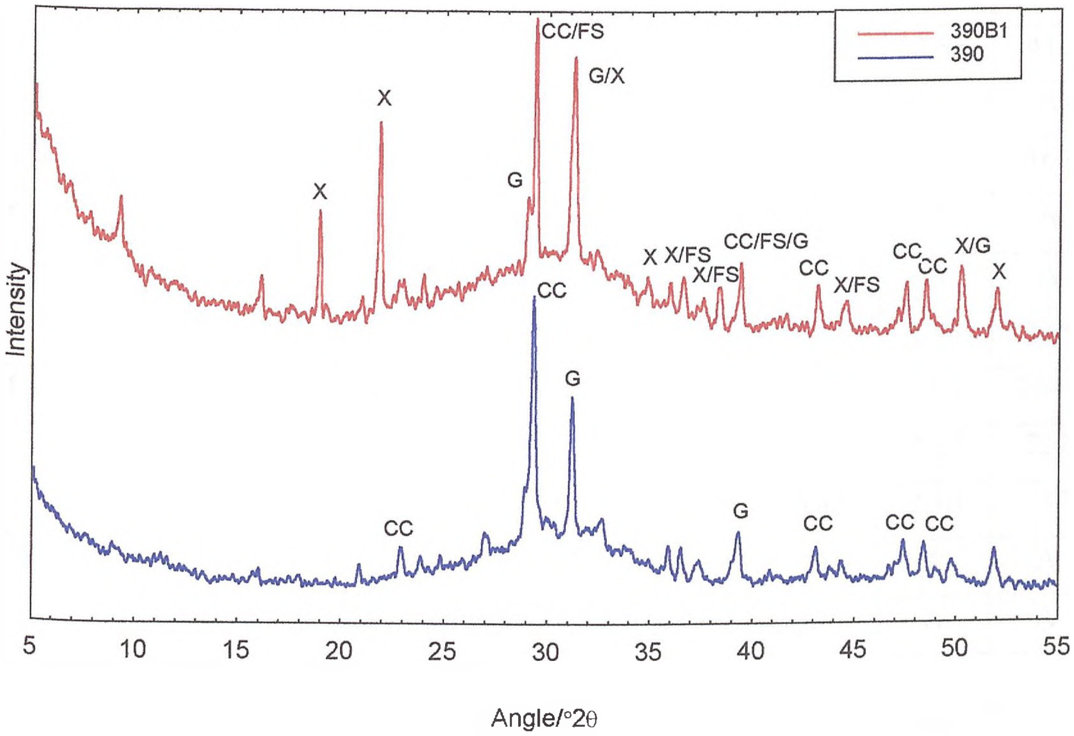

Figure 4.3.16 9:1 BFS:OPC (390) & 9:1 BFS:OPC + 5% $SnCl_2$ (390B1) Hydrated for 90 Days

Days		**7**		**28**		**90**		**180**	
	JCPDS	**d**	**I**	**d**	**I**	**d**	**I**	**d**	**I**
X	4.06	4.08	343	4.06	294	4.07	355	4.07	386
	4.69	4.70	185	4.70	165	4.69	238	4.71	224
	2.87	2.87	380	2.86	332	2.86	441	2.86	412
FS	2.88	2.87	380	2.86	332	2.86	441	2.86	412
	7.92	A	A	A	A	A	A	A	A
	2.45	2.46	147	2.45	124	2.46	153	2.45	167
CH	2.63	A	A	A	A	A	A	A	A
	4.90	A	A	A	A	A	A	A	A
	1.93	1.93	98	1.93	84	1.93	111	1.93	128
CC	3.04	A	A	3.04	281	3.04	492*	3.04	804*
	2.29	2.30	109	2.29	95	2.29	171	2.29	227
	2.10	A	A	2.10	84	2.10	142	2.10	177
E	9.73	A	A	A	A	A	A	A	A
	5.61	A	A	A	A	A	A	A	A
	3.88	A	A	3.89	102	3.87	149	3.86	167
G	2.86	2.87	380	2.86	332	2.86	441	2.86	412
	1.93	1.93	98	1.93	84	1.93	111	1.93	128
	3.72	3.72	139	3.72	124	3.71	156	3.72	156

* = 100% peak A = absent

Table 4.3.9 d-Spacings and Raw Intensities for 9:1 BFS:OPC + 5% $SnCl_2$

Figure 4.3.17 shows the x-ray data for 3:1 PFA:OPC with and without the addition of 5% $SnCl_2$ (43B1 and 43, respectively). It can be seen that after 3 days hydration the neat cement showed evidence of quartz and mullite present from the anhydrous PFA and also clear evidence for the presence of some calcium hydroxide (around 18° and 34°2θ). There was also strong evidence for the presence of calcium carbonate which, whilst apparent, was not as strong at this age in either of the slag cements.

Addition of the $SnCl_2$ appeared to have similar effects to those seen previously in other cement systems. That is, there was little or no production of calcium hydroxide but there was evidence for the formation of $CaSn(OH)_6$ (phase X). There was also an indication that Friedel's salt was being formed although, as with the 9:1 BFS:OPC system, this was not as strong as in either the OPC or 3:1 BFS:OPC systems.

After 180 days hydration (Fig. 4.3.18) both systems looked significantly different. The neat cement (4180) mainly showed evidence for calcium carbonate although there was a little quartz remaining from the PFA. The system with the metal salt addition (4180B1) showed a significant increase in the amount of phase X present as well as in the calcium carbonate phase although phase X was beginning to decrease by 180 days hydration. This is more clearly illustrated in Table 4.3.10 but it can also be seen that, even though it had begun to decrease the intensities after 180 days were still greater than after 3 days. Another interesting point from this table was that the quartz followed a similar trend to phase X. This was in contrast to the neat cement in which the peak intensity decreased substantially with time between 3 and 180 days hydration (Table 4.3.3). The intensity of the peaks due to Friedel's salt increased significantly from that seen after 3 days hydration and indicated that the phase formed eventually. From the data in Table 4.3.10 this appears to be similar to the 9:1 BFS:OPC system. However, when studying the XRD trace it is possible to see the peak at approximately 31°2θ clearly as it is no longer overlapping with a gehlenite peak (as there is none present in the PFA system) which makes the phase easier to identify.

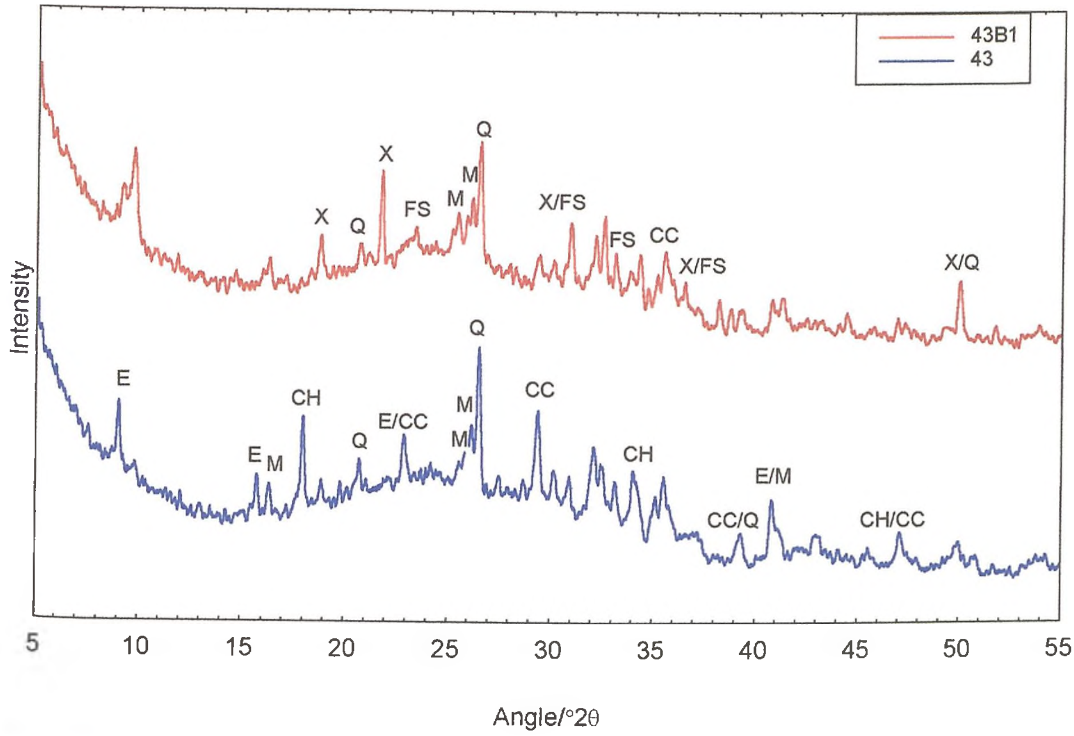

Figure 4.3.17 3:1 PFA:OPC (43) & 3:1 PFA:OPC + 5% $SnCl_2$ (43B1) Hydrated for 3 Days

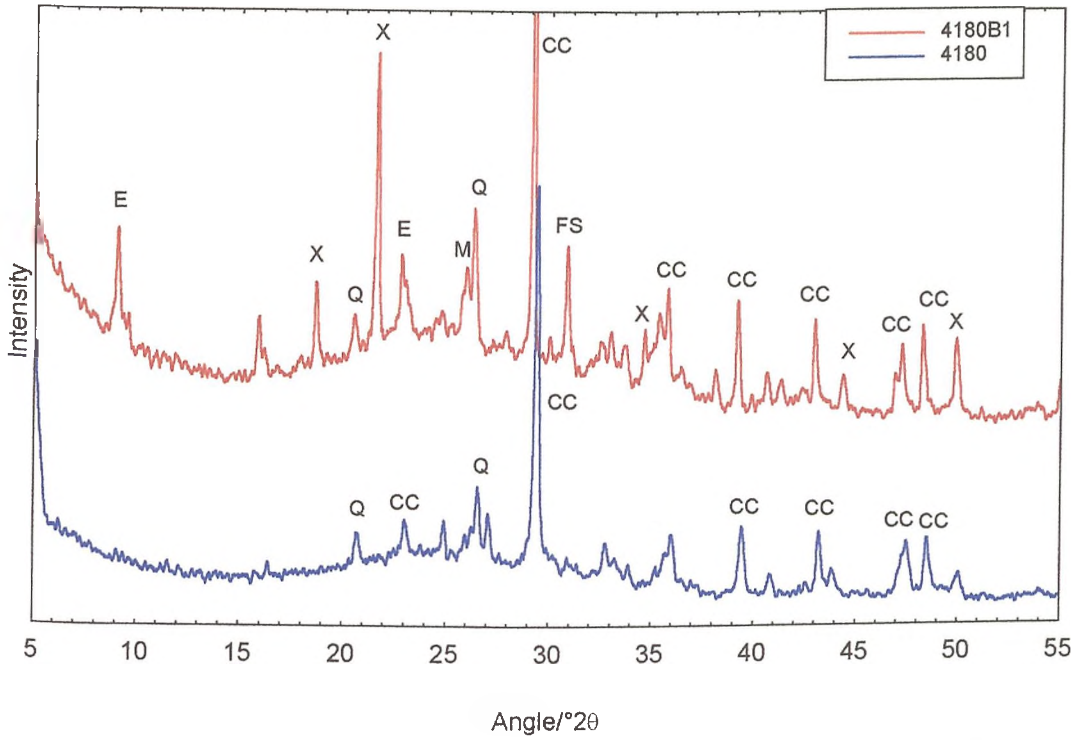

Figure 4.3.18 3:1 PFA:OPC (4180) & 3:1 PFA:OPC + 5% $SnCl_2$ (4180B1) Hydrated for 180 Days

Days		**3**		**28**		**90**		**180**	
	JCPDS	**d**	**I**	**d**	**I**	**d**	**I**	**d**	**I**
X	4.06	4.08	290	4.08	302	4.08	445	4.10	345
	4.69	4.72	205	4.71	212	4.71	301	4.75	247
	2.87	2.89	223	2.88	227	2.88	260	2.87	166
FS	2.88	2.89	223	2.88	227	2.88	260	2.87	166
	7.92	A	A	A	A	A	A	A	A
	2.45	2.46	146	2.45	123	2.46	164	2.47	138
CH	2.63	2.65	160	2.64	132	2.65	164	A	A
	4.90	A	A	A	A	A	A	A	A
	1.93	1.93	98	A	A	1.92	133	1.92	165
CC	3.04	3.03	181	3.04	200	3.04	455*	30.6	798*
	2.29	2.29	26	A	A	2.29	156	2.29	224
	2.10	A	A	A	A	2.10	142	2.10	198
E	9.73	A	A	A	A	A	A	9.75	315
	5.61	A	A	A	A	A	A	A	A
	3.88	A	A	A	A	A	A	3.86	250
Q	3.34	3.36	330	3.36	247	3.36	347	3.38	344
	4.26	4.28	194	4.28	168	4.28	211	4.32	205
	1.82	1.82	146	1.82	119	1.82	291	1.83	172

* = 100% peak A = absent

Table 4.3.10 d-Spacings and Raw Intensities for 3:1 PFA:OPC + 5% $SnCl_2$

4.3.3 $SnCl_2$ Systems (1% Addition)

As mentioned previously, it was necessary to carry out a limited study at the 5% loading because some of the phases formed in the presence of 1% additions were at the limits of detection of the x-ray diffractometer. The following section will illustrate the difficulties encountered and also show how the 5% data helped to clarify the results obtained with 1% additions.

Figure 4.3.19 shows OPC (128) and OPC + 1% $SnCl_2$ (128B2) hydrated for 28 days. It is immediately apparent that differences between the two systems were not as great as those between the neat cement and the 5% loading. Firstly, the amount of calcium hydroxide present (at 18°2θ), whilst less in the tin containing system was not as significantly reduced as with a 5% addition. Also, any $CaSn(OH)_6$ present was associated with other hydration phases which were present in both systems and could not, therefore, be definitely said to be present. The main difference was that there was some evidence for the formation of Friedel's salt (at around 11°θ) in the tin-containing system which was not present in the neat system. Again, this was quite often associated with some other phase although the peak at around 11°2θ was solitary. This was an indication that the reaction proposed in equation 4.2 was taking place although to a lesser extent than in the 5% systems due to the decreased amount of $SnCl_2$ present. There was very little difference between 28 and 90 days hydration (Figure 4.3.20) except that the amount of calcium hydroxide in both systems had decreased (as expected) and the amount of calcium carbonate had increased. There was still no definite evidence for phase X although, as at 28 days, Friedel's salt was still clearly present. However, from Table 4.3.11 it can be seen that there is some evidence for phase X at all ages from the second strongest peak position (d = 4.69Å) and, after 180 days, there is evidence from the two strongest peaks. The third strongest peak listed coincides with a peak due to Friedel's salt and cannot, therefore, be considered on its own. It has to be noted that the intensities of these peaks are relatively low and this highlights the problems of using just the x-ray trace when working at the limits of detection of the equipment. Combining Figures 4.3.19 and 4.3.20 with Table 4.3.11 it can be concluded that after 180 days there is some evidence for phase X having formed although, the peak intensities suggest that the amount is restricted.

The results for all the cement systems containing 1% $SnCl_2$ were similar in that there was no definite evidence of phase X, but combined with the 5% results and the fact that Friedel's salt was being formed, it could be said to be present, although in such small quantities that it was at the limits of detection of the equipment. Therefore, the results for this section of work have been condensed into tables for ease of reference.

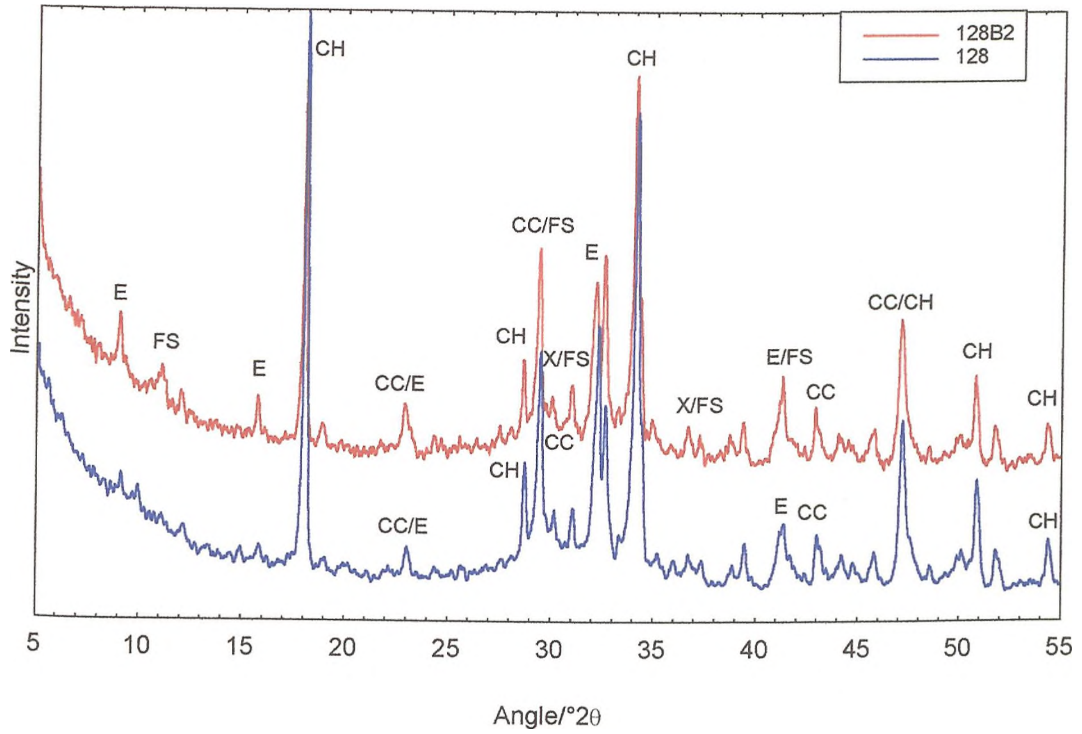

Figure 4.3.19 100% OPC (128) & 100% OPC + 1% $SnCl_2$ (128B2) Hydrated for 28 Days

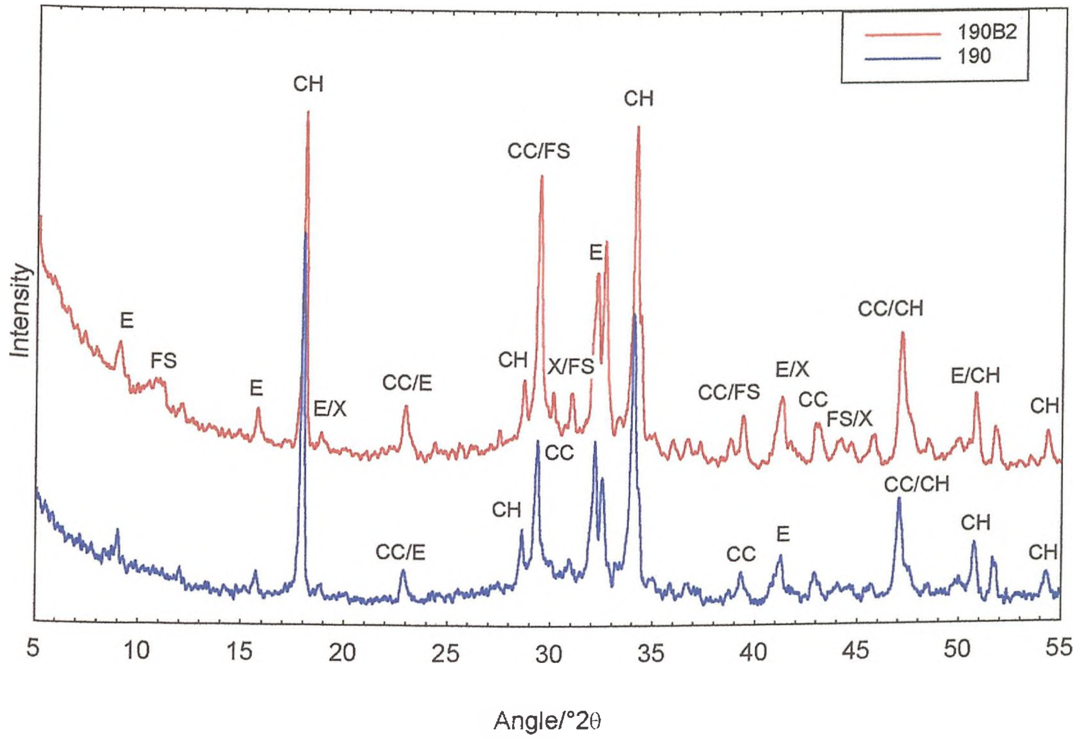

Figure 4.3.20 100% OPC (190) & 100% OPC + 1% $SnCl_2$ (190B2) Hydrated for 90 Days

Days		**3**		**28**		**90**		**180**	
	JCPDS	**d**	**I**	**d**	**I**	**d**	**I**	**d**	**I**
X	4.06	A	A	A	A	A	A	4.08	96
	4.69	4.69	105	4.70	122	4.71	114	4.72	108
	2.87	2.89	170	2.88	187	2.88	180	2.88	205
FS	2.88	2.89	170	2.88	187	2.88	180	2.88	205
	7.92	7.97?	206	7.97?	215	7.89?	192	7.96?	195
	2.45	2.45	118	2.45	121	2.45	105	2.45	111
CH	2.63	2.63	602*	2.63	695	2.63	615	2.63	675
	4.90	4.92	598	4.92	699*	4.92	634*	4.92	780*
	1.93	1.93	241	1.93	294	1.93	274	1.93	315
CC	3.04	3.04	376	3.04	412	3.04	534	3.04	484
	2.29	2.29	104	2.29	128	2.29	142	2.29	135
	2.10	2.11	123	2.11	152	2.11	129	2.11	134
E	9.73	9.73	253	9.77	300	9.75	258	9.79	237
	5.61	5.62	132	5.62	166	5.62	152	5.62	135
	3.88	3.88	141	3.88	155	3.88	158	3.88	141

* = 100% peak A = absent

Table 4.3.11 d- Spacings and Raw Intensities for OPC + 1% $SnCl_2$

Tables 4.3.12 to 4.3.14 show the d-spacings and raw intensities for 3:1 BFS:OPC, 9:1 BFS:OPC and 3:1 PFA:OPC all with the addition of 1% $SnCl_2$. The trends observed in all these systems were very similar. There was very little calcium hydroxide present after 28 days hydration and in most systems it was absent. The amount of calcium carbonate formed increased with time in all systems although the greatest increase was seen in the 3:1 PFA:OPC system. This followed trends seen previously with the neat system and with the 5% loading of $SnCl_2$. Evidence for the formation of phase X varied between systems. The 3:1 BFS:OPC system (Table 4.3.12) showed no real evidence at all for the formation of any phase X other than from the third most intense peak. However, as mentioned previously, this peak coincides with the most intense peak of the Friedel's salt phase and cannot, therefore, be taken alone as confirmation of the formation of phase X.

Figure 4.3.21 illustrates this more clearly. It shows 3:1 BFS:OPC (290) and 3:1 BFS:OPC + 1% $SnCl_2$ (290B2) after 90 days hydration. It can be seen that, as suggested in Table 4.3.12, the evidence for the formation of phase X was not conclusive and that all peaks overlapped with peaks for other hydration products. However, what was clear was that, as with the OPC system, there were some differences between the tin-containing system and the neat cement. The most obvious of these was that there was clear evidence for the formation of Friedel's salt and ettringite in the tin-containing system whereas there was none in the neat cement. Also, although there was only a small amount of calcium hydroxide present in the neat cement, there was none at all in the tin-containing cement. This again ties in with the results obtained with the 5% loading but the differences between the two systems were not as significant.

Days		**7**		**28**		**90**		**180**	
	JCPDS	**d**	**I**	**d**	**I**	**d**	**I**	**d**	**I**
X	4.06	A	A	A	A	A	A	A	A
	4.69	A	A	A	A	A	A	A	A
	2.87	2.88	349	2.87	440*	2.88	323	2.87	305
FS	2.88	2.88	349	2.89	254	2.88	323	2.89	236
	7.92	A	A	A	A	A	A	7.92	245
	2.45	2.47	136	2.45	122	2.46	113	2.46	124
CH	2.63	2.64	182	2.64	174	A	A	A	A
	4.90	A	A	A	A	A	A	A	A
	1.93	1.94	122	1.93	117	1.94	119	1.92	153
CC	3.04	3.06	318	3.05	442*	3.05	654*	30.4	664*
	2.29	2.30	122	2.29	140	2.30	173	2.29	183
	2.10	2.11	112	2.10	124	2.10	149	2.10	143
E	9.73	9.84?	214	9.88?	220	9.88?	238	9.79	222
	5.61	5.66?	126	5.58?	122	5.65?	133	5.61	131
	3.88	3.89	168	3.89	164	3.89	181	3.88	179
G	2.86	2.88	349	2.87	440*	2.88	323	2.87	305
	1.93	1.94	122	1.94	117	1.94	119	1.92	153
	3.72	3.74	136	3.73	137	3.74	123	3.73	140

* = 100% peak A = absent

Table 4.3.12 d-Spacings and Raw Intensities for 3:1 BFS:OPC + 1% $SnCl_2$

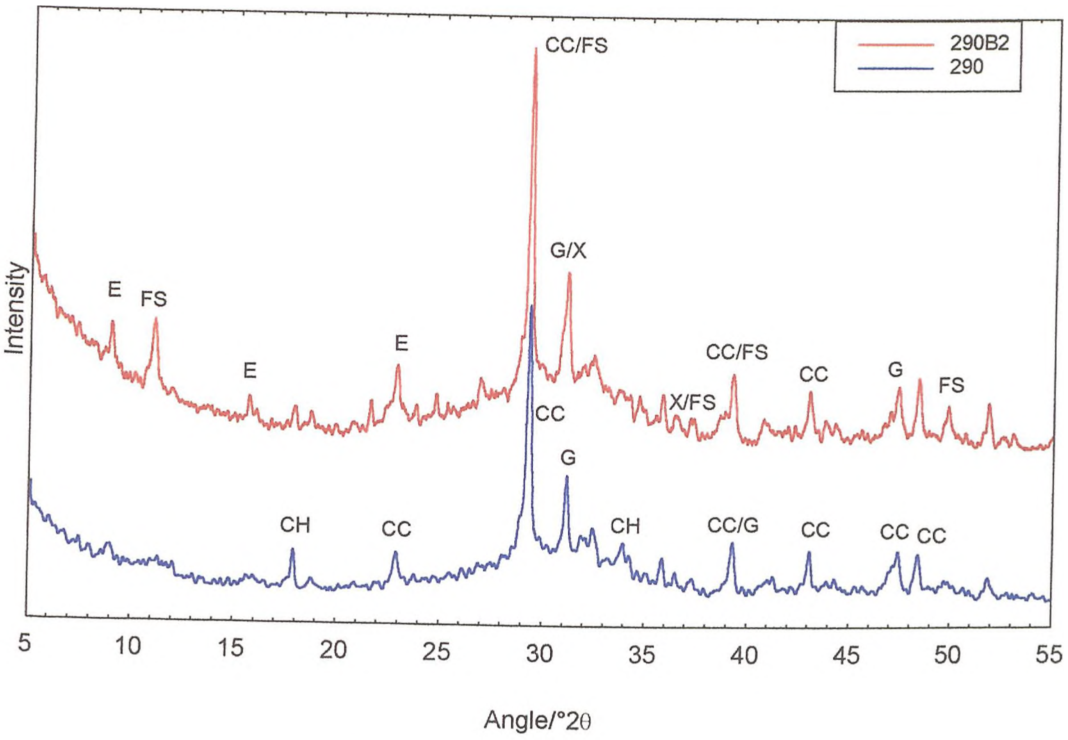

Figure 4.3.21 3:1 BFS:OPC (290) & 3:1 BFS:OPC + 1% $SnCl_2$ (290B2) Hydrated for 90 Days

In contrast to the 3:1 BFS:OPC system, the 9:1 BFS:OPC system (Table 4.3.13 and Figure 4.3.22) showed some evidence for the formation of phase X. Although the peak expected to be the most intense was not in evidence after 7 days, all three were apparent, if weak, after this time. Also, there was definite evidence for the formation of ettringite and Friedel's salt, both of which were absent in the neat system. Figure 4.3.22 clearly illustrates these observations where the presence of Friedel's salt and phase X are confirmed by the XRD trace after hydration for 180 days.

Figures 4.3.23 and 4.3.24 show 3:1 PFA:OPC (428 & 490) 3:1 PFA:OPC + 1% $SnCl_2$ (428B2 & 490B2) hydrated for 28 and 90 days, respectively. As mentioned previously, it can be seen that the amount of calcium carbonate in the PFA system increased substantially (see also Table 4.3.14). After 28 days (Figure 4.3.23) there was definite evidence for the formation of phase X. Although the peaks were small, they occurred independently of any other phase, i.e. there was evidence for the most intense peak as well as those which overlapped with other phases. However, when the cement had hydrated for 90 days (Figure 4.3.24) there was no longer any evidence for phase X. This can be seen clearly in Table 4.3.14 as well as very little evidence for the formation of Friedel's salt although, at all ages the most intense peak was present. The decrease in the amount of phase X present was not evident at the 5% loading but it is possible that the reason for this occurring is due to the pozzolanic reaction of the PFA cement. That is, as there was no calcium hydroxide present the $CaSn(OH)_6$ phase enters into the pozzolanic reaction instead and is, therefore, consumed.

Days		**7**		**28**		**90**		**180**	
	JCPDS	**d**	**I**	**d**	**I**	**d**	**I**	**d**	**I**
X	4.06	A	A	4.08	120	4.08	103	4.08	130
	4.69	4.72?	114	A	A	4.71	71	4.71	107
	2.87	2.86	369*	2.86	411	2.86	374	2.86	360
FS	2.88	2.88	265	2.86	411	2.86	374	2.86	360
	7.92	7.99?	259	A	A	A	A	7.89	228
	2.45	2.46	147	2.46	141	2.46	104	2.46	123
CH	2.63	2.63	177	A	A	A	A	A	A
	4.90	4.92	154	A	A	A	A	A	A
	1.93	1.93	120	1.93	111	1.93	114	1.91	177
CC	3.04	3.04	332	3.04	703*	3.04	1050*	3.04	807*
	2.29	A	A	2.29	181	2.29	207	2.29	195
	2.10	2.11	109	2.10	160	2.09	179	2.10	167
E	9.73	9.75	220	A	A	A	A	9.71	222
	5.61	A	A	A	A	A	A	5.60	128
	3.88	3.87	143	3.87	175	3.86	146	3.87	187
G	2.86	2.86	369*	2.86	411	2.86	374	2.86	360
	1.93	1.93	120	1.93	111	1.93	114	1.91	177
	3.72	A	A	3.72	134	3.71	109	A	A

* = 100% peak A = absent

Table 4.3.13 d-Spacings and Raw Intensities for 9:1 BFS:OPC + 1% $SnCl_2$

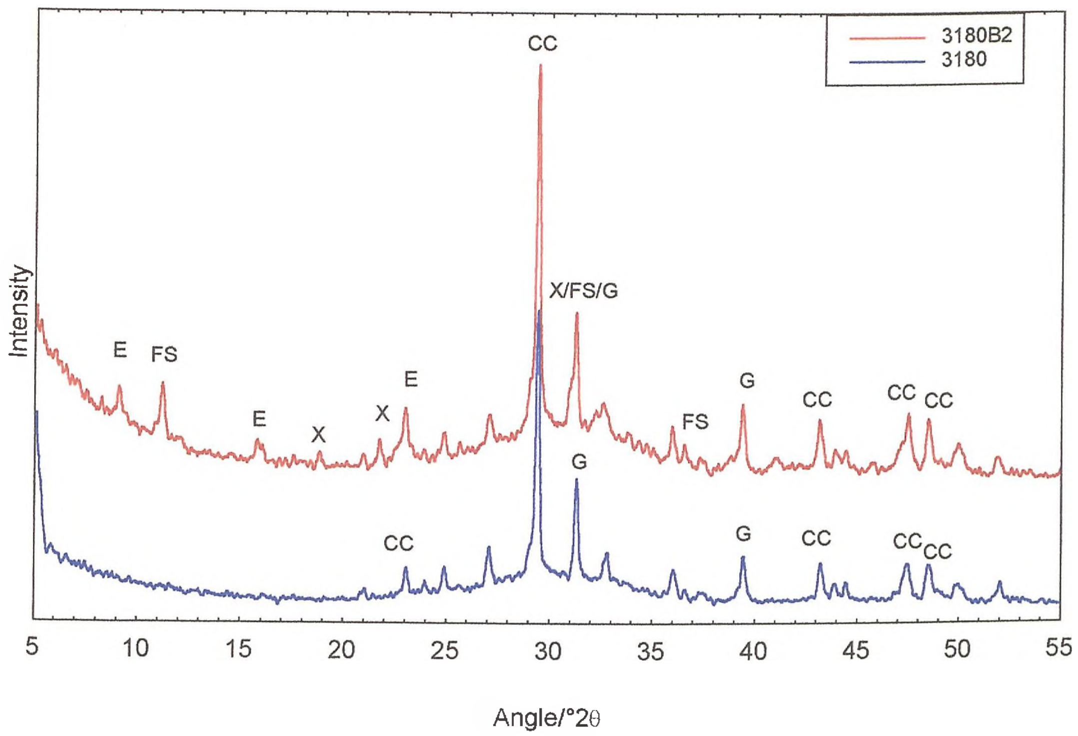

Figure 4.3.22 9:1 BFS:OPC (390) & 9:1 BFS:OPC + 1% $SnCl_2$ (390B2) Hydrated for 180 Days

Days		3		28		90		180	
	JCPDS	d	I	d	I	d	I	d	I
X	4.06	4.08	184	4.08	245	A	A	A	A
	4.69	4.69	170	4.72	185	A	A	A	A
	2.87	2.89	167	2.88	213	2.89	176	2.89	167
FS	2.88	2.89	167	2.88	213	2.89	176	2.89	167
	7.92	A	A	7.87	211	A	A	A	A
	2.45	A	A	A	A	A	A	A	A
CH	2.63	2.64	154	A	A	A	A	A	A
	4.90	4.92	174	A	A	A	A	A	A
	1.93	1.92	106	1.92	143	A	A	1.92	217
CC	3.04	3.04	259	3.04	1550*	3.05	1080*	3.05	1247*
	2.29	2.29	108	2.29	172	2.29	237	2.29	271
	2.10	2.10	110	2.10	154	2.10	225	2.10	240
E	9.73	A	A	9.66?	331	9.69?	299	9.71	276
	5.61	A	A	5.57?	197	5.57?	197	5.57	195
	3.88	3.87	248	3.87	285	3.87	288	3.87	283
Q	3.34	3.36	346	3.34	258	3.36	389	3.36	364
	4.26	4.28	206	4.28	210	4.29	205	4.3	201
	1.82	1.83	101	1.83	117	1.84	87	1.83	90

* = 100% peak A = absent

Table 4.3.14 d-Spacings and Raw Intensities for 3:1 PFA:OPC + 1% $SnCl_2$

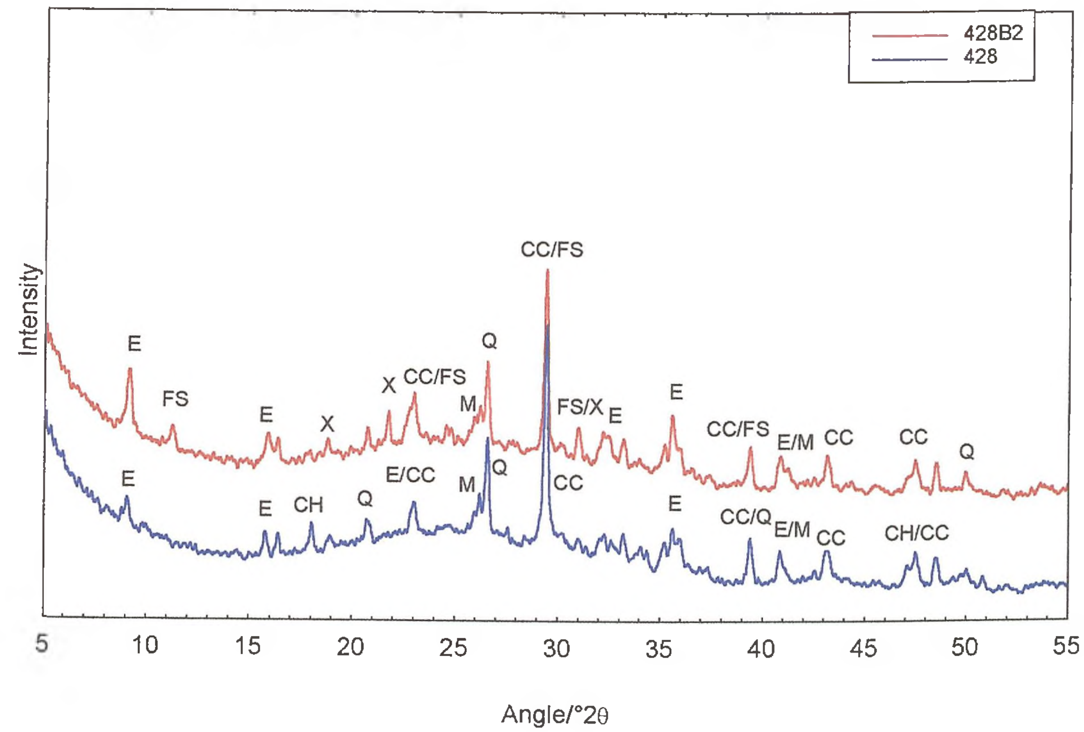

Figure 4.3.23 3:1 PFA:OPC (428) & 3:1 PFA:OPC + 1% $SnCl_2$ (428B2) Hydrated for 28 Days

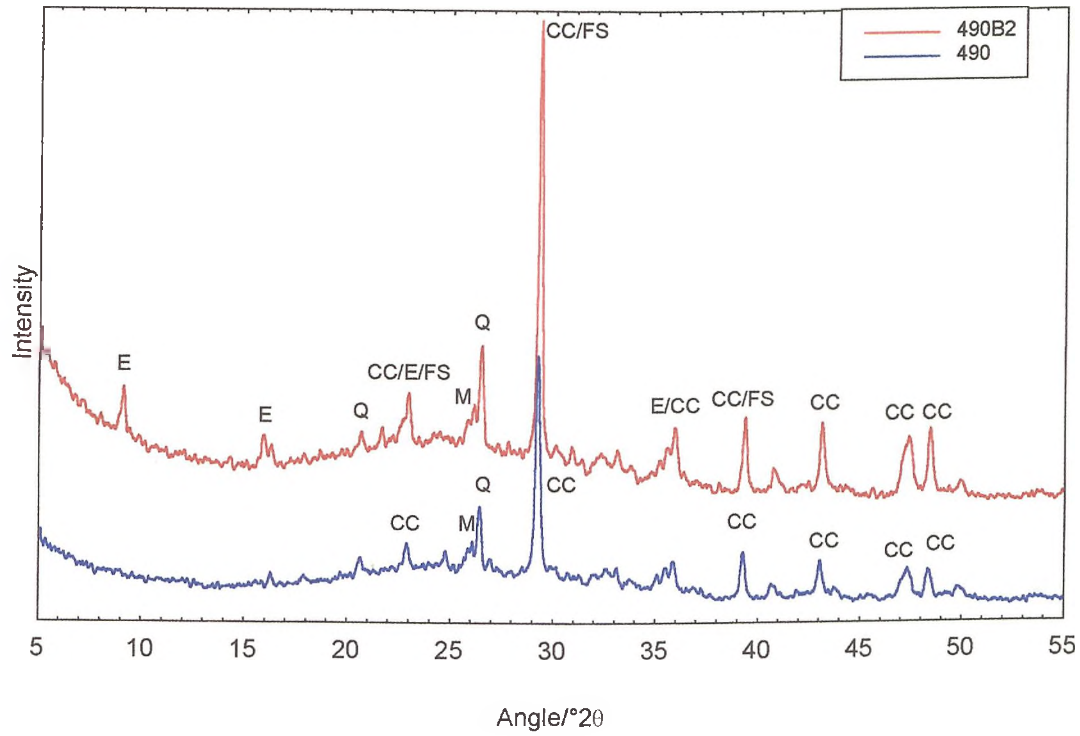

Figure 4.3.24 3:1 PFA:OPC (490) & 3:1 PFA:OPC + 1% $SnCl_2$ (490B2) Hydrated for 90 Days

4.3.4 $SnCl_4$ Systems

As mentioned previously the addition of the metal salts at 5% loading was only carried out on a limited scale. It was not possible to add 5% $SnCl_4$ to any of the cement systems as the amount of heat generated on adding the water was such that the water boiled off and there was insufficient remaining to form a paste. Therefore, the only data available for the $SnCl_4$ system was that at 1% loading and, as seen in the previous section, this was near the limits of detection of the phases by the diffractometer. Also, it was not possible to form a cement paste with the 9:1 BFS:OPC system with the $SnCl_4$ salt, therefore, there will be no data presented for this system. However, enough information was available to give an idea of what was occurring although this was obviously limited. From the results of the addition of $SnCl_2$ to the cement systems it was proposed that the tin(II) oxidised to tin(IV) in solution and then combined with the cement phases to form Friedel's salt and calcium hydroxo stannate (Eqn. 4.3). It would, therefore, be expected that much the same products would be formed with the addition of $SnCl_4$.

Figures 4.3.25 and 4.3.26 show 100% OPC (128) and 100 % OPC + 1% $SnCl_4$ hydrated for 28 and 90 days respectively. It can be seen that after, 28 days, the main difference between the neat cement and the tin-containing cement was that there was evidence for the formation of ettringite and Friedel's salt in the tin system but not in the neat cement. There was also some evidence for the formation of phase X although, as in the 1% tin(II) system, the peaks were combined with other hydration phases. This was confirmed by the data presented in Table 4.3.15 where it can be seen that the most intense peak at 4.06Å was absent. Figure 4.3.26 shows the systems after 90 days hydration and it can be seen that there was very little change from that seen after 28 days hydration apart from an increase in the amount of calcium carbonate and a decrease in the amount of calcium hydroxide in both systems.

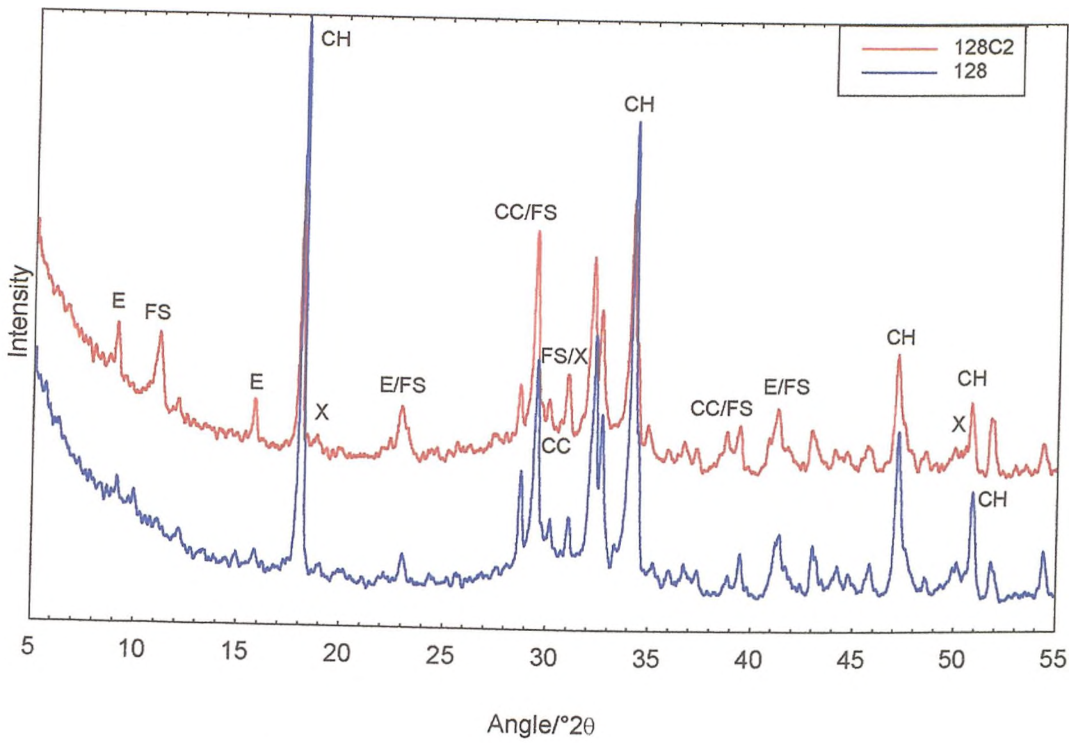

Figure 4.3.25 100% OPC (128) & 100% OPC + 1% $SnCl_4$ (190C2) Hydrated for 28 Days

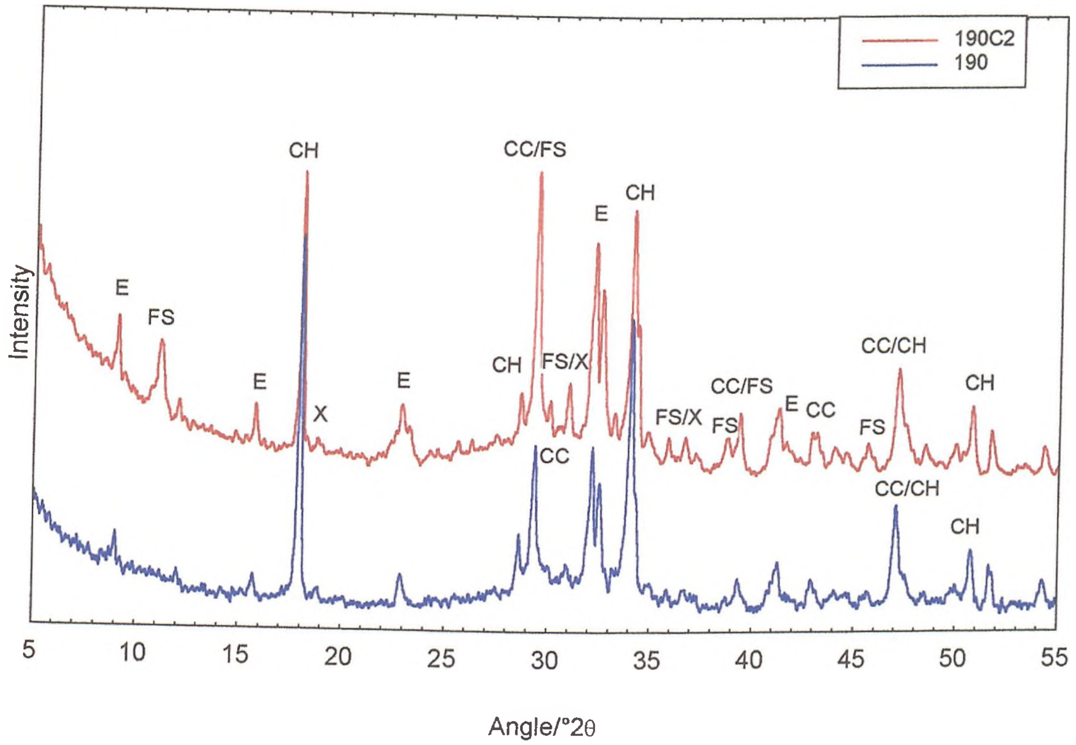

Figure 4.3.26 100% OPC (190) & 100% OPC + 1% $SnCl_4$ (190C2) Hydrated for 90 Days

Days		**3**		**28**		**90**		**180**	
	JCPDS	**d**	**I**	**d**	**I**	**d**	**I**	**d**	**I**
X	4.06	A	A	A	A	A	A	A	A
	4.69	4.71	110	4.71	112	4.72	110	4.71	115
	2.87	2.88	196	2.89	218	2.88	206	2.88	192
FS	2.88	2.88	196	2.89	218	2.87	206	2.88	192
	7.92	7.89	270	7.96	275	7.96	264	7.94	269
	2.45	2.45	125	2.45	112	2.45	118	2.45	112
CH	2.63	2.63	157	2.63	507	2.63	487	2.63	530
	4.90	4.91	639	4.92	532*	4.93	542	4.92	492
	1.93	1.93	282	1.93	256	1.93	229	1.93	224
CC	3.04	3.03	303	3.04	455	3.04	549*	3.04	550*
	2.29	2.29	119	2.29	138	2.29	157	2.29	153
	2.10	2.11	164	2.11	132	2.11	126	2.1	125
E	9.73	9.67	266	9.77	289	9.77	302	9.73	273
	5.61	5.58	151	5.63	169	5.63	164	5.60	161
	3.88	3.88	149	3.88	162	3.89	167	3.88	163

* = 100% peak A = absent

Table 4.3.15 d-Spacings and Raw Intensities for 100% OPC + 1% $SnCl_4$

Figures 4.3.27 and 4.3.28 show x-ray diffraction patterns for the 3:1 BFS:OPC (228 & 290) and 3:1 BFS:OPC + 1% $SnCl_4$ (228C2 & 290C2) systems hydrated for 28 and 90 days, respectively. After 28 days it can be seen that there was no calcium hydroxide present in the tin-containing system and very little ettringite in the neat cement. Also, there was some evidence for the presence of Friedel's salt, but no direct confirmation of the production of phase X in the tin system. This is illustrated more clearly in Table 4.3.16 where the two strongest peaks for phase X were mostly absent, whereas those for Friedel's salt were evident at all intensities and all ages. After 90 days hydration (Figure 4.3.28) there appeared to be less Friedel's salt present and a definite decrease in the amount of calcium hydroxide in the neat cement. Also, there appeared to be more calcium carbonate in both systems although this was not as great as in either the OPC system (Figures

4.3.25 & 4.3.26) or in the 3:1 BFS:OPC system with 1% $SnCl_2$ added (Figure 4.3.27 & 4.3.28). However, there was one major difference between this system and all other systems studied which was the appearance of two relatively strong peaks, identified as being due to the presence of $SnCl_4$ and which occurred around 27°2θ and 33°2θ (Figure 4.3.28). These peaks have not been identified anywhere else other than in the 3:1 BFS:OPC system after 90 and 180 days hydration. It is possible that these results were an aberration even though they were identified after two hydration times. However, they may also be a phenomenon unique to the slag cements but, without further studies on the 3:1 BFS:OPC cement or any data available from the 9:1 BFS:OPC system it would be difficult to comment further.

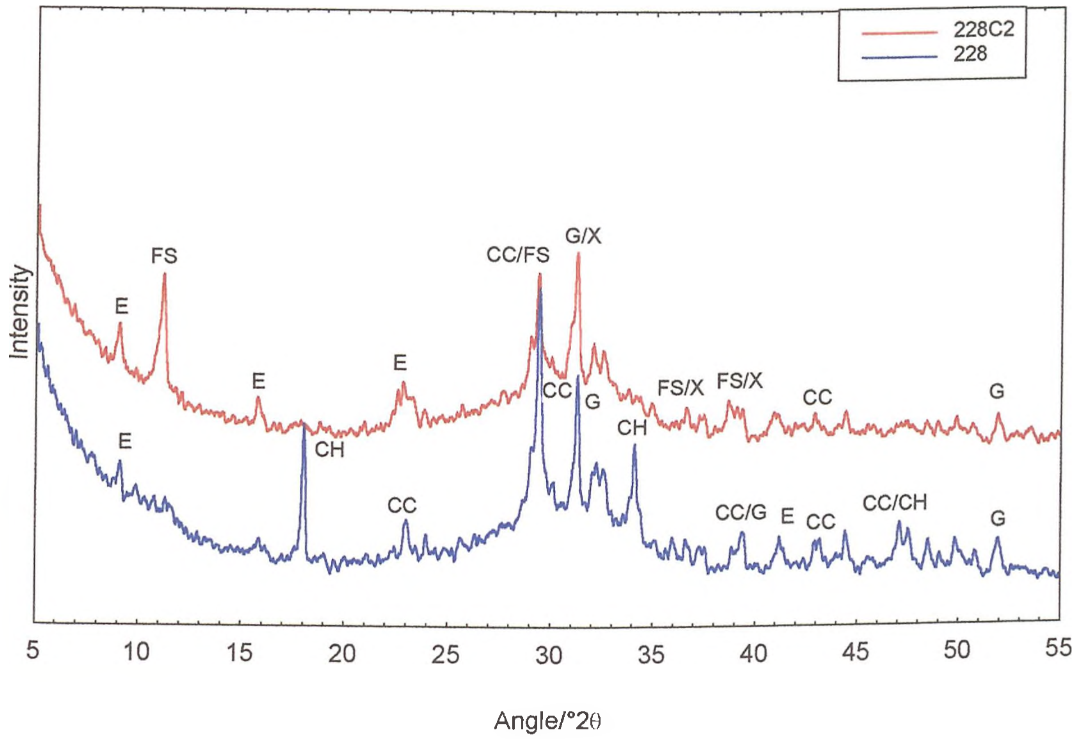

Figure 4.3.27 3:1 BFS:OPC (228) & 3:1 BFS:OPC + 1% $SnCl_4$ (228C2) Hydrated for 28 Days

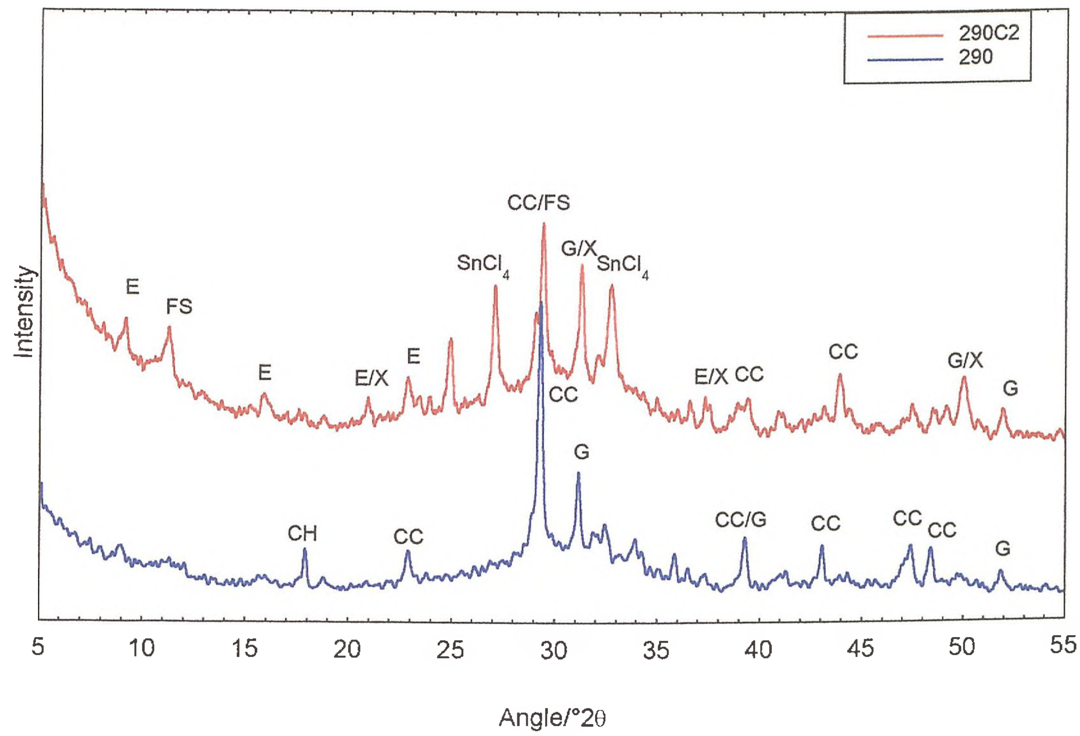

Figure 4.3.28 3:1 BFS:OPC (290) & 3:1 BFS:OPC + 1% $SnCl_4$ (290C2) Hydrated for 90 Days

Days		**3**		**28**		**90**		**180**	
	JCPDS	**d**	**I**	**d**	**I**	**d**	**I**	**d**	**I**
X	4.06	4.08	117	A	A	A	A	A	A
	4.69	A	A	A	A	4.70	100	4.68	107
	2.87	2.87	338	2.86	347	2.86	328	2.86	311
FS	2.88	2.88	286	2.86	347	2.86	328	2.86	311
	7.92	7.89	317	7.91	311	7.85	232	7.83	245
	2.45	2.46	136	2.45	120	2.46	127	2.46	110
CH	2.63	2.62	162	A	A	A	A	2.65	153
	4.90	A	A	A	A	A	A	A	A
	1.93	1.94	112	A	A	1.92	119	1.92	130
CC	3.04	3.04	254	3.04	316	3.04	389	3.04	500*
	2.29	A	A	2.29	118	2.29	130	2.29	151
	2.10	A	A	2.11	110	2.10	118	2.10	128
E	9.73	9.77	242	9.77	238	9.65	245	9.71	256
	5.61	5.61	144	5.62	133	5.62	131	5.60	138
	3.88	A	A	3.89	157	3.89	160	3.89	171
G	2.86	2.87	338	2.86	347	2.86	328	2.86	311
	1.93	1.94	112	A	A	1.92	119	1.92	130
	3.72	3.72	133	A	A	3.72	132	3.72	134

* = 100% peak A = absent

Table 4.3.16 d-Spacings and Raw Intensities for 3:1 BFS:OPC + 1% $SnCl_4$

Figures 4.3.29 and 4.3.30 show x-ray diffraction traces for the 3:1 PFA:OPC (428 and 4180) and 3:1 PFA:OPC + 1% $SnCl_4$ (428C2 and 4180C2) systems hydrated for 28 and 180 days, respectively. The trend seen in this system mirrors that of the $SnCl_2$ system (Figures 4.3.23 and 4.3.24). That is, after 28 days there was some evidence for the formation of phase X but after 180 days there was no conclusive evidence of its presence at all. Also, the amount of Friedel's salt was again small but in this system it disappeared after 90 days hydration (Table 4.3.17).

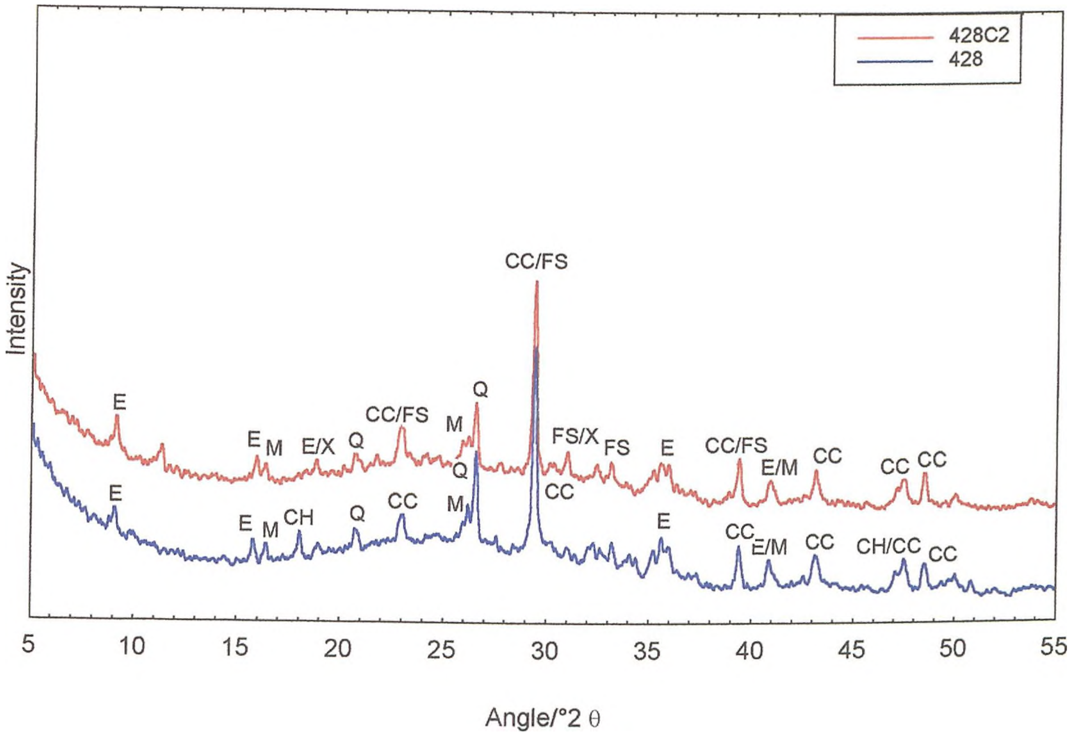

Figure 4.3.29 3:1 PFA:OPC (428) & 3:1 PFA:OPC + 1% $SnCl_4$ (428C2) Hydrated for 28 Days

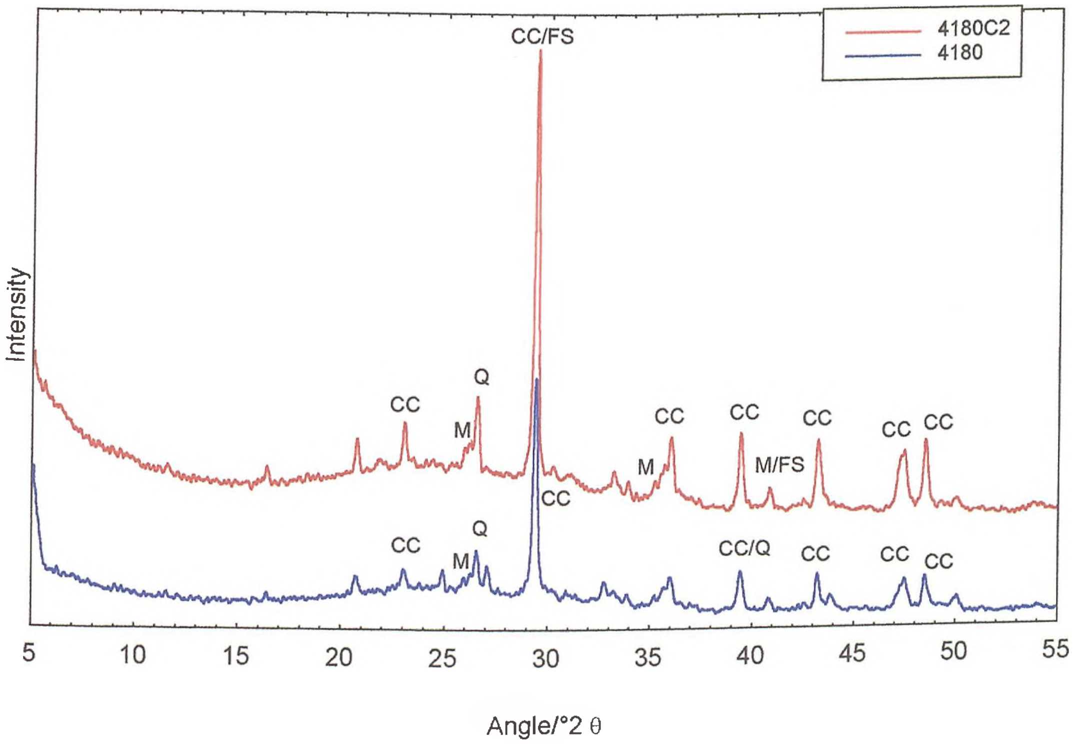

Figure 4.3.30 3:1 PFA:OPC (4180) & 3:1 PFA:OPC + 1% $SnCl_4$ (4180C2) Hydrated for 180 Days

Days		**3**		**28**		**90**		**180**	
	JCPDS	**d**	**I**	**d**	**I**	**d**	**I**	**d**	**I**
X	4.06	4.09	254	4.08	181	4.07	199	A	A
	4.69	4.73	195	4.71	198	A	A	A	A
	2.87	2.89	231	2.88	192	A	A	A	A
FS	2.88	2.89	231	2.88	192	A	A	A	A
	7.92	7.87	197	A	A	A	A	A	A
	2.45	2.46	122	A	A	A	A	A	A
CH	2.63	2.61	157	A	A	A	A	A	A
	4.90	4.94	161	A	A	A	A	A	A
	1.93	A	A	1.93	110	1.92	188	1.92	189
CC	3.04	3.05	191	3.04	583*	3.04	1050*	3.04	1121*
	2.29	2.30	112	2.29	178	2.29	249	2.29	247
	2.10	2.11	112	2.10	150	2.09	221	2.10	230
E	9.73	9.73	293	9.67	266	A	A	A	A
	5.61	5.59	198	5.56	175	A	A	A	A
	3.88	3.89	278	3.87	249	3.86	255	3.86	274
Q	3.34	3.36	342	3.36	302	3.36	328	3.36	333
	4.26	4.29	197	4.28	186	4.28	213	4.28	236
	1.82	1.83	119	A	A	1.82	99	A	A

* = 100% peak A = absent

Table 4.3.17 d-Spacings and Raw Intensities for 3:1 PFA:OPC + 1% $SnCl_4$

The reason for this is probably that the pozzolanic reaction utilised the $CaSn(OH)_6$ formed as there was no calcium hydroxide present.

In summary, the addition of $SnCl_2$ or $SnCl_4$ to any of the cement systems caused two non-standard hydration phases to be formed which were calcium hydroxo stannate ($CaSn(OH)_6$) and Friedel's salt ($Ca_3Al_2O_6.CaCl_2.10H_2O$). As a consequence of this, the amount of calcium hydroxide present decreased substantially to that identified in the neat cement. This was most clearly illustrated in the 100% OPC cement system with a loading of 5% $SnCl_2$ and Eqn. 4.3 suggests a reason for this observation.

The main difference between the cement systems was in the formation of Friedel's salt. There was much less evidence for it's presence in the 9:1 BFS:OPC and 3:1 PFA:OPC cement systems and one reason for this cold be the lack of C_3A in these systems due to the decreased amount of OPC present. C_3A was one of the phases in the cement which, according to Eqn. 4.3, contributed to the formation of the Friedel's salt and the calcium hydroxo stannate. There was also some possible evidence for the consumption of the calcium hydroxo stannate phase for the pozzolanic reaction in both the 3:1 PFA:OPC and 9:1 BFS:OPC cements which was utilised due to the lack of calcium hydroxide present.

4.3.5 $ZnCl_2$ Systems

The addition of $ZnCl_2$ to the cement systems caused significant retardation of set as shown by the calorimetry data in section 4.2. Therefore, it was difficult to form a cement paste which would set within the time needed for this work. This meant that, for the 5% loading the only system which was feasible to study was the 9:1 BFS:OPC system, and at 1% loading only the 9:1 BFS:OPC and 3:1 PFA:OPC cements were available for investigation.

Figure 4.3.31 shows the x-ray diffraction pattern for the 9:1 BFS:OPC (314) and 9:1 BFS:OPC + 5% $ZnCl_2$ (314A1) systems hydrated for 14 days. This was the earliest age at which it was possible to grind the cement paste to a powder to prepare for x-ray diffraction due to the high level of retardation occurring in this system. Before this age the pastes were too wet to grind even if placed in a vacuum desiccator for 3 days. It can be seen from Figure 4.3.31 that the main constituents present were gehlenite, Friedel's salt and phase Z. However, the occurrence of phase Z overlapped with other hydration products being formed and the only peak due to this phase on its own was a very small peak around 17°2θ. This was not very conclusive evidence that this phase was being formed. The results after 28 days were not dissimilar and have, therefore, not been included.

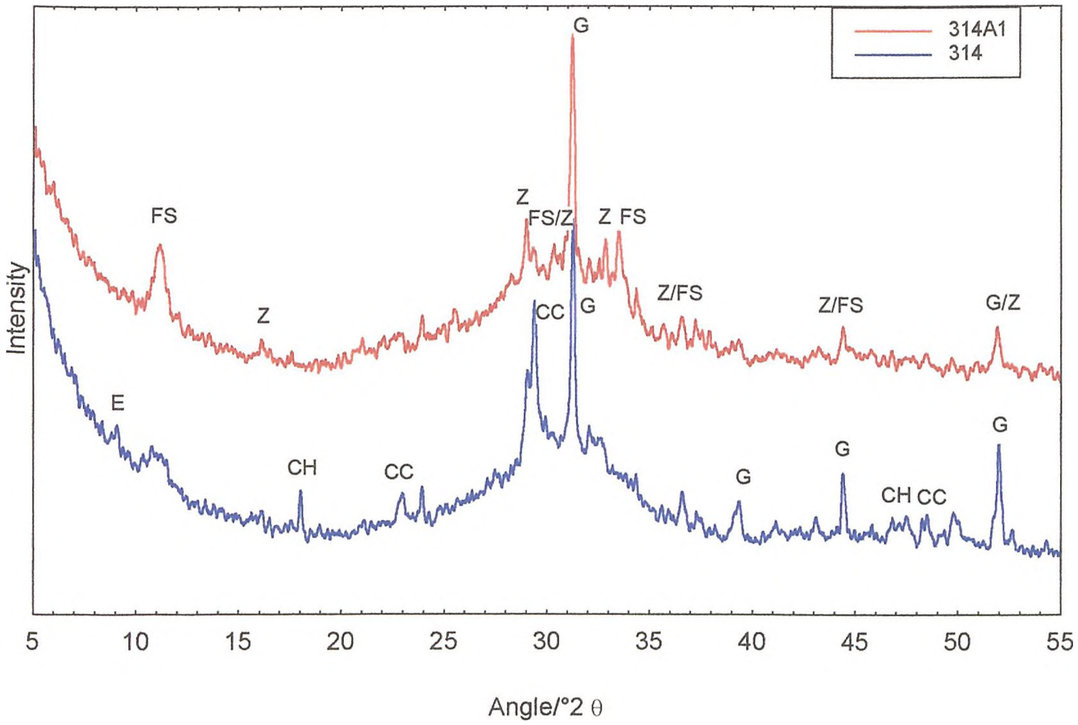

Figure 4.3.31 9:1 BFS:OPC (314) & 9:1 BFS:OPC + 5% $ZnCl_2$ (314A1) Hydrated for 14 Days

After 90 days (Figure 4.3.32) it can be seen that, whilst there was not a significant difference, the amount of phase Z appeared to be increasing and there was some evidence for it occurring on its own, although these peaks were still relatively small. However, after 180 days hydration (Figure 4.3.33), there were significant differences. There was still clear evidence for the presence of gehlenite and also, some calcium carbonate started to form which hadn't been detected previously. However, the main difference was that the amount of phase Z had increased significantly and it became clear that this phase was forming. It was possible it took so long as the system was very retarded and the hydration required time to proceed.

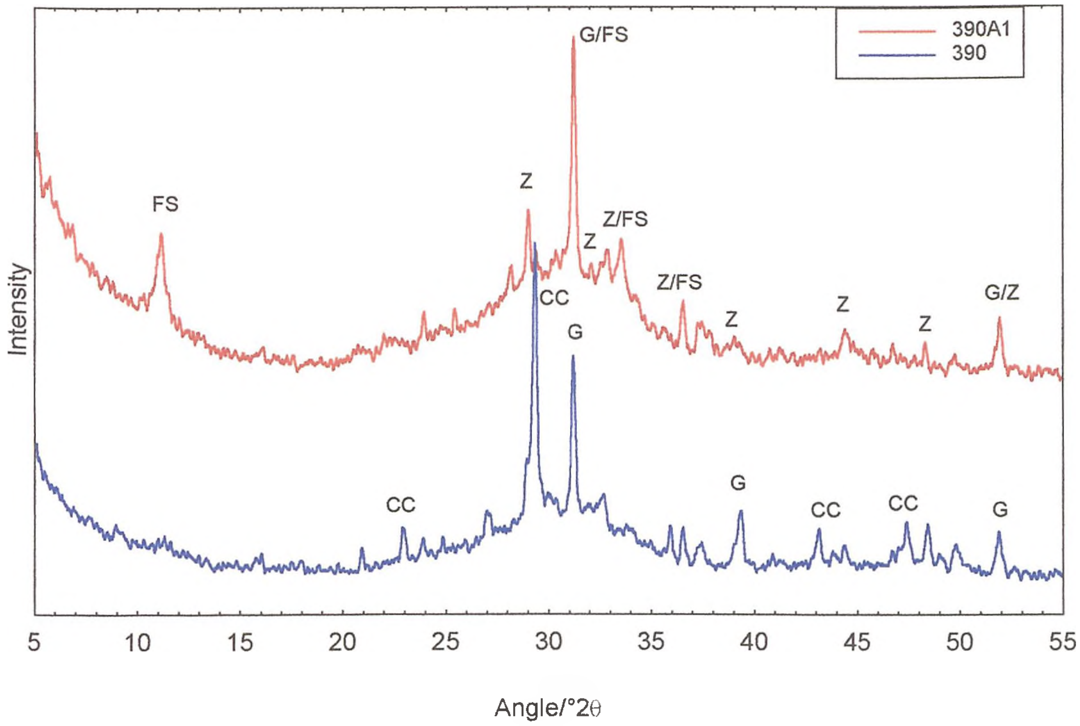

Figure 4.3.32 9:1 BFS:OPC (390) & 9:1 BFS:OPC + 5% $ZnCl_2$ (390A1) Hydrated for 90 Days

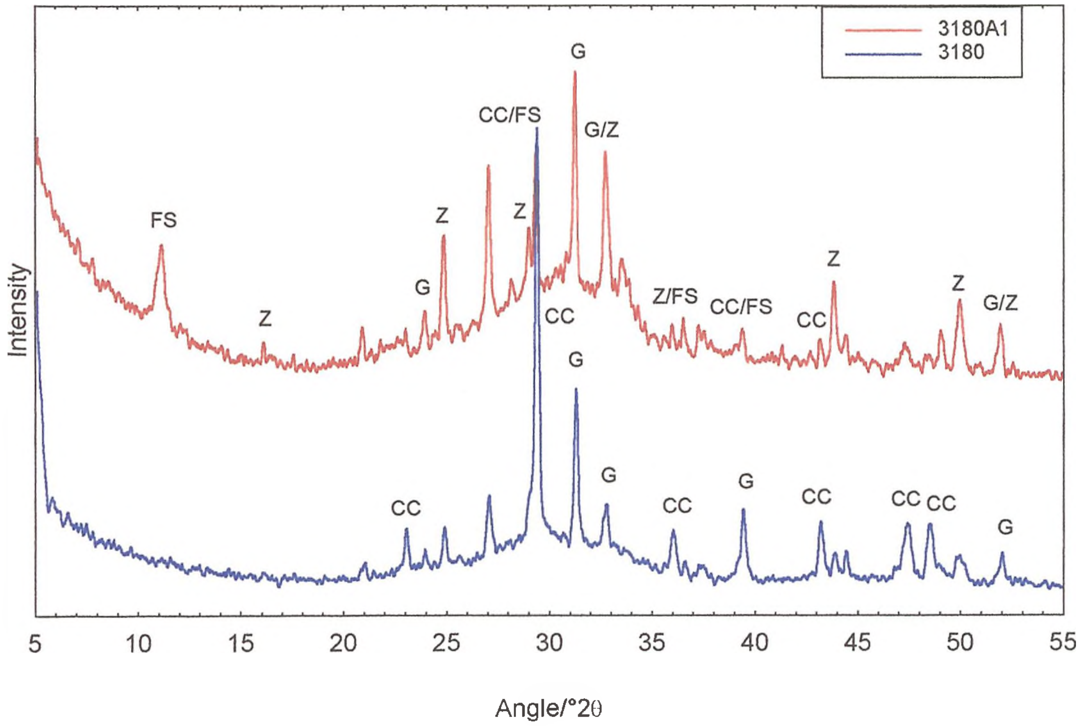

Figure 4.3.33 9:1 BFS:OPC (3180) & 9:1 BFS:OPC + 5% $ZnCl_2$ (3180A1) Hydrated for 180 Days

It has been well documented in the literature[36,41,43,44,46,49-51] that, when zinc is added to a cement, a calcium zinc hydroxide hydrate – $CaZn_2(OH)_6.2H_2O$ - is formed. The peaks labelled Z on the x-ray diffraction traces were identified as being indicative of this phase.

Table 4.3.18 shows d-spacings for the three strongest peaks for the calcium zincate as identified by the JCPDS card system along with those for Friedel's salt. The angles were calculated using Bragg's Law (Eqn. 4.1) and the experimental d-spacings are also shown. The values were taken from the 9:1 BFS:OPC cement with 5% $ZnCl_2$ added after being hydrated for 180 days. It can be seen that the values agree well and, therefore, it can be stated that the calcium zincate phase was formed.

Phase	**d-spacing/Å**	**Angle/°2θ**	**Experimental d-spacing/Å**
Z	2.88	31.05	2.89
	3.56	25.01	3.57
	1.82	50.12	1.82
	2.45	36.68	2.45
	2.39	37.64	2.40
	2.04	44.41	2.04
	2.74	32.68	2.73
	2.06	43.95	2.06
	5.49	16.14	5.50
	3.07	29.09	3.08
FS	2.88	31.05	2.89
	7.92	11.17	7.93
	2.45	36.68	2.46
	3.86	23.04	3.86
	3.04	29.38	3.04
	2.03	44.64	2.04
	2.28	39.53	2.29
	2.17	41.62	2.18

Card numbers: Z = 25-1449; FS = 28-207

Table 4.3.18 d-Spacings and Angles for the Non-Standard Hydration Phases

As indicated in Figures 4.3.31 – 4.3.33, there was evidence for the formation of Friedel's salt in the zinc-containing systems, but not in the neat cements. These results were similar to those observed in the tin-containing systems and, therefore, an equation can be proposed for the formation of calcium zincate and Friedel's salt:

$$\begin{array}{c} 2ZnCl_2 + 2Ca_3Al_2O_6 + 3Ca(OH)_2 + 22\ H_2O \\ \downarrow \\ \underset{\text{(Friedel's Salt)}}{2Ca_3Al_2O_6.CaCl_2.10\ H_2O} + \underset{\text{(Phase Z)}}{CaZn_2(OH)_6.2H_2O} \end{array} \qquad \text{Equation 4.4}$$

As the evidence for the formation of $CaZn_2(OH)_6.2H_2O$ was not as strong as for the parallel tin phase in the cements loaded with 5% $ZnCl_2$, it could be assumed that at 1% loading there may be very little evidence. These observations highlight the difficulties in working with systems in which the phases formed are close to the limits of detection of the equipment. The problems discussed for the tin-containing systems were even greater for the zinc-containing cements due to the weak intensities of the peaks and the greatly retarded systems.

Figure 4.3.34 shows the 9:1 BFS:OPC neat cement and 9:1 BFS:OPC with 1% $ZnCl_2$ added both hydrated for 28 days. It can be seen that very little hydration had occurred in either cement but, especially in the zinc-containing system. Gehlenite was the only phase present and the XRD trace was very similar to that of the anhydrous material, indicating that very little hydration had proceeded. However, after 90 days hydration (Figure 4.3.35) it can be seen that there was quite substantial evidence for the formation of phase Z as well as the appearance of some calcium carbonate, especially around 29°2θ. This is in comparison to the 5% sample (Figure 4.3.32) where, even though the scales are different, it can be clearly seen that there was no calcium carbonate formation at 5% loading. The other main difference between 1% and 5% additions of $ZnCl_2$ was that with the 1% there was no evidence of any Friedel's salt formation, whereas at 5% there was no doubt that Friedel's salt had been formed at all ages. There was also no ettringite formed in either system.

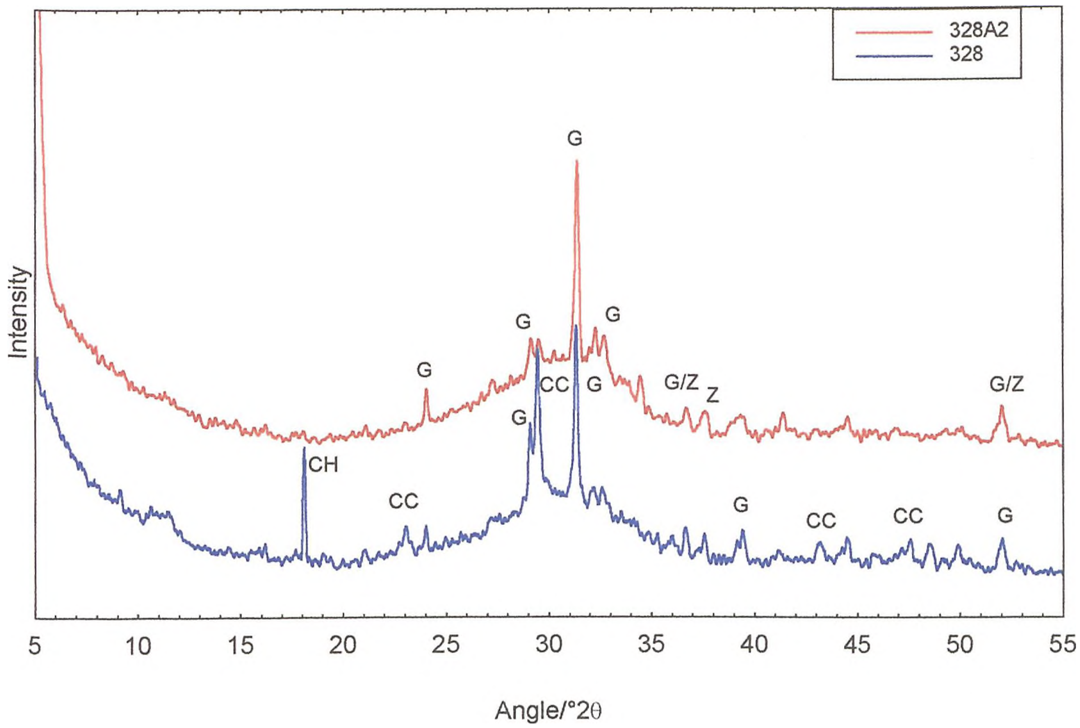

Figure 4.3.34 9:1 BFS:OPC (328) & 9:1 BFS:OPC + 1% $ZnCl_2$ (328A2) Hydrated for 28 Days

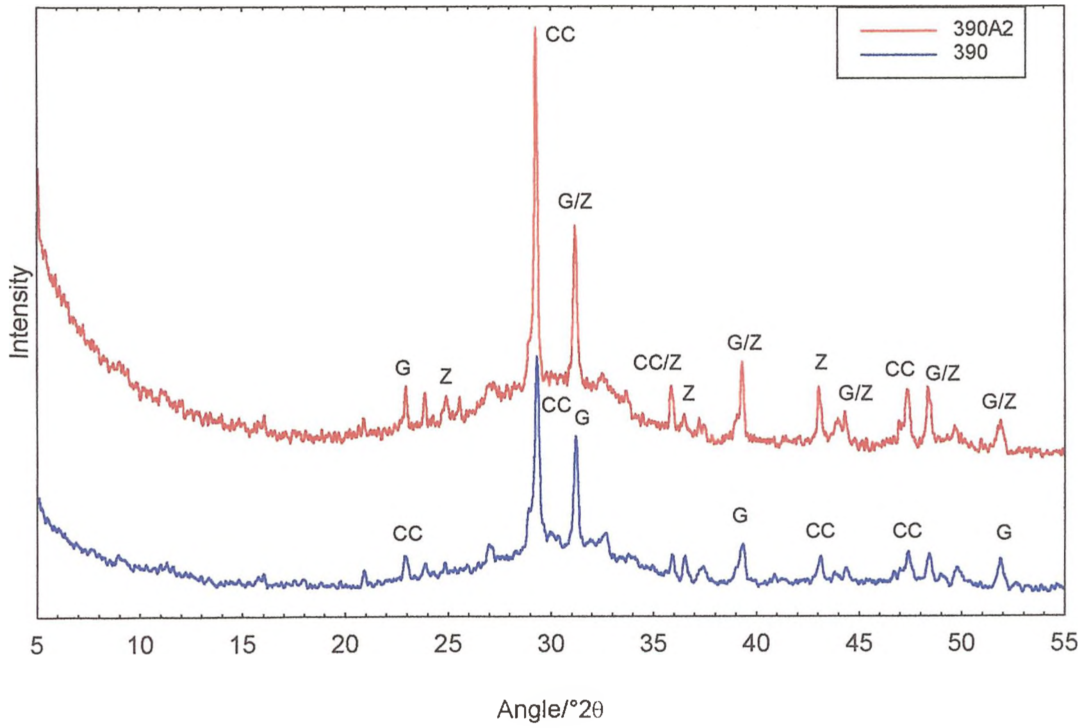

Figure 4.3.35 9:1 BFS:OPC (390) & 9:1 BFS:OPC + 1% $ZnCl_2$ (390A2) Hydrated for 90 Days

The 3:1 PFA:OPC system with 1% addition of $ZnCl_2$ exhibited different behaviour to that of the 9:1 BFS:OPC system. Figure 4.3.36 shows x-ray diffraction traces for the 3:1 PFA:OPC (414) and 3:1 PFA:OPC + 1% $ZnCl_2$ (414A2) systems hydrated for 14 days. There was not much difference between the neat and zinc-containing cements at this age except that there were some weak peaks attributable to the formation of phase Z in the zinc-containing cements. There was no evidence for Friedel's salt formation but both systems showed evidence for the formation of ettringite. However, after 28 days (Figure 4.3.37), there was a significant difference in the zinc-containing system (428A2). The ettringite had disappeared, the amount of calcium carbonate present appeared to have decreased and there was a relatively large peak around 32-33°2θ indicative of the formation of phase Z. Of all the cement systems studied this peak for phase Z was the most significant seen. There were also some smaller peaks similar to those seen previously which were further evidence for the formation of this phase.

After 180 days hydration (Figure 4.3.38) it can be seen that the zinc-containing cement consisted mainly of calcium carbonate with some residual quartz, however, the peaks due to phase Z had largely disappeared. This mirrored what occurred with both the 1% $SnCl_2$ and 1% $SnCl_4$ systems. The reason put forward was that it was possible that because of the lack of calcium hydroxide present in the cement system the $CaZn_2(OH)_6.2H_2O$ phase (or the corresponding tin phase) was utilised for the pozzolanic reaction. It was not clear if this decrease was occurring in the 5% $SnCl_2$ system as there was significant amounts of the phase present. There was no formation of Friedel's salt in this system at any age, as observed with the 9:1 BFS:OPC cement. Ettringite did, however, form at early ages.

The effect of adding $ZnCl_2$ to the cement systems studied was the formation of calcium zincate ($CaZn_2(OH)_6.2H_2O$) and Friedel's salt ($Ca_3Al_2O_6.CaCl_2.10H_2O$) which was a very similar result to the addition of the tin salts. A similar mechanism was suggested in Eqn. 4.4 for the formation of these phases. Although the study of the zinc-containing cements was restricted due to difficulties with cement preparation, the results obtained corresponded well with the published data and the results of the addition of the tin salts.

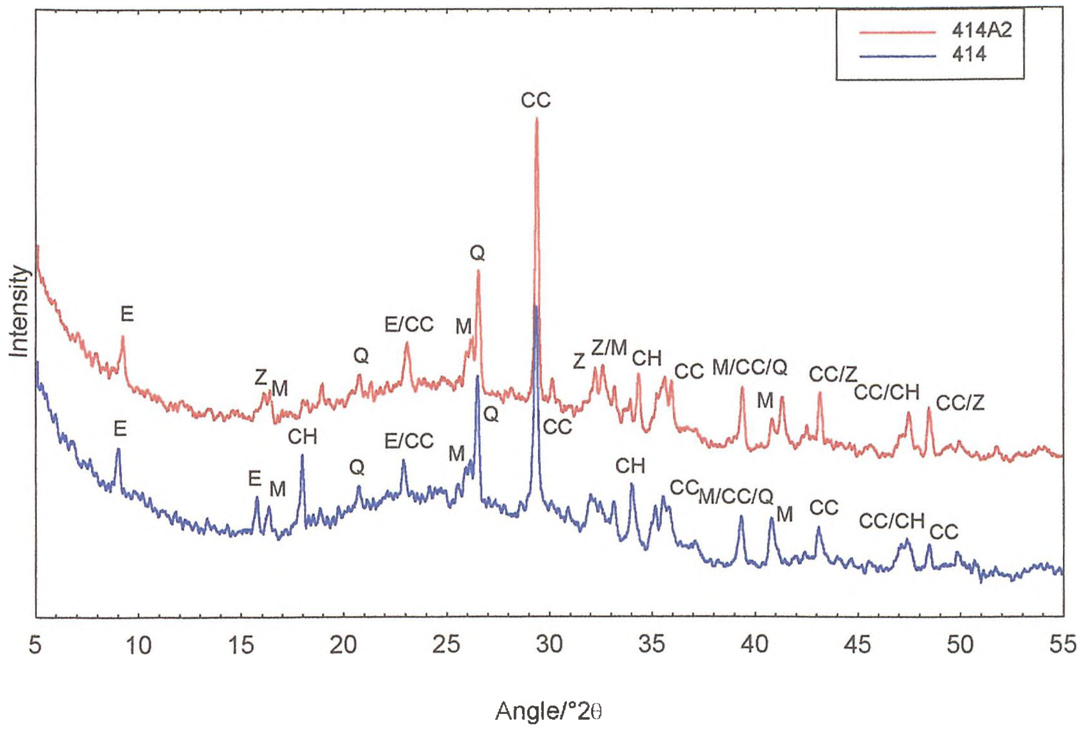

Figure 4.3.36 3:1 PFA:OPC (414) & 3:1 PFA:OPC + 1% $ZnCl_2$ (414A2) Hydrated for 14 Days

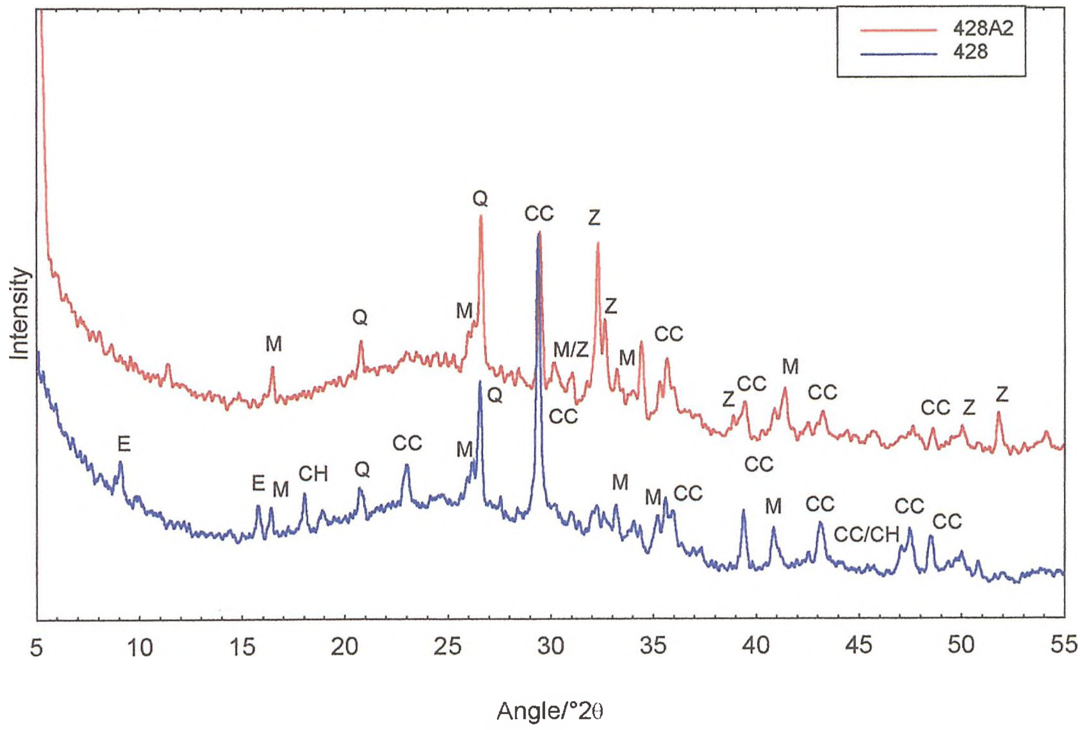

Figure 4.3.37 3:1 PFA:OPC (428) & 3:1 PFA:OPC + 1% $ZnCl_2$ (428A2) Hydrated for 28Days

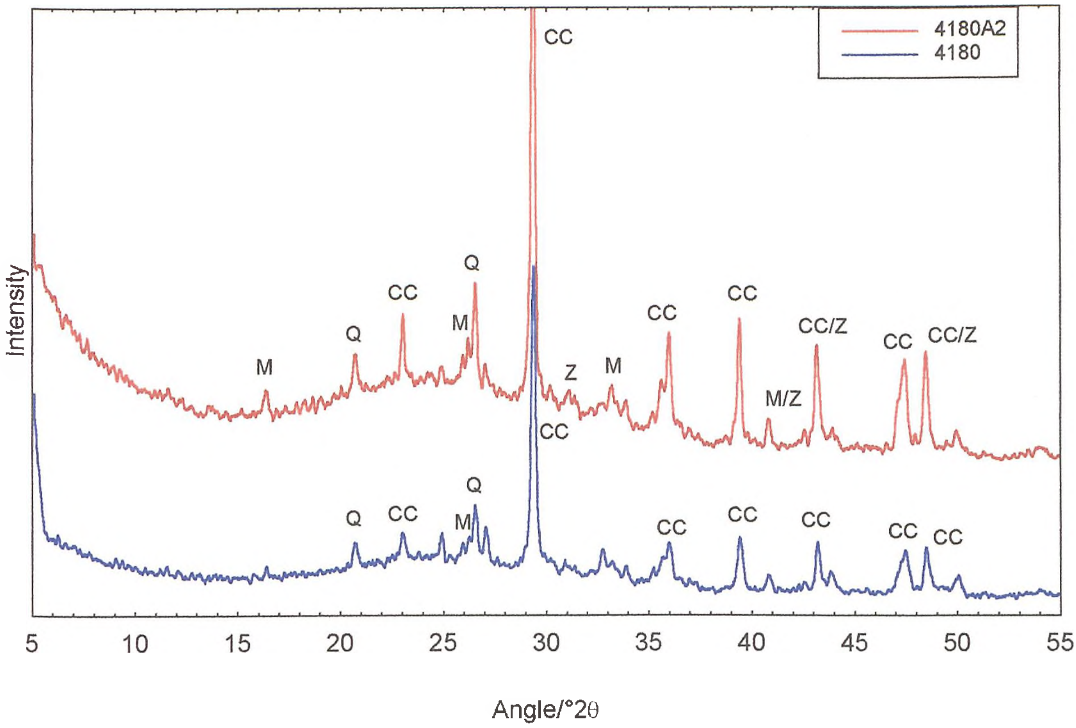

Figure 4.3.38 3:1 PFA:OPC (4180) & 3:1 PFA:OPC + 1% $ZnCl_2$ (4180A2) Hydrated for 180 Days

4.4 THERMAL ANALYSIS

Thermal analysis covers several different techniques. The main one used for this study was differential thermal analysis and will, therefore, be the one described in detail in this section. Differential thermal analysis is described as a technique in which the difference in temperature between the sample and the reference material is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed.[58] The discovery of this technique is usually credited to Le Chatelier, who in 1887 devised a heating-curve method to measure temperature as a function of time. The method was used to investigate the constitution and decomposition of clays and limestone.[59,60] Over the last twenty years the application of differential thermal analysis to investigate cement hydration has become diverse. The ability of the technique to detect minor chemical changes and provide analytical information for cements, with or without inorganic additives, has made it an invaluable tool, especially alongside other techniques such as x-ray diffraction.[60] Differential thermal analysis (DTA) works by measuring the temperature of the sample along with a reference material which, in this study, was fired alumina. The temperature difference between the sample and the reference is zero until the sample undergoes a thermal change. When this occurs there is either an absorption or evolution of heat which means that the temperature of the sample becomes lower or higher than that of the reference material. The differential temperature is plotted against the actual temperature which then shows endothermic or exothermic peaks which can be identified, enabling the hydration of the cement to be monitored.

The thermal analysis carried out was a limited study to help clarify the results obtained from the x-ray diffraction (section 4.3). As a consequence, the samples were chosen to attempt to illustrate the differences between the neat cement systems and those containing 5% $SnCl_2$. Some work was also done on the 9:1 BFS:OPC cement containing 5% $ZnCl_2$. All samples were run in a nitrogen atmosphere from room temperature to 600°C at 10°/minute.

4.4.1 Differential Thermal Analysis

The aim of this limited study was to attempt to identify standard and non-standard phases which would help to clarify the x-ray diffraction results. Using the x-ray diffraction results, the main phases to be identified were: calcium hydroxide, C-S-H, ettringite, Friedel's salt and $CaSn(OH)_6$ or $CaZn_2(OH)_6.2H_2O$ (depending on the metal salt present). It would not be possible to identify calcium carbonate as the maximum temperature used in this study was not high enough for this purpose. However, there was sufficient evidence for the formation of calcium carbonate from the x-ray diffraction results.

From the literature, the approximate peak temperatures at which the endotherms relating to these phases would be expected are shown in Table 4.4.1:

Phase	**Endotherm Temperature/°C**			
	Bye [54]		Taylor [1]	Birnin-Yauri[61]
	15 minutes	16 hours		
Calcium hydroxide	492	501/528 (doublet)	530-550	-
C-S-H	-	111	115-125	-
Ettringite	125	132	135-140	-
Friedel's salt	-	-	-	120

Table 4.4.1 Endotherm Peak Temperatures for Some Standard Cement Phases

It can be seen from Table 4.4.1 that there are discrepancies between the temperatures for any given endotherm. This is because the exact temperature at which the endotherm occurs can be affected by a number of factors. For example, if the equipment used differs then the results will differ. Also, the size of the sample and the amount of phase present contribute significantly to the differences in endotherm temperature. Therefore, these temperatures should be used as guidelines only and should not necessarily be matched exactly. It was not possible to find endotherm temperatures for the calcium hydroxo stannate or the calcium zincate phases and they are, therefore, not included in the table.

As this study was limited and the traces obtained from the chart recorder not readily available for computer manipulation, it was decided that all results would be tabulated and a few traces shown as an illustration of the tabular results. Therefore, Table 4.4.2 shows all the endotherm temperatures obtained for both neat cement systems and those containing 5% $SnCl_2$. There are also two results from the 9:1 BFS:OPC system containing 5% $ZnCl_2$. The cement systems have been entered by code for ease and the explanation of this can be found in Chapter 3.

4.4.1.1 OPC Systems

From Table 4.4.2 it can be seen that, as expected from the x-ray diffraction results, there were some differences between the neat and the tin-containing systems. Considering the neat cements first (128 - 1180), it can be seen that there were three endotherms common to this cement which were around 120°C, 170°C and 480°C. Figure 4.4.1 shows a 100% OPC cement having been hydrated for 28 days and clearly illustrates the endotherms. The y-axes on Figures 4.4.1 and 4.4.6 are greater than the other traces, which all have comparable y-axes. Therefore, the peaks observed in Figures 4.4.1 and 4.4.6 cannot be compared directly with any other trace although, the peak positions (endotherm temperatures) are comparable. This could not be avoided as putting all traces on the same axes resulted in diminished information from the smaller peaks.

Cement	Endotherm Temperatures/°C			
128	120	170	-	476
190	120	-	-	485
1180	107	170	-	467
128B1	120	158	270/311	457
190B1	120	158	280/311	448
1180B1	107	146	270/301	448
228	107	-	-	476
290	107	133	-	457
2180	107	-	-	-
228B1	80	133	280/341	-
290B1	107	158	301/361	-
2180B1	107	146	301	-
328	107	215	-	467
390	94	-	-	-
3180	107	-	-	-
328B1	107	-	331	-
390B1	80	-	311	-
3180B1	107	-	321	-
328A1	107	181	-	-
390A1	94	181	-	-
428	107	-	-	457
490	107	133	-	-
4180	120	-	-	-
428B1	107	-	311	-
490B1	94	-	311	-
4180B1	80	-	321	-

Table 4.4.2 Endotherm Temperatures for Results Obtained from DTA

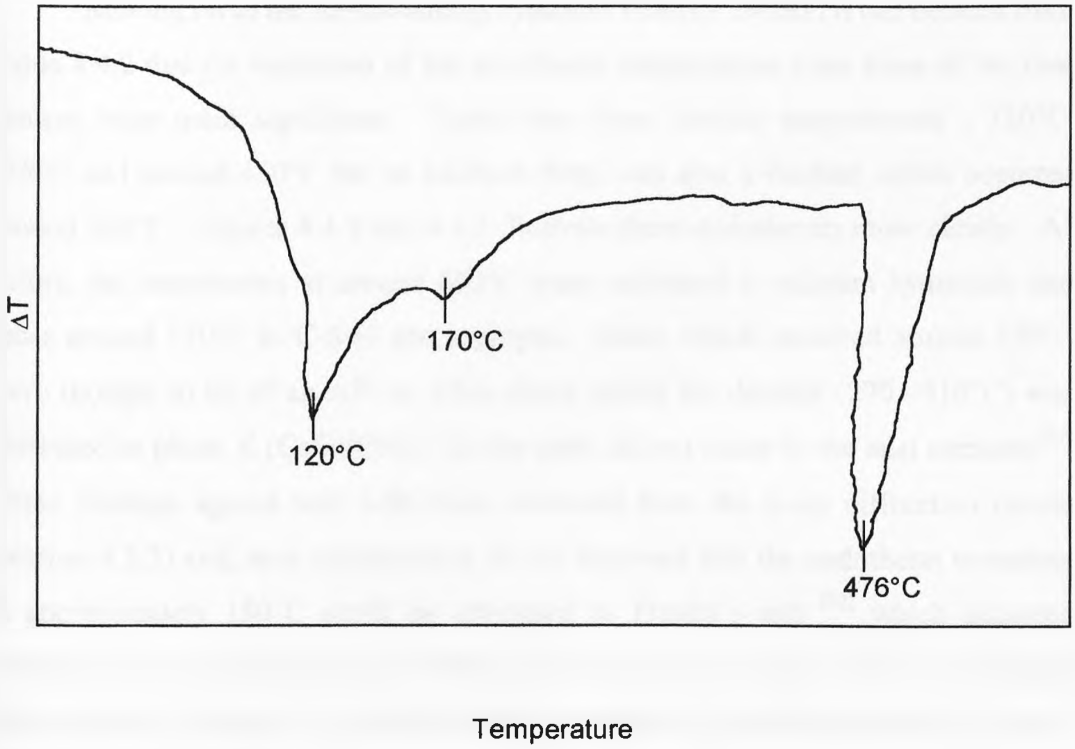

Figure 4.4.1 DTA Trace of a 100% OPC Hydrated for 28 Days

These endotherms were attributed to the following phases :

Calcium hydroxide ≈ 480°C.
C-S-H ≡ 120°C.

The endotherm which occurred around 170°C could have been either an AFt or an AFm phase. However, from the x-ray diffraction results (section 4.3.1), the only phase this could be attributed to would be ettringite and the temperatures given for this phase in Table 4.4.1 were much lower than that found by experiment. This would suggest that the endotherm indicating ettringite was probably occurring at around 120°C which would mean it would be masked by the C-S-H peak. Also, it is possible that the peak at around 170°C was attributable to some AFm phase just forming as it is a weak peak and the fact that it was not observed by x-ray diffraction does not mean that it was not present. Taylor[1] states that much of the AFm material is poorly crystalline which would mean that it would not be identified by x-ray diffraction.

Moving on to the tin-containing systems (128B1 - 190B1) it can be seen from Table 4.4.2 that the variations of the endotherm temperatures from those of the neat cement were quite significant. There were three similar temperatures - 120°C, 158°C and around 450°C but in addition there was also a doublet which occurred around 300°C. Figures 4.4.2 and 4.4.3 illustrate these endotherms more clearly. As before, the endotherms at around 450°C were attributed to calcium hydroxide and those around 120°C to C-S-H and ettringite. Those which occurred around 150°C were thought to be of an AFt or AFm phase whilst the doublet (270 –310°C) was attributed to phase X ($CaSn(OH)_6$) as this peak did not occur in the neat cements.[62] These findings agreed well with those observed from the x-ray diffraction results (section 4.3.2) and, as a consequence, it was reasoned that the endotherm occurring at approximately 150°C could be attributed to Friedel's salt [62] which occurred alongside the calcium hydroxo stannate (see Figures 4.3.10 and 4.3.11) even though the endotherm occurred at a slightly higher temperature than that recorded by Birnin-Yauri and Glasser.[61]

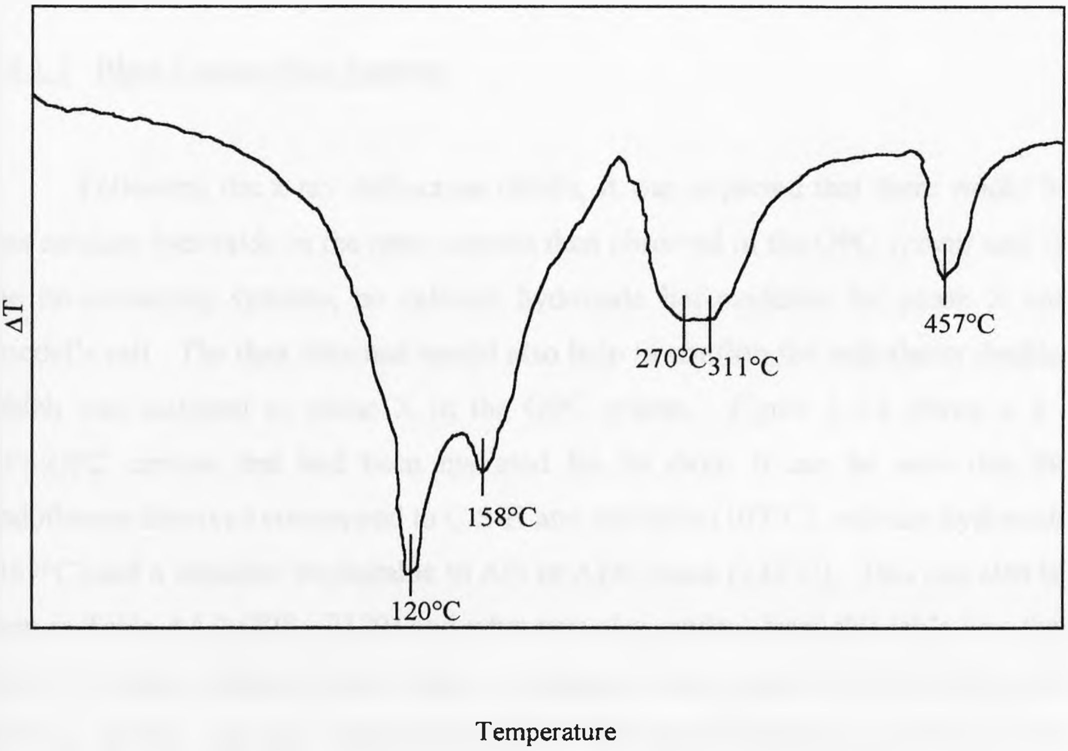

Figure 4.4.2 DTA Trace of a 100% OPC + 5% $SnCl_2$ Hydrated for 28 Days

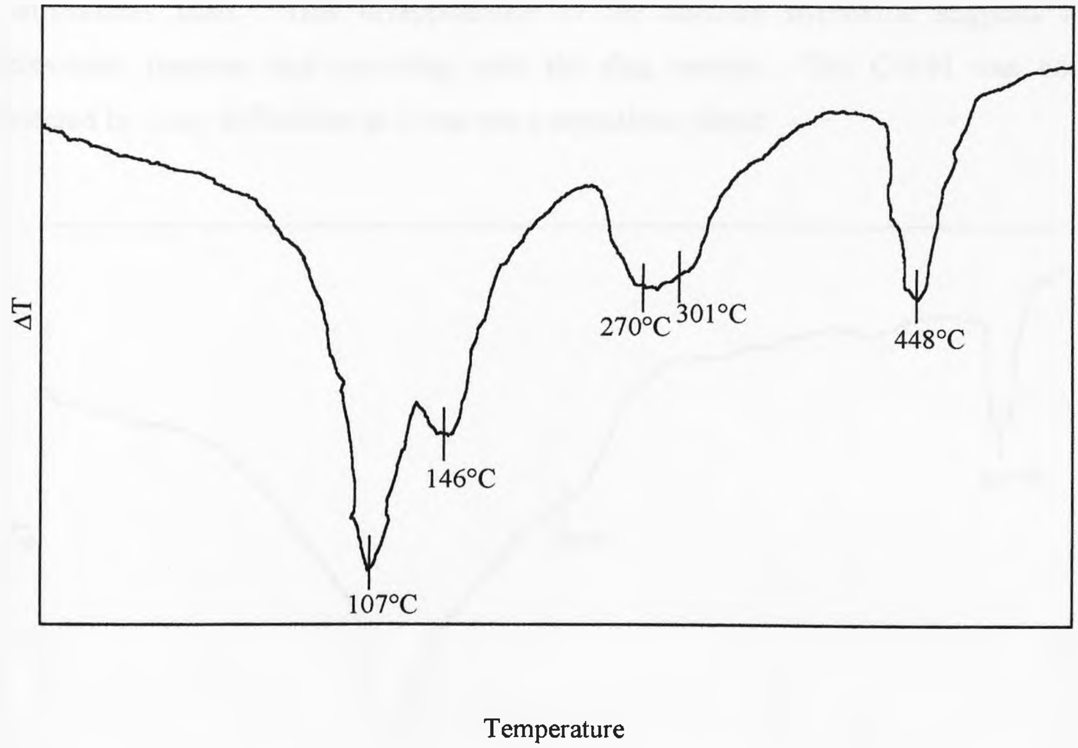

Figure 4.4.3 DTA Trace of a 100% OPC + 5% $SnCl_2$ Hydrated for 1180 Days

4.4.1.2 Blast Furnace Slag Systems

Following the x-ray diffraction results, it was expected that there would be less calcium hydroxide in the neat cements than observed in the OPC system and, in the tin-containing systems, no calcium hydroxide but evidence for phase X and Friedel's salt. The data obtained would also help to confirm the endotherm doublet which was assigned as phase X in the OPC system. Figure 4.4.4 shows a 3:1 BFS:OPC cement that had been hydrated for 90 days. It can be seen that the endotherms observed correspond to C-S-H and ettringite (107°C), calcium hydroxide (457°C) and a shoulder attributable to AFt or AFm phase (133°C). This can also be seen in Table 4.4.2 (228 - 2180) and what was also evident from this table was that after 180 days hydration there was no evidence of any calcium hydroxide in the system. In fact, the only endotherm present was that attributable to C-S-H. This confirmed the x-ray diffraction results (Figure 4.3.3) in that the amount of calcium hydroxide decreased up to 180 days and the only phases then present were calcium carbonate and gehlenite, neither of which were detected by DTA due to the temperatures used. This disappearance of the calcium hydroxide suggests a pozzolanic reaction was occurring with the slag cement. The C-S-H was not detected by x-ray diffraction as it was not a crystalline phase.

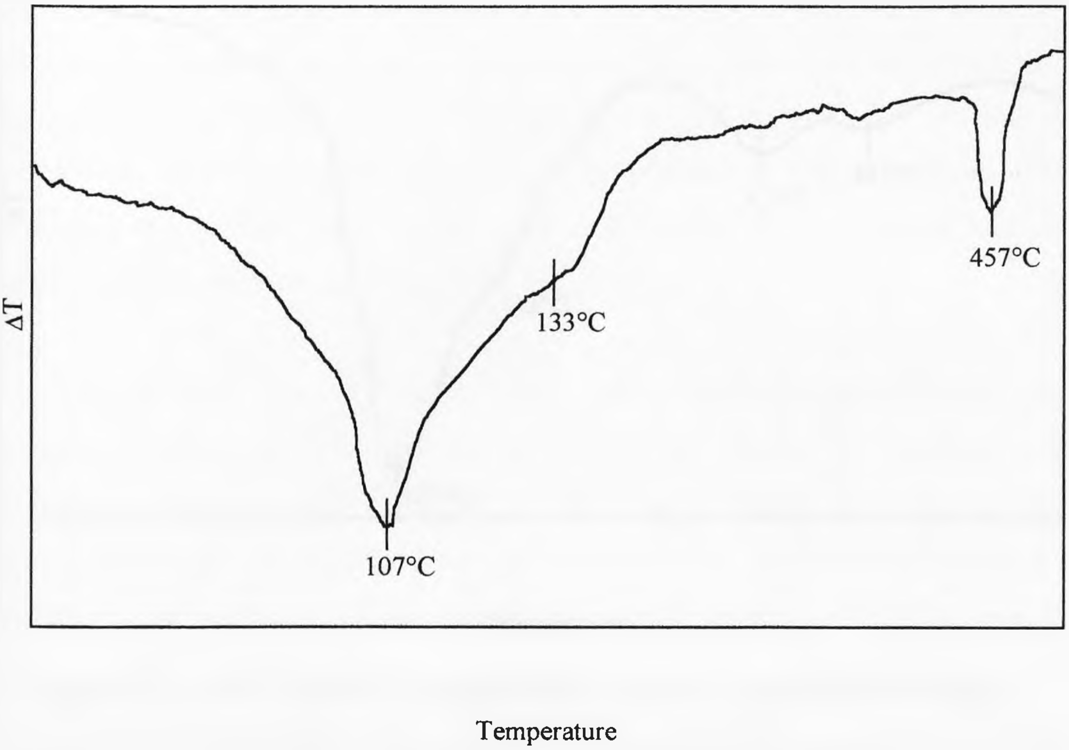

Figure 4.4.4 DTA Trace of 3:1 BFS:OPC Hydrated for 90 Days

A similar effect was seen in the 9:1 BFS:OPC cement systems (Table 4.4.2, 328-3180) but the evidence for calcium hydroxide and an AFt/AFm phase disappeared at an even earlier age than in the 3:1 BFS:OPC cement. This also confirmed the x-ray diffraction results (Figure 4.3.4) and gave further evidence for a pozzolanic reaction consuming the calcium hydroxide.

The results for both slag systems containing 5% $SnCl_2$ were similar in that there was a complete absence of calcium hydroxide at all ages and there was also evidence of an endotherm between 250°C and 330°C, although in the 3:1 BFS:OPC cement this was a doublet until after 90 days hydration when it became a single peak whereas in the 9:1 BFS:OPC system it was only a single peak at all ages. Another difference was the absence of an AFt/AFm peak at all ages in the 90% slag system, but evidence of it at all ages in the 75% system (Table 4.4.2). Figures 4.4.5 (75%

slag cement hydrated for 90 days) and 4.4.6 (90% slag system hydrated for 28 days) clearly illustrate this even though the hydration times were different.

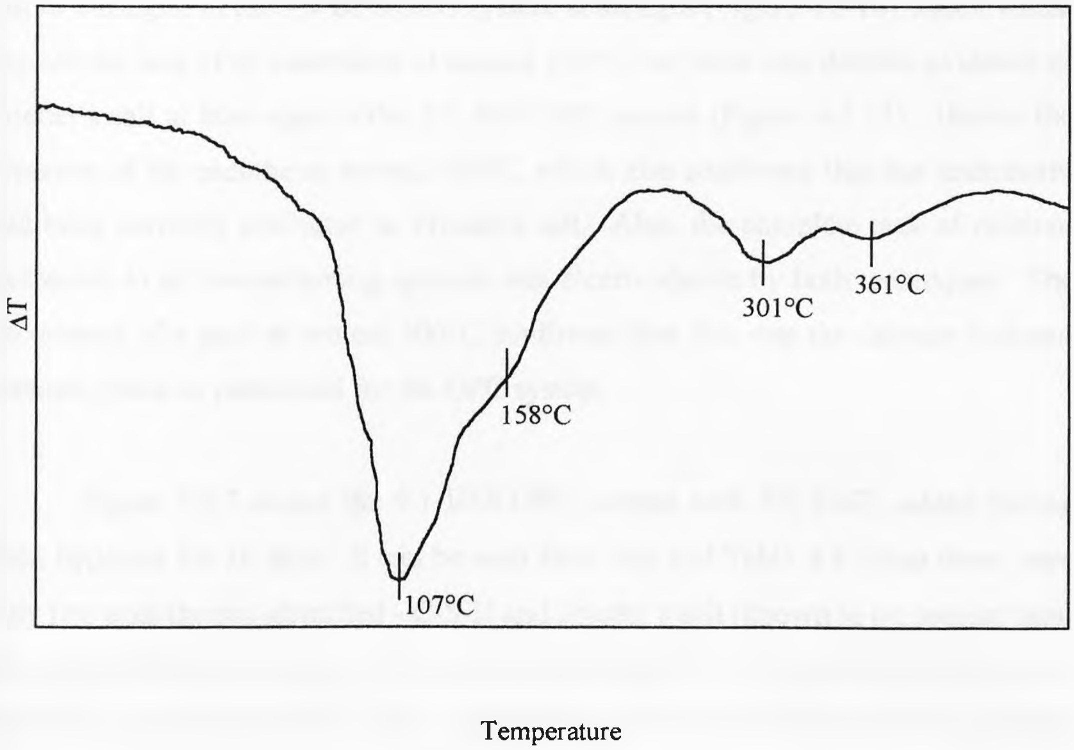

Figure 4.4.5 DTA Trace of 3:1 BFS:OPC + 5% $SnCl_2$ Hydrated for 90 Days

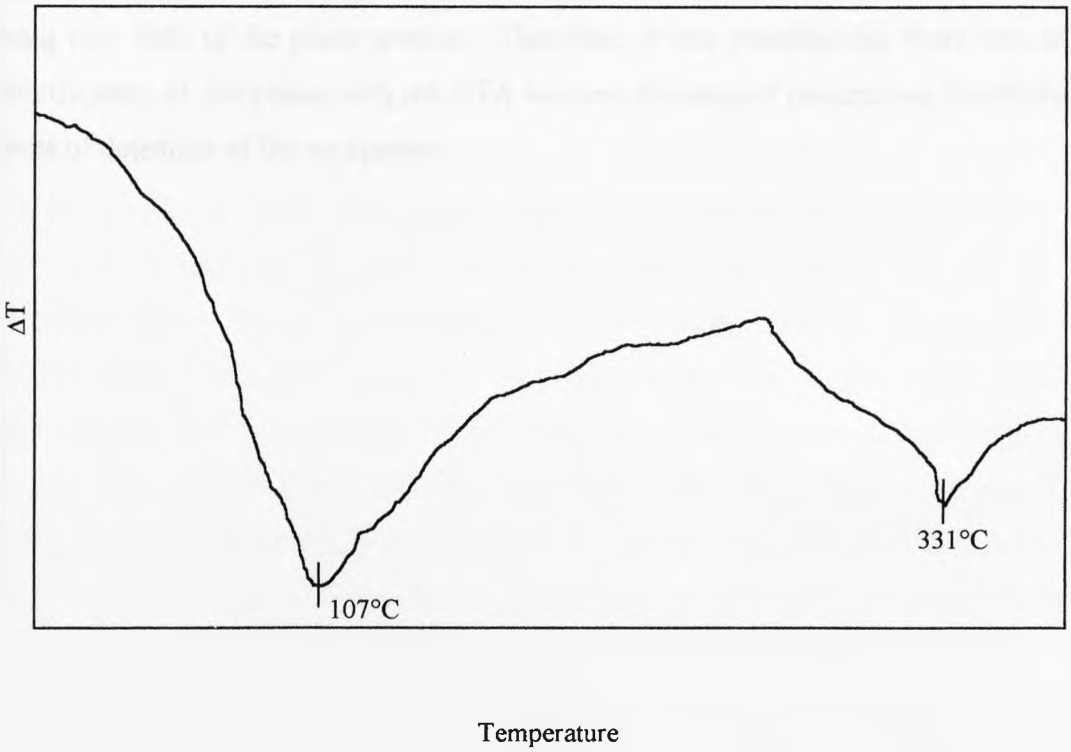

Figure 4.4.6 DTA Trace of 9:1 BFS:OPC + 5% $SnCl_2$ Hydrated for 28 Days

Again, the results from the DTA correlated well with those from x-ray diffraction. For example there was very little x-ray diffraction evidence for Friedel's salt or ettringite in the 9:1 BFS:OPC system at all ages (Figure 4.3.16) which would explain the lack of an endotherm at around 150°C, but there was definite evidence of Friedel's salt at later ages in the 3:1 BFS:OPC cement (Figure 4.3.14). Hence, the presence of the endotherm around 150°C, which also confirmed that this endotherm had been correctly attributed to Friedel's salt. Also, the complete lack of calcium hydroxide in all tin-containing systems was clearly shown by both techniques. The occurrence of a peak at around 300°C confirmed that this was the calcium hydroxo stannate phase as postulated for the OPC system.

Figure 4.4.7 shows the 9:1 BFS:OPC cement with 5% $ZnCl_2$ added having been hydrated for 28 days. It can be seen from this and Table 4.4.2 that there were only two endotherms identified - C-S-H and Friedel's salt (known to be present from the x-ray diffraction results - for example Figure 4.3.31). The work undertaken on this system was limited but it was disappointing not to have identified the presence of $CaZn_2(OH)_6.2H_2O$. However, the peaks present in the x-ray diffraction results for the identification of calcium zincate were weak which was indicative of there being very little of the phase present. Therefore, it was possible that there was no identification of this phase with the DTA because the amount present was below the limits of detection of the equipment.

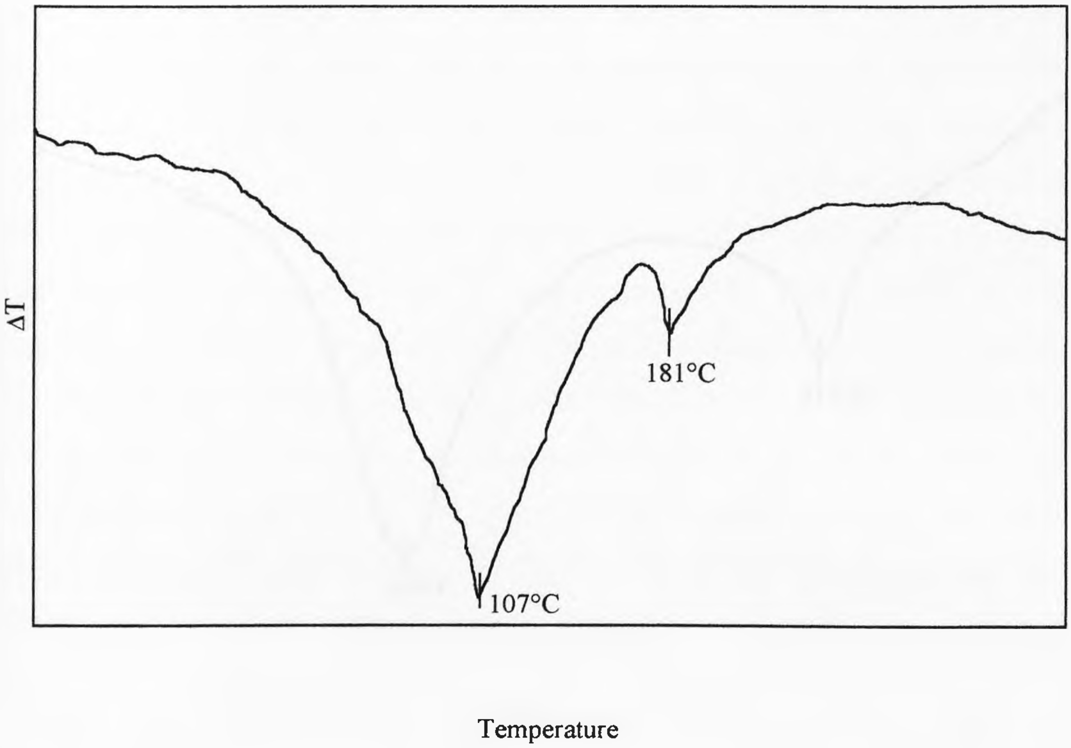

Figure 4.4.7 DTA Trace of 9:1 BFS:OPC + 5% $ZnCl_2$ Hydrated for 28 Days

4.4.1.3 Pulverised Fuel Ash Systems

Table 4.4.2 lists the results from the 3:1 PFA:OPC cement systems (428 - 4180 and 428B1 - 4180B1) and it can be seen that they followed a similar trend to that found in the 3:1 BFS:OPC cement. In the neat cement, the main evidence was for C-S-H (around 110°C) with some calcium hydroxide (457°C) after 28 days hydration but no calcium hydroxide after this time. Also, there was some evidence of an AFt/AFm phase (133°C) after 90 days hydration but not at other times. In the tin-containing system (428B1 - 4180B1) there was evidence in the DTA curves for only two phases - C-S-H (≈100°C) and $CaSn(OH)_6$ (≈ 310°C - again a single peak as in the 9:1 BFS:OPC system) with no evidence for calcium hydroxide or Friedel's salt. This can also be seen in Figure 4.4.8. All these results, again, correlate with the x-ray diffraction results (Figures 4.3.2 and 4.3.23) and confirm those findings.

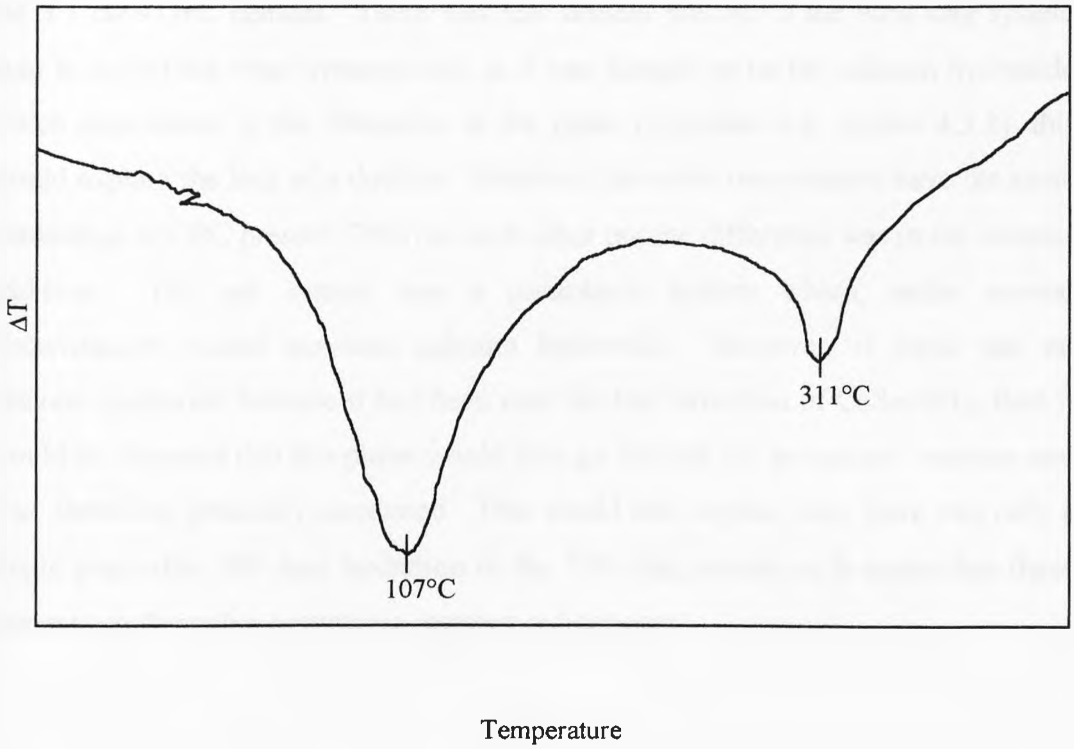

Figure 4.4.8 DTA Trace of 3:1 PFA:OPC + 5% $SnCl_2$ Hydrated for 28 Days

4.4.1.4 Summary

The DTA results for all the cement systems correlated well with those obtained from the x-ray diffraction technique which confirmed the previous findings. The endotherm temperatures varied between cements and also from those given in the literature. However, the temperatures were consistent enough for it to be possible to identify phases from them. In all cements there was evidence for C-S-H which could not be identified by x-ray diffraction due to it being a non-crystalline phase. There was also evidence for calcium hydroxide but only in the systems in which it had been identified from x-ray diffraction. The endotherm temperatures which were assigned to the calcium hydroxo stannate phase only appeared when there was $SnCl_2$ present which helped to confirm that the peak was assigned correctly. Also, in some systems this peak was a doublet and in others it was a single peak. One explanation for this was that there was more $CaSn(OH)_6$ present in the systems in which a doublet appeared than in the others. A single peak occurred in the 9:1 BFS:OPC cement, 3:1 PFA:OPC cement and after 180 days hydration in the 3:1 BFS:OPC cement. There was less cement present in the 90% slag system than in any of the other systems and, as it was thought to be the calcium hydroxide which contributed to the formation of the phase (Equation 4.3, section 4.3.2), this would explain the lack of a doublet. However, the other two systems have the same percentage of OPC present (25%) as each other but the difference was in the mineral addition. The ash system was a pozzolanic system which, under normal circumstances would consume calcium hydroxide. However, if there was no calcium hydroxide because it had been used for the formation of $CaSn(OH)_6$ then it would be expected that this phase would then go through the pozzolanic reaction and was, therefore, gradually consumed. This would also explain why there was only a single peak after 180 days hydration in the 75% slag system as it seems that these cements go through a pozzolanic reaction at later ages.

4.5 SCANNING ELECTRON MICROSCOPY

Scanning electron microscopy (SEM) has been used to study the effects of the addition of the different inorganic metal salts on the microstructure of the cements. Combined with SEM, electron dispersive x-ray analysis (EDS) was used in an attempt to locate the position of the metal within the microstructure to help to determine the stability of the material. The sample preparation was described in section 3.3.3 and, as mentioned, backscattered electron imaging was used throughout. A flat polished sample was important for backscattered electron imaging and EDS analysis so as to minimise the topographical effects.

Backscattered electron imaging (BEI) has become a useful tool in the study of cement microstructures. Secondary electron imaging (SEI) only provides topographical information on the system under investigation whereas BEI allows the microstructure to be examined in terms of its composition, that is, the atomic number contrast. The secondary electron coefficient (δ) and the backscattered electron coefficient (η) of a sample are the number of secondary and backscattered electrons emitted from a specimen for each incident electron, respectively, and the backscattered electron coefficient of an element increases monotonically with the atomic number.[63] Therefore, higher atomic number elements look brighter in BEI than lower atomic number elements which means that, in hydrated Portland cements any remaining anhydrous material, hydration products and porosity can be distinguished on the basis of the level of grey on the image.[64] It should also be possible to distinguish the metals within the microstructure in a similar way and, combined with the EDS analysis, give a full picture of the location of the metals. The different levels of grey seen in BEI's of neat cements are assigned, in descending order of brightness, to: anhydrous material, calcium hydroxide, hydration products and porosity.[65]

4.5.1 Neat Cements

Plates 1 and 2 show 100% OPC after 3 days and 180 days hydration respectively. After 3 days hydration it can be seen that the microstructure was dominated by large, bright areas which could be attributed to anhydrous material as the cement was still quite young. There was some evidence of hydration rims beginning to appear around the outside of the bright areas (A) although this was not extensive and there was a significant amount of porosity. However, after 180 days hydration (plate 2) it can be seen that the microstructure was more dense than after 3 days hydration and there was more evidence of outer product (OP). Although the magnifications of the micrographs were not the same, the differences between them can be clearly seen.

Plates 3 and 4 show the 3:1 BFS:OPC cement after 3 and 90 days hydration. Again these micrographs are of different magnifications but still illustrate the point. The most striking thing about the microstructures were the proliferation of large angular slag grains (A). These were apparent after both hydration times and dominated the microstructure. This was because, in this system, there was 75% blast furnace slag and only 25% OPC and, therefore, it would be expected that the slag would dominate. It can be seen that after 3 days hydration there was no evidence of any hydration of the slag particles, little cement hydration and a lot of porosity. It can also be seen that the cement appeared to be secreted in pockets throughout the microstructure. Again, as would be expected, after 90 days hydration the microstructure had changed, although, possibly not as significantly as in the neat OPC system. It can be seen from plate 4 that, although the evidence for hydration rims around the slag particles was not conclusive, the cement fraction was hydrated (A). The hydration of the cement was having the effect of building up the matrix between the slag particles and, therefore, reducing porosity and this continued to longer hydration times as the cement hydration continued.

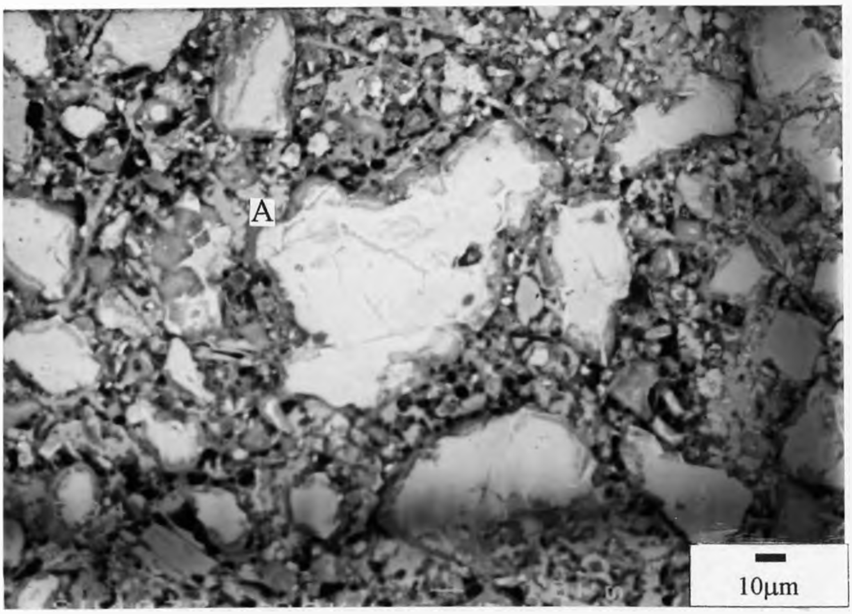

Plate 1 BEI of 100% OPC Hydrated for 3 Days

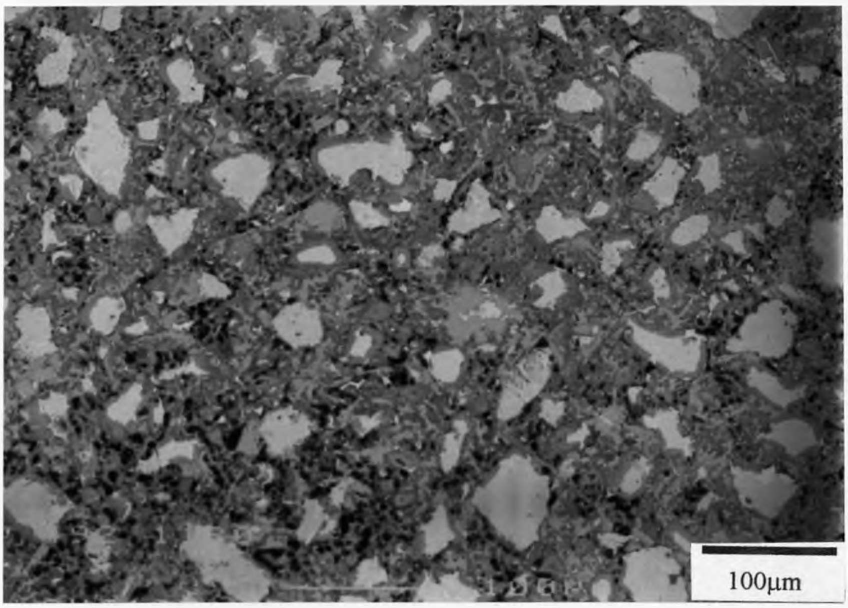

Plate 2 BEI of 100% OPC Hydrated for 180 Days

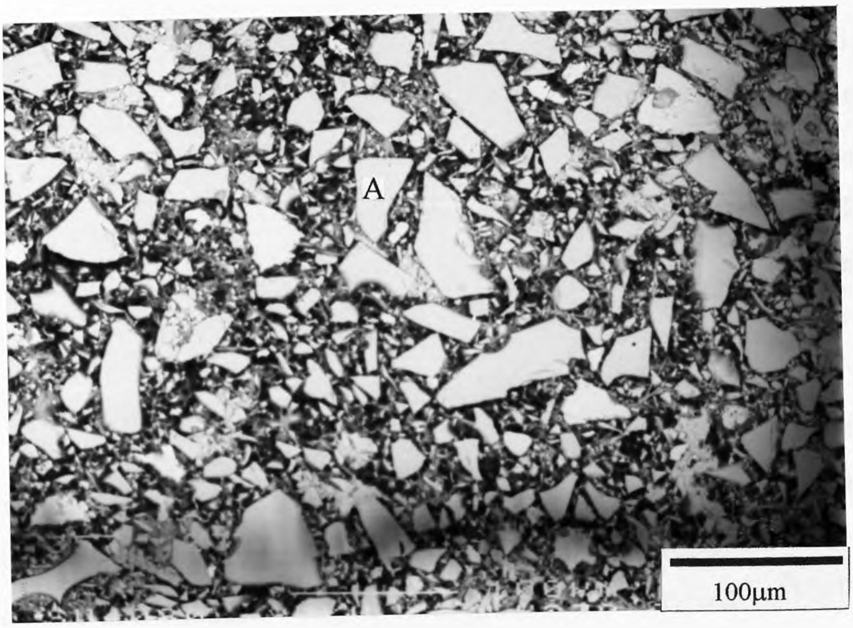

Plate 3 BEI of 3:1 BFS:OPC Hydrated for 3 Days

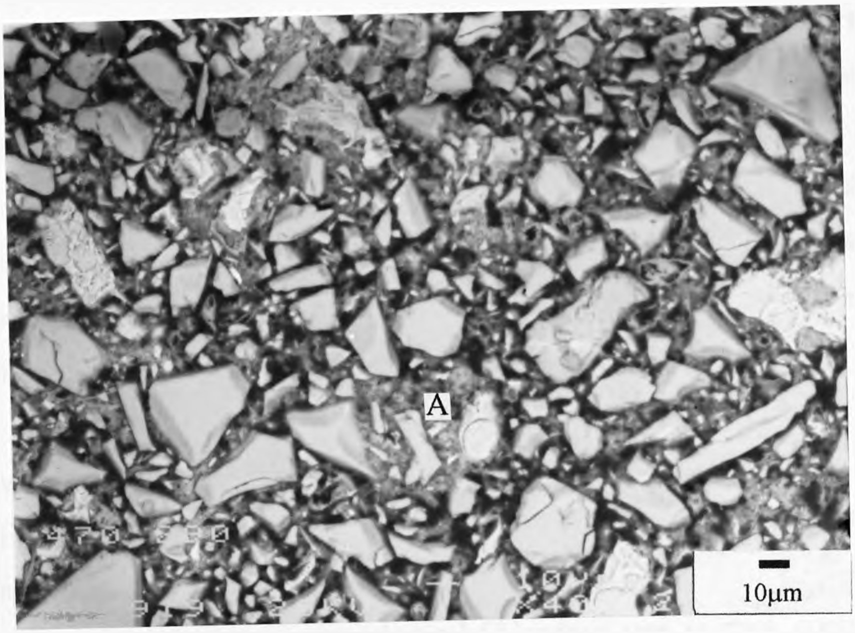

Plate 4 BEI of 3:1 BFS:OPC Hydrated for 90 Days

Plate 5 shows a 9:1 BFS:OPC cement that has been hydrated for 90 days. It would be expected that, as this system contained 90% slag with only 10% OPC, the angular slag grains would dominate even more than in the previous system and, therefore, there would be less hydrating cement visible and more porosity. If the two slag systems are compared (plates 4 and 5) it can be seen that this was indeed the case (the magnifications of the micrographs are the same to allow direct comparison). At first glance it would appear that the microstructures are very similar. However, in the 9:1 BFS:OPC system there were more slag grains of a larger size because, in the 3:1 BFS:OPC system they appeared to have broken down more. Also, as expected, in the 75% slag system, the pockets of cement were forming a more dense matrix with the consequence that there was more porosity in the 90% slag system. Again, as with the OPC system, these micrographs only confirmed what was already known about these systems as they hydrated.

Figure 4.5.1 shows an EDS trace of a typical slag grain taken from the same sample as plate 5 (i.e. 9:1 BFS:OPC hydrated for 90 days). It can be seen that there was a lot of calcium, silicon and aluminium with lesser amounts of magnesium and sulphur and traces of potassium and titanium. If this is compared with the chemical analysis shown in Chapter 3 (Table 3.1.1) it can be seen that they correlate well. That is, the chemical analysis shows the greatest amounts of CaO, SiO_2 and Al_2O_3 with lesser amounts of MgO and K_2O. All EDS data taken for slag grains showed very similar results after all hydration times.

A 3:1 PFA:OPC cement having been hydrated for 90 days is shown in plate 6 with an EDS trace of a typical PFA particle (again having been hydrated for 90 days) shown in figure 4.4.2. It can be seen from plate 6 that the PFA particles, which dominate the microstructure, were spherical (A) which was in stark contrast to the angular grains of the blast furnace slag (plates 3-5). Again, as with the slag cements, it would be expected that the ash particles would dominate as there was 75% ash and only 25% OPC in the cement. Also visible was an area of hydrating cement (B) with a lot of anhydrous material but also with a hydration rim around the outside. It can

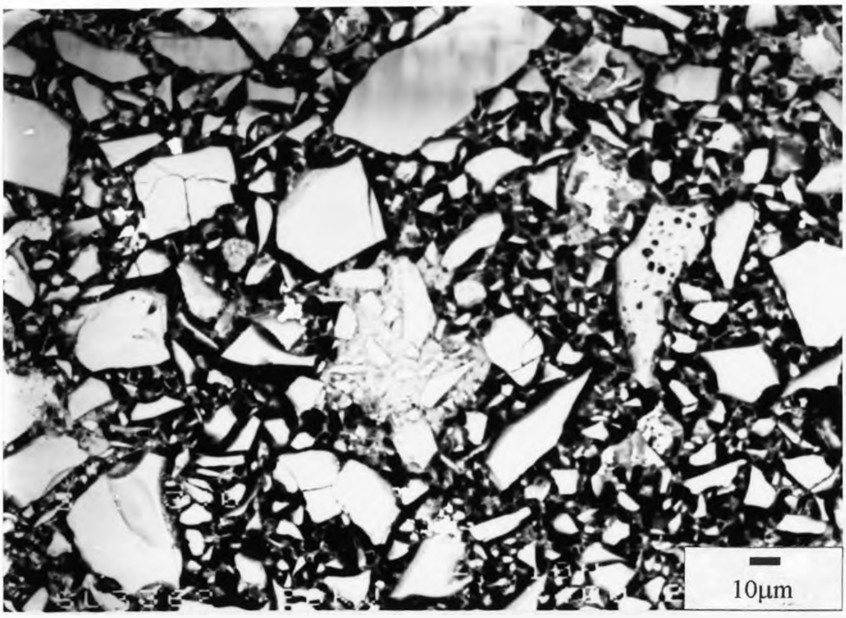

Plate 5 BEI of 9:1 BFS:OPC Hydrated for 90 Days

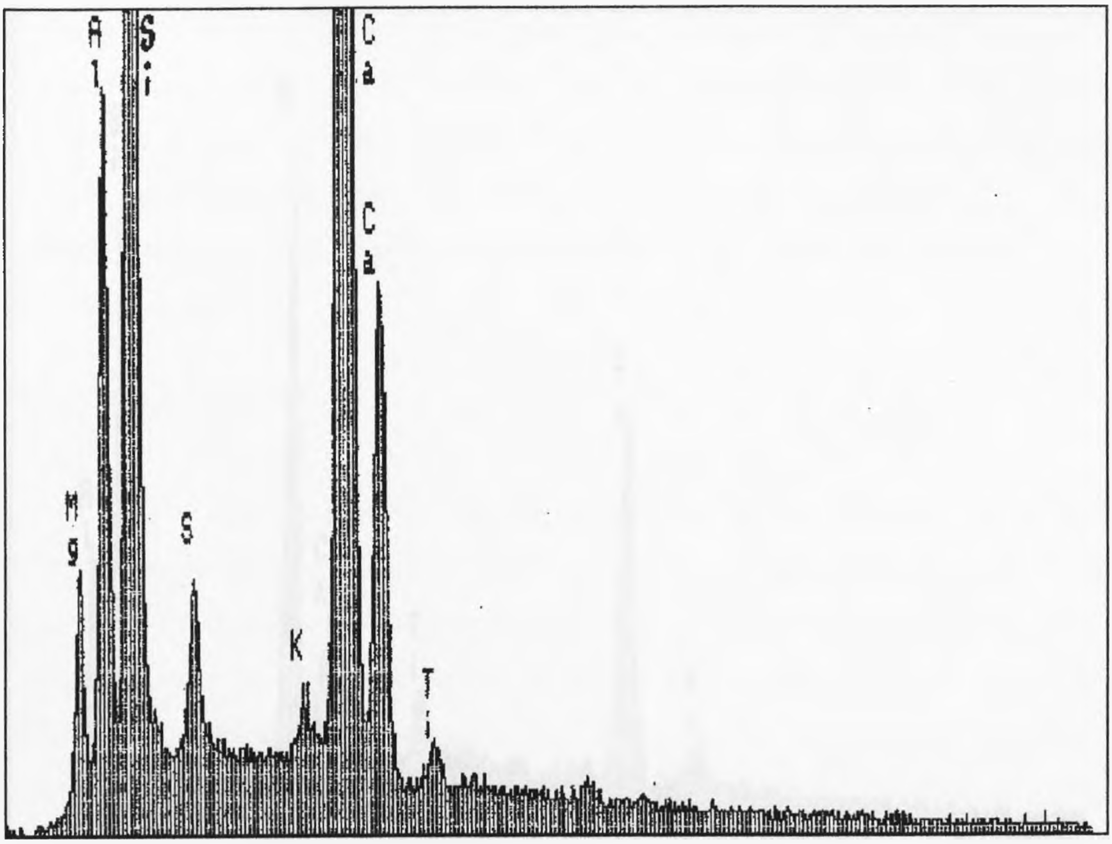

Figure 4.5.1 EDS Trace of a Slag Grain

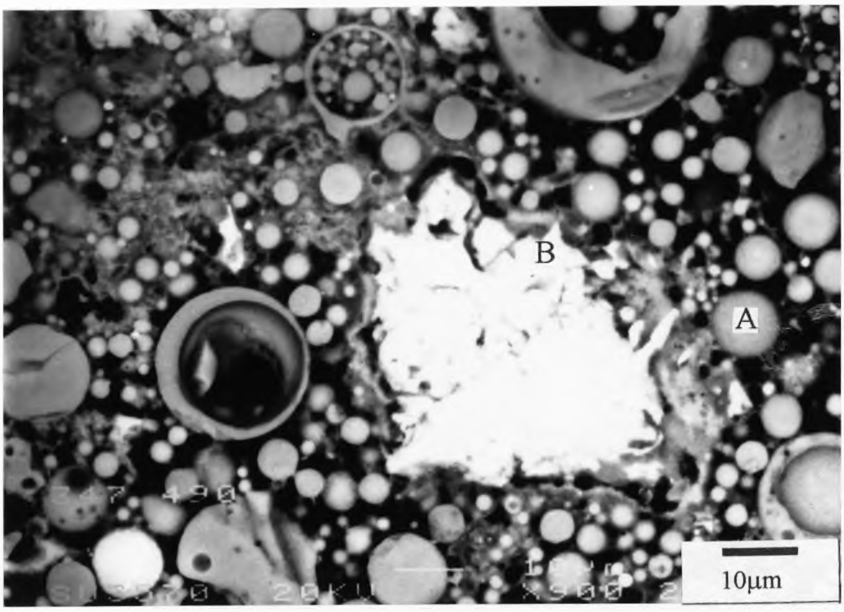

Plate 6 BEI of 3:1 PFA:OPC Hydrated for 90 Days

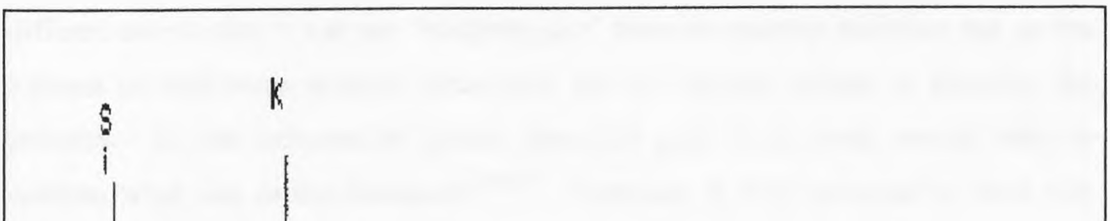

Figure 4.5.2 EDS Trace of a PFA Particle

also be seen that, as with the slag systems, the OP of the cement has started to connect the PFA particles and, consequently, the porosity has begun to decrease. The EDS trace (Figure 4.5.2) shows the PFA grain to be dominated by potassium, silicon and iron with lesser amounts of aluminium, calcium and titanium. Although there was no chemical analysis available for the PFA used for this work, the constituents shown in the EDS trace were similar to the example of a typical fly ash shown in Chapter 2 (Table 2.2). It can be seen, from the results of the EDS analysis, that the fly ash used was a low lime fly ash.

In summary, the neat composite cements appear to behave in a similar way to each other. That is, the mineral addition (PFA or BFS) did not appear to have hydrated significantly (at least after 90 days hydration) and the cement fraction created a dense matrix between the mineral addition particles as hydration proceeded, thereby reducing the porosity as the sample aged. The OPC system differed only in that it was not 'bridging gaps' between mineral additions but, as the amount of anhydrous material decreased, the OP formed helped to decrease the porosity. All the information gained from this part of the study served only to confirm what was in the literature[1,66,67]. However, it was important to have this information for comparison with the systems containing the metal salt additions.

4.5.2 $SnCl_2$ Systems

Unlike the x-ray diffraction section of the results (section 4.3.2), the examples shown here were only carried out at the 5% loading of the metal salt. This was because it was virtually impossible to identify tin through EDS analysis at lower loadings due to the positioning of the tin peak. Figure 4.5.3 illustrates this more clearly. It can be seen that the tin peak splits off from the calcium peak. This was not a problem at 5% loadings as the peak was strong enough to be identified as being separate from the calcium peak. However, at 1% it was not clear for most samples whether tin had been identified or if there was some noise on the calcium peak. Therefore, the work concentrated on the 5% loadings which also meant no data were obtained for the $SnCl_4$ system because, as mentioned previously, it was not possible to make a cement paste with $SnCl_4$ at this loading.

Plates 7 and 8 show 100% OPC + 5% $SnCl_2$ after hydration for 3 and 90 days, respectively. From plate 7 it can be seen that there were pockets of anhydrous cement (A) but the matrix was relatively pore free which, following on from the neat cement system, would indicate significant hydration. There were also small bright areas which were not present in the neat cement (B). From the atomic number contrast seen with BEI, it was assumed that these bright areas were of a higher atomic number than the other, grey areas. As tin has an atomic number of 50[63], it was decided that this would be a good area to start to search, using EDS analysis, for the tin. Figure 4.5.3 shows a typical EDS trace for such an area. It can be seen that there were significant amounts of calcium, tin and chlorine with lesser amounts of silicon and trace amounts of aluminium, sulphur and iron. This differed from an EDS trace of, for example, the matrix in that there was significantly less silicon, and there was evidence for tin and chlorine.

Plate 8 shows the same cement after 90 days hydration and there were a few differences. The matrix appeared to be a darker grey than after 3 days hydration, indicating a greater amount of hydration product[65] and around the anhydrous material hydration rims could be seen. Both of these observations point to hydration having continued since 3 days and, therefore, the amount of hydration having occurred would have increased. Also, although the bright areas (identified as containing tin) were still visible, they appeared to have been better incorporated into the matrix than after 3 days hydration, when they were visible as seemingly separate particles.

Plates 9-11 show both 3:1 and 9:1 BFS:OPC with the addition of 5% $SnCl_2$. Plate 9 is the 3:1 BFS:OPC system after 90 days hydration and plates 10 and 11 show the 9:1 BFS:OPC system after 28 and 180 days respectively. It can be seen from Plate 9 that the microstructure was similar to the neat cement (plate 4) in that there were large angular grains of slag with the OPC starting to form a dense matrix. There was still a lot of porosity. However, there were also some differences.

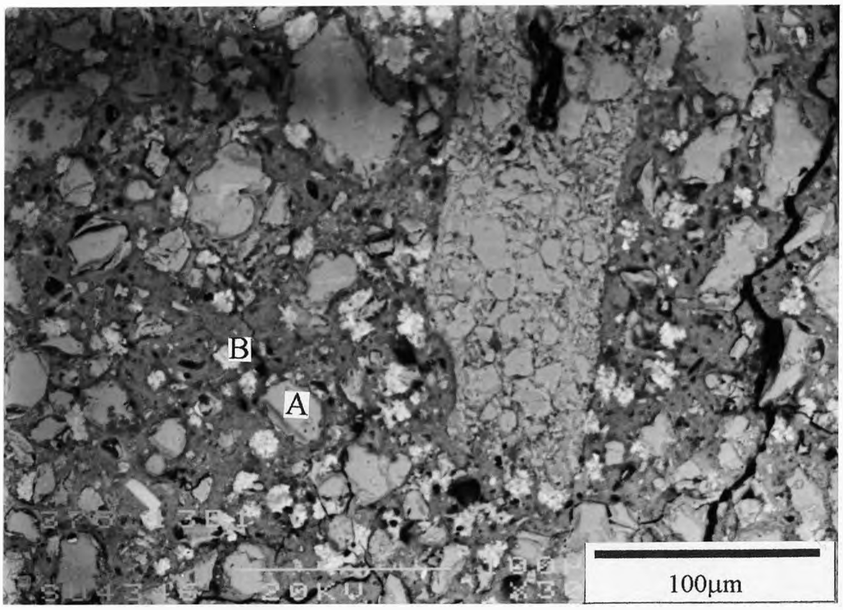

Plate 7 BEI of 100% OPC + 5% $SnCl_2$ Hydrated for 3 Days

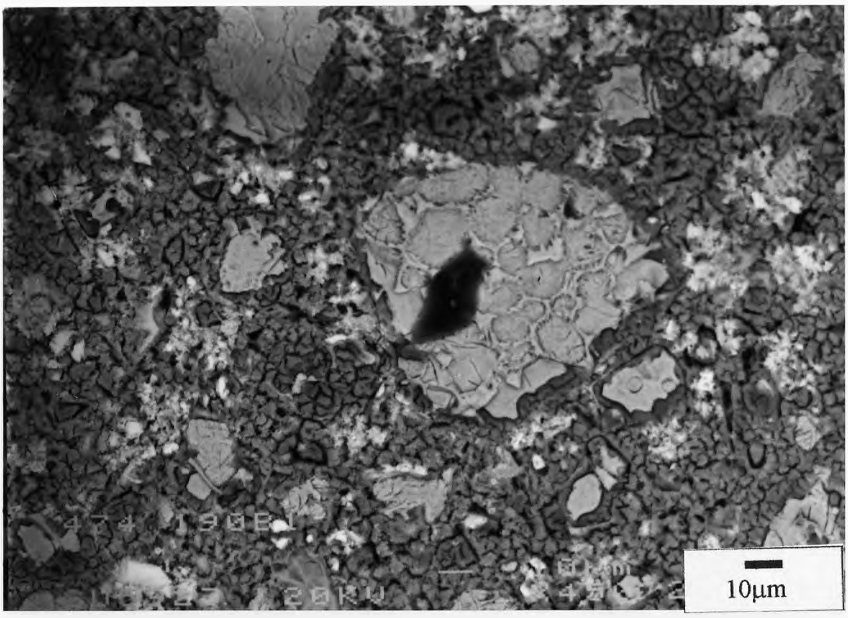

Plate 8 BEI of 100% OPC + 5% $SnCl_2$ Hydrated for 90 Days

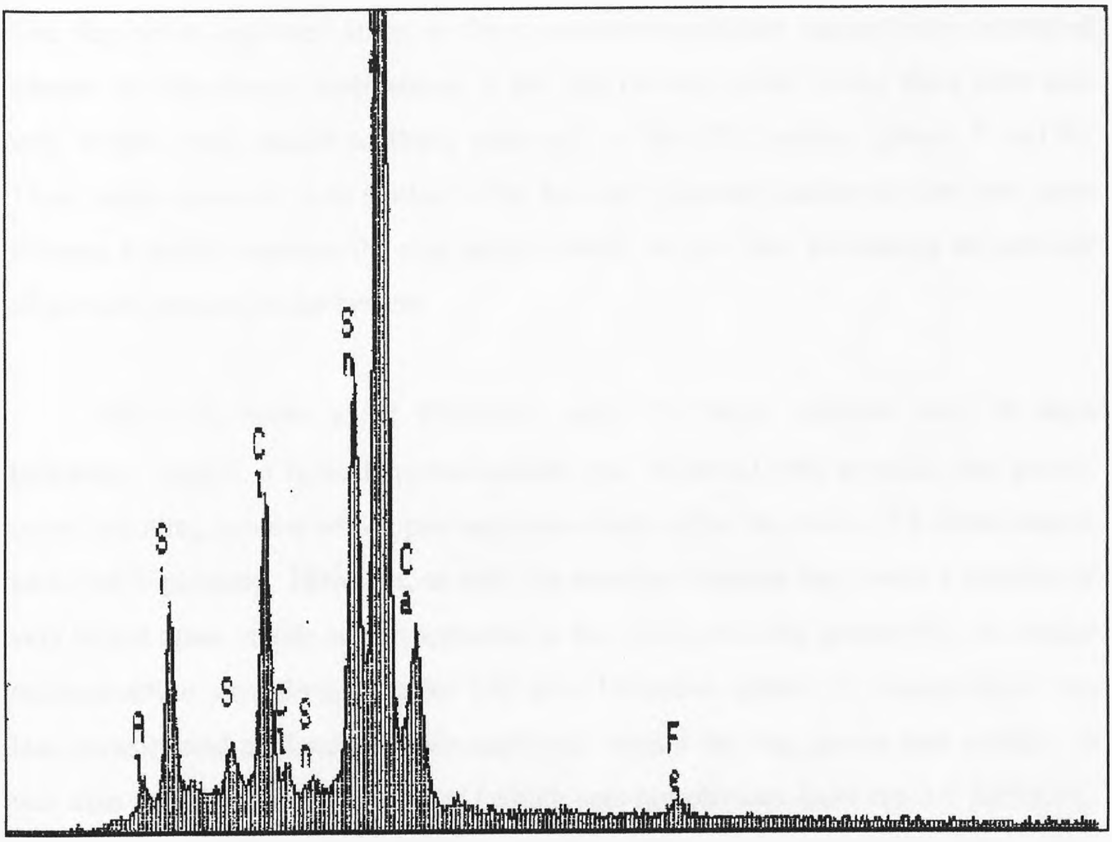

Figure 4.5.3 EDS of Bright Area taken from Plate 7

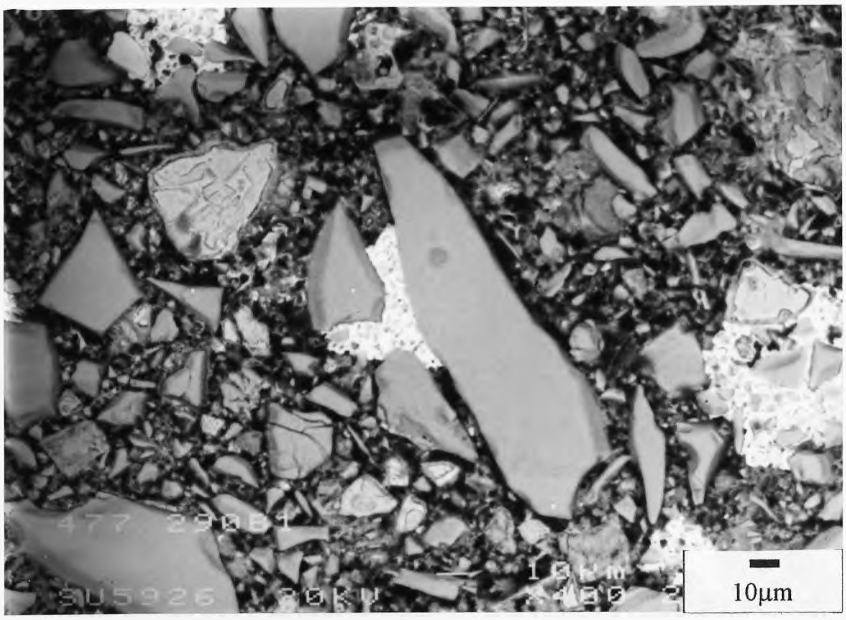

Plate 9 BEI of 3:1 BFS:OPC + 5% $SnCl_2$ Hydrated for 90 Days

The slag grains appeared larger in the tin-containing system suggesting a decreased amount of hydration in comparison to the neat cement (plate 4) and there were also very bright areas similar to those observed in the OPC system (plates 7 and 8). These areas appeared to be similar to the hydrating cement fraction in that they were forming a matrix between the slag grains which, in turn, was decreasing the amount of porosity present in the system.

Plate 10 shows a 9:1 BFS:OPC with 5% $SnCl_2$ addition after 28 days hydration. Again, a typical microstructure was observed with angular slag grains, some hydrating cement whose products contribute to the formation of a dense matrix and a lot of porosity. However, as with the previous systems there were a number of very bright areas visible which appeared to be linking the slag grains (A). A similar microstructure was observed after 180 days hydration (plate 11) except there was less porosity and evidence of hydration rims around the slag grains was visible. It was also apparent from this system (which was not obvious from the 3:1 BFS:OPC system) that the darker areas within the bright phases were particles of slag which confirms the earlier point that the bright, tin-containing areas were linking the slag particles.

Figures 4.5.4 and 4.5.5 are EDS traces for 9:1 BFS:OPC cements containing 5% $SnCl_2$ after 28 and 180 days respectively. Figure 4.5.4 was taken from a bright area which, as before, gives an indication of a lot of calcium and tin with lesser amounts of silicon, chlorine and trace amounts of magnesium, aluminium and titanium. Figure 4.5.5 shows a slag grain after 180 days hydration. The results are similar to the previous slag grain and also show that the tin was not deposited within the slag grain itself.

Plates 12-15 show 3:1 PFA:OPC + 5% $SnCl_2$ after 3, 28, 90 and 180 days hydration respectively. It can be seen that, up to 90 days hydration (plates 12-14), the microstructure was very similar to that of the neat PFA cement (plate 6). That is, a microstructure dominated by the spherical PFA particles with some areas of OPC between the particles (A on plate 12). There were also some relatively bright areas similar to those observed for the slag cements. Again, it was these areas which were

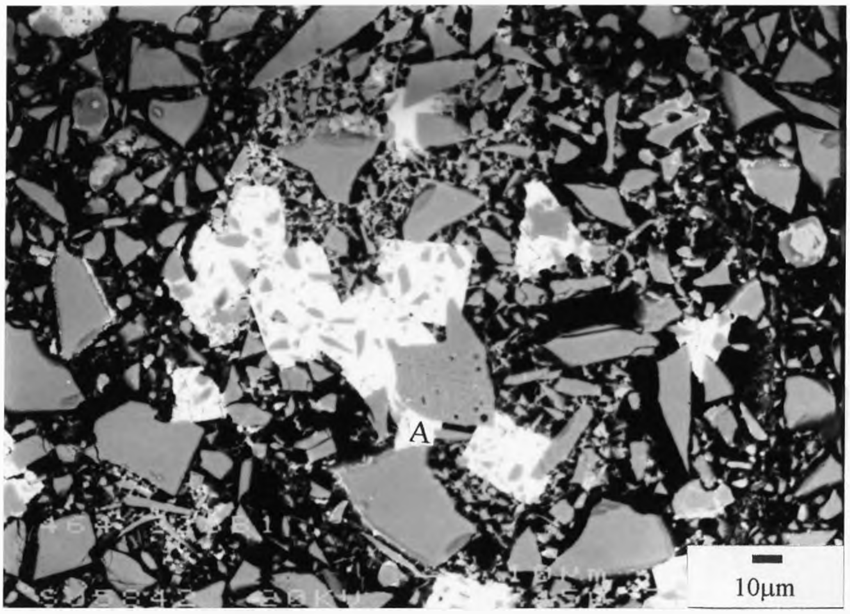

Plate 10 BEI of 9:1 BFS:OPC + 5% $SnCl_2$ Hydrated for 28 Days

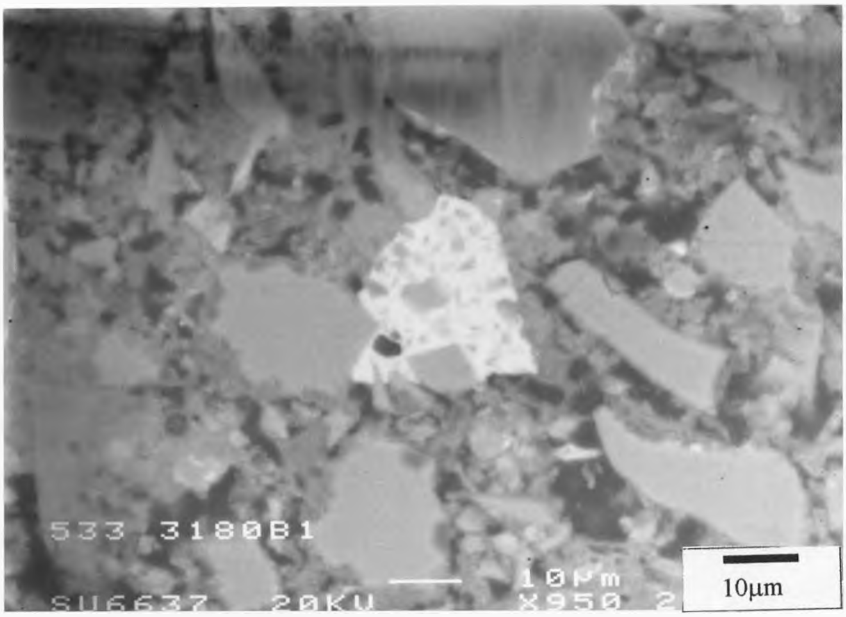

Plate 11 BEI of 9:1 BFS:OPC + 5% $SnCl_2$ Hydrated for 180 Days

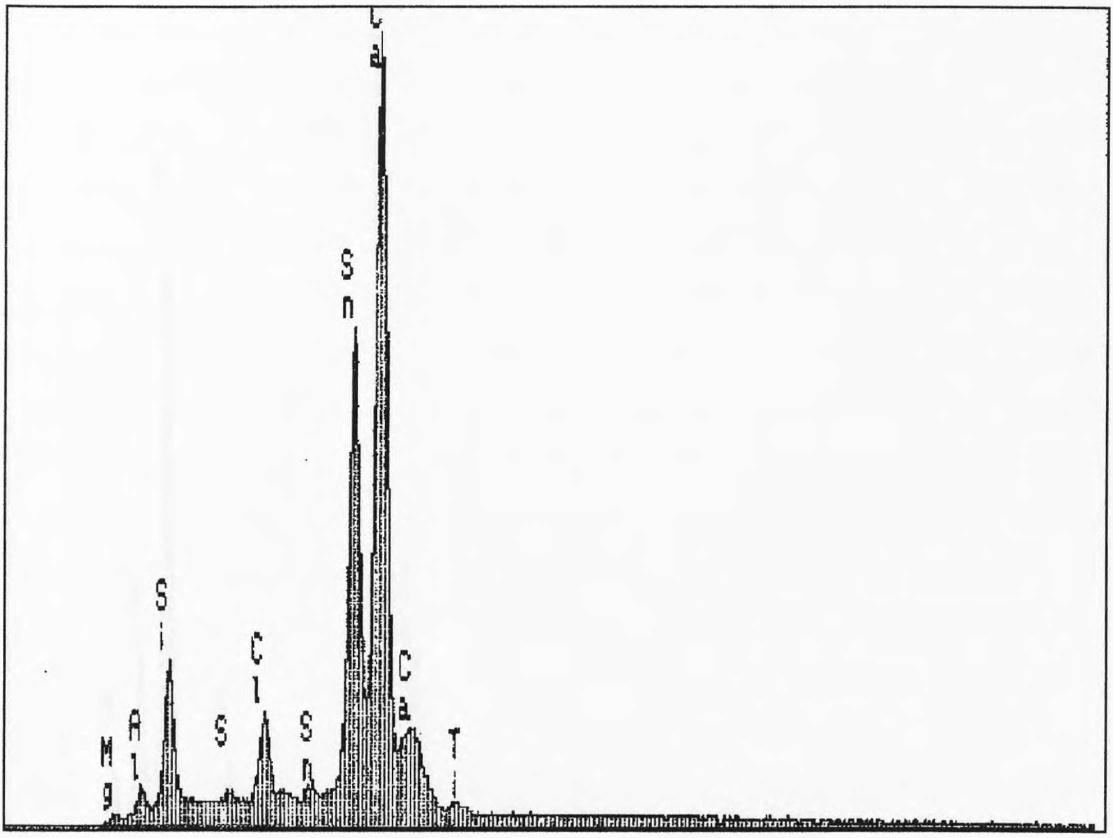

Figure 4.5.4 EDS of Bright Area taken from Plate 10

concentrated on for the initial search for tin within this system. Also, from plate 13, it was clear that within the bright areas were spherical PFA particles in a similar way to the slag particles seen in plate 11. Figures 4.5.6 and 4.5.7 show EDS traces from the cement system hydrated for 3 days. Figure 4.5.6 shows the analysis from a bright area within the microstructure and it can be seen that, as before, it was dominated by significant amounts of calcium and tin with lesser amounts of chlorine and silicon and trace amounts of aluminium, titanium and iron. Figure 4.5.7 shows a PFA particle taken from the same sample as Figure 4.5.6 and it can be seen that there was no evidence of either tin or chlorine and that it was similar in composition to the PFA particle analysed in the neat cement (Figure 4.5.2). These analyses showed that, as with the slag system, the tin was not concentrated in the PFA particle but, rather in the matrix. It can, therefore, be concluded from these micrographs that the PFA cement system behaves in a very similar way to the slag systems in that the mineral additions appeared to take no part in incorporating the tin within the microstructure and that the tin was deposited within the matrix of the composite cements. As a consequence of this the tin helps to reduce the porosity.

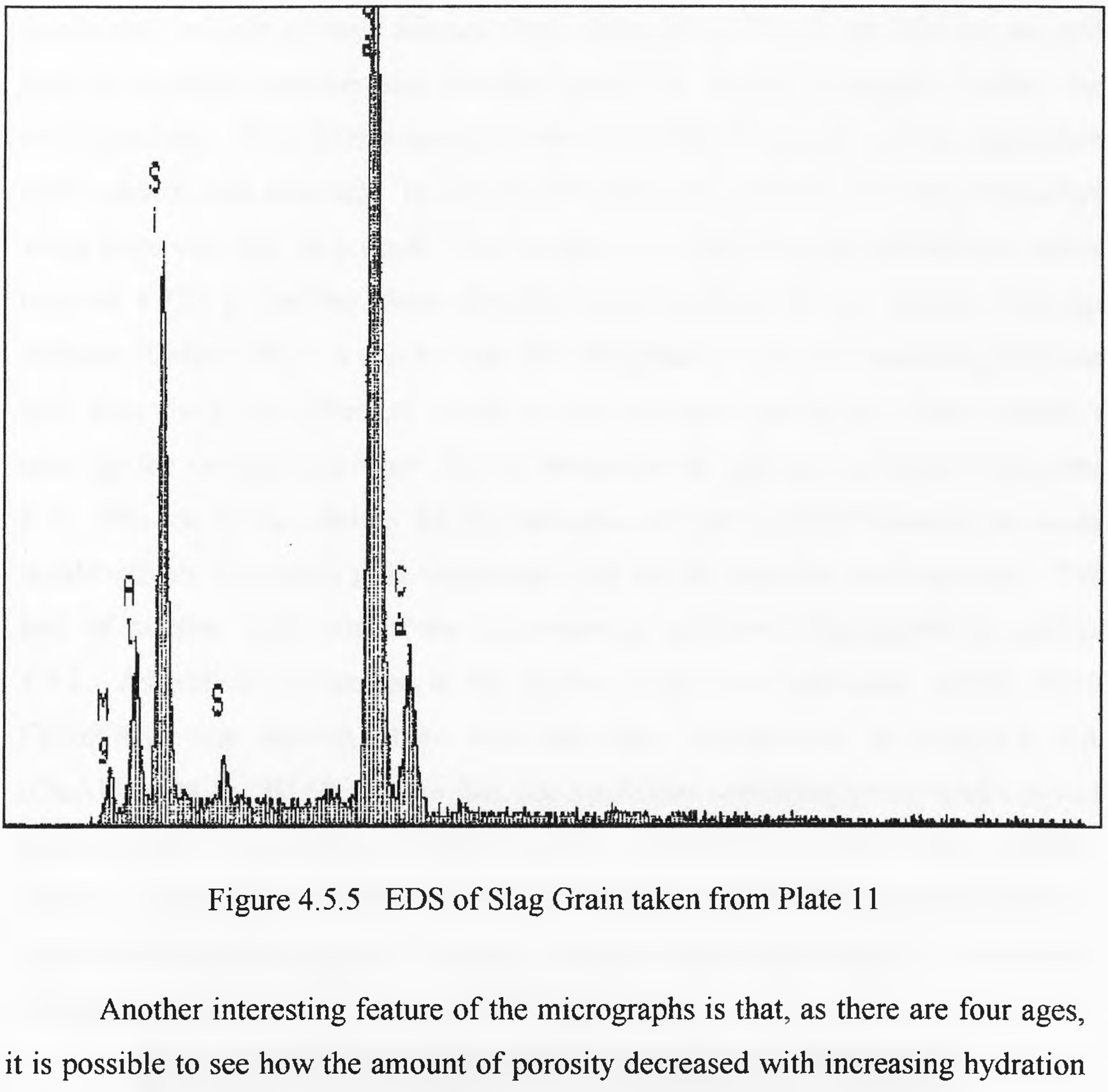

Figure 4.5.5 EDS of Slag Grain taken from Plate 11

Another interesting feature of the micrographs is that, as there are four ages, it is possible to see how the amount of porosity decreased with increasing hydration time. There was not much difference between 3 and 28 days hydration (Plates 12 and 13). However, after 90 days hydration (Plate 14) it can be seen that the PFA particles appeared to be more joined together and that the pockets of cement which were hydrating along with the tin-containing bright areas were helping to achieve this. After 180 days hydration (Plate 15) the effect of the reduction of porosity is quite obvious, especially if this is compared with the 3 day hydration micrograph (Plate 12). There was also a large cement grain in the middle of the micrograph and, if this is compared with the cement grain seen after 90 days hydration (Plate 14), it can be seen that the products were much darker which is indicative of more advanced hydration.

In summary, the composite cement systems appeared to behave in a similar way with regards to the hydration of the cement and the location of the tin within the microstructure. That is, the tin was not associated with the mineral additions (either pulverised fuel ash or blast furnace slag) although it did help to bind the mineral addition particles together and, thereby reduce the amount of porosity within the microstructure. From EDS analysis it was found that the tin was always associated with calcium and chlorine. In fact, in all cases, the chlorine was only identified when there was also tin present. This would tie in with the x-ray diffraction results (section 4.3.2) in that the phase identified as containing tin was calcium hydroxo stannate ($CaSn(OH)_6$). It can be seen that the phase is calcium containing and that also, from the x-ray diffraction results, it was postulated that as this phase formed it used up the calcium necessary for the formation of calcium hydroxide (Equation 4.3). The use of the calcium for the formation of non-standard hydration products would explain the strong peak associated with the tin from the EDS analysis. The lack of calcium hydroxide in the tin-containing systems is highlighted in section 4.3.2. As well as a decrease in the amount of calcium hydroxide present when $CaSn(OH)_6$ was formed, there was also the identification of Friedel's salt ($Ca_3Al_2O_6.CaCl_2.10H_2O$). Again this was a calcium containing phase which would help to explain the amount of calcium present in the EDS trace but it also contains chlorine. This phase was also only identified by x-ray diffraction when $CaSn(OH)_6$ was present and may explain the reason for the definite identification of a substantial chlorine peak when tin was present via EDS analysis.

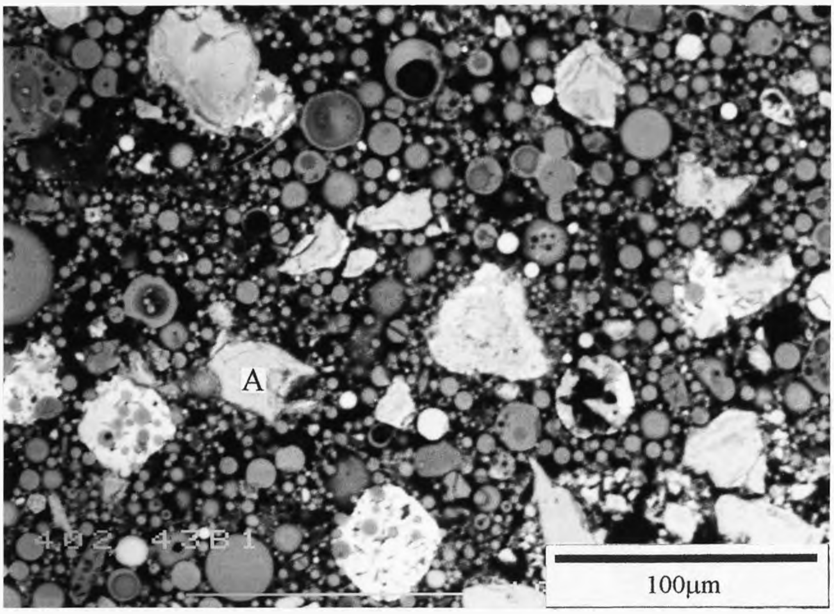

Plate 12 BEI of 3:1 PFA:OPC + 5% $SnCl_2$ Hydrated for 3 Days

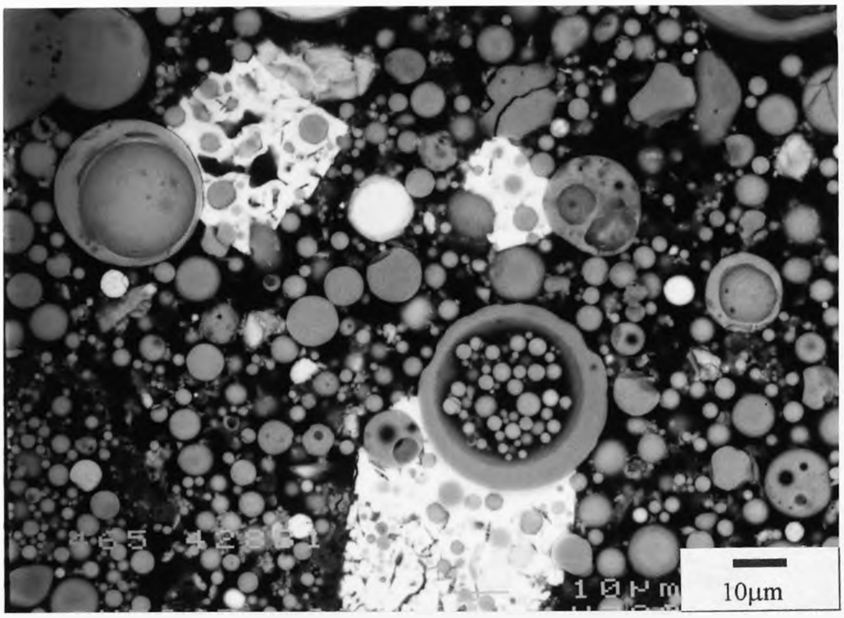

Plate 13 BEI of 3:1 PFA:OPC + 5% $SnCl_2$ Hydrated for 28 Days

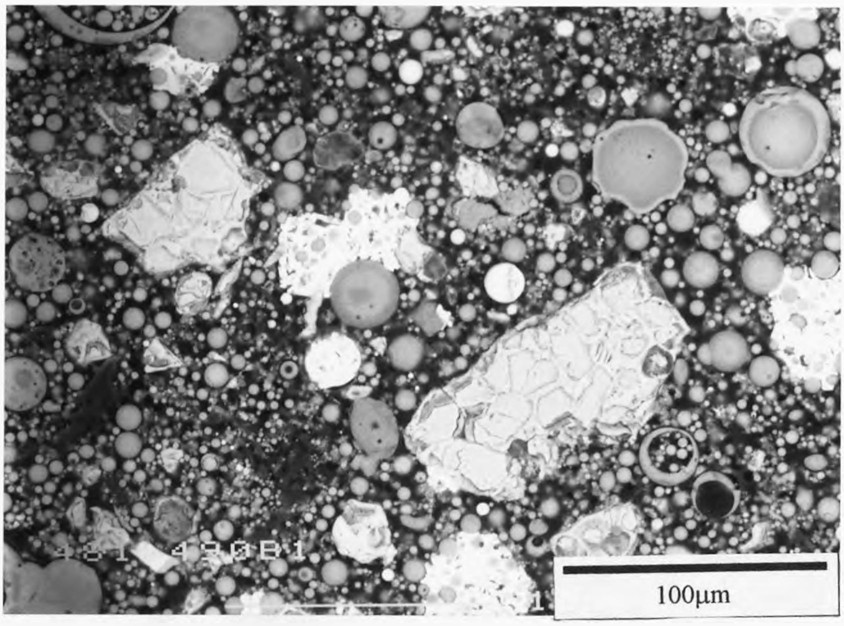

Plate 14 BEI of 3:1 PFA:OPC + 5% $SnCl_2$ Hydrated for 90 Days

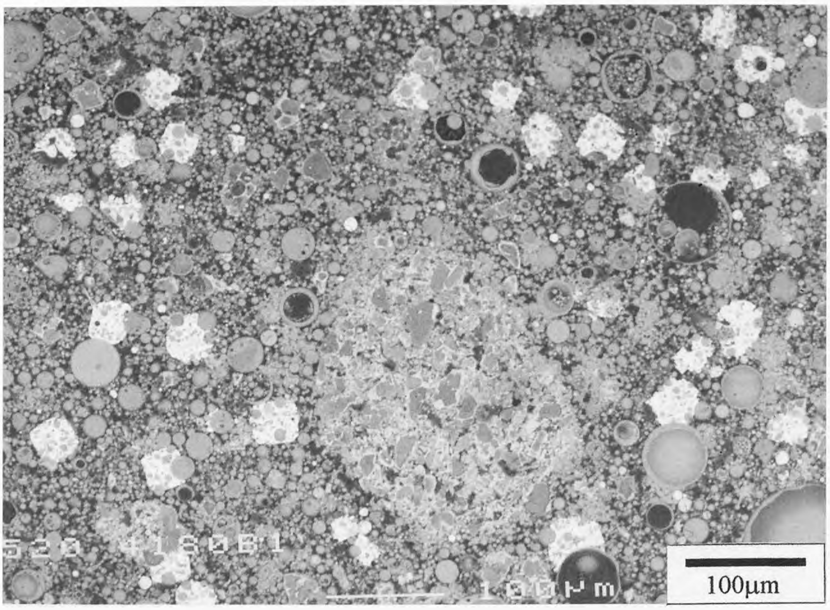

Plate 15 BEI of 3:1 PFA:OPC + 5% $SnCl_2$ Hydrated for 180 Days

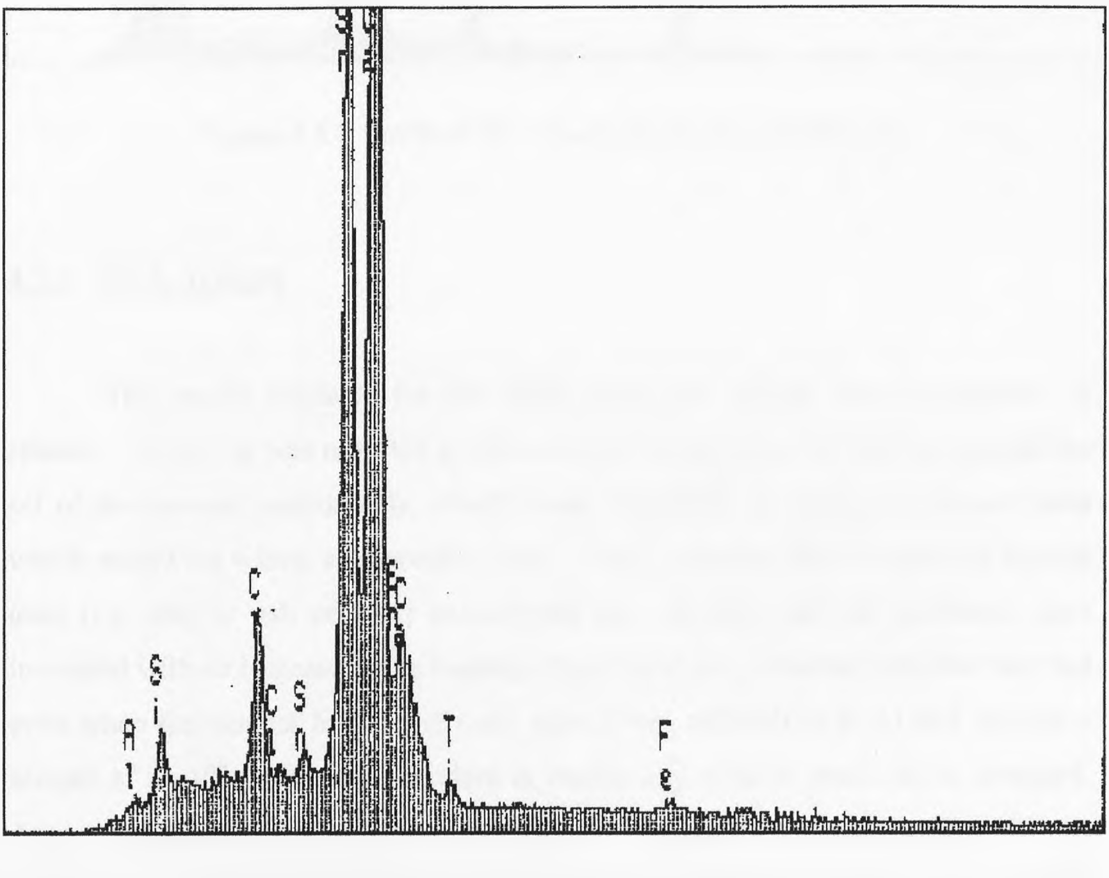

Figure 4.5.6 EDS of Bright Area taken from Plate 12

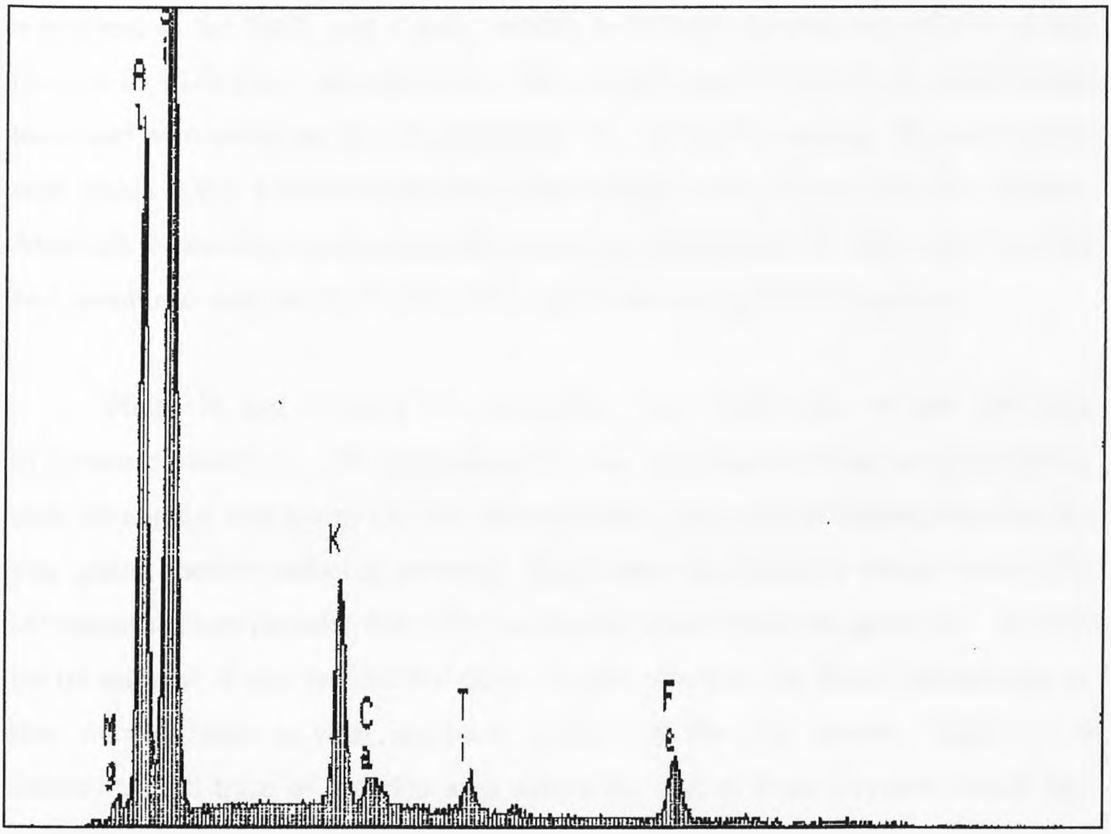

Figure 4.5.7 EDS of PFA Particle taken from Plate 12

4.5.3 ZnCl$_2$ Systems

The results available for the ZnCl$_2$ work are limited due to a number of reasons. Firstly, as was reported in the calorimetry section (4.2), ZnCl$_2$ retarded the set of the cement considerably, which made it difficult to prepare a cement paste which would set within a reasonable time. Also, it seemed that the type of cement used (i.e. slag or ash cement) exacerbated this situation and the problems were increased with an increase in the loading of the metal salt. Another problem was that even when the cement had set, at early ages it was difficult to grind and prepare a sample of a sufficiently high standard to enable any reliable results to be obtained. As a consequence, there were relatively few samples for examination in the microscope. At 1% loading it was possible to manufacture cements with the 9:1 BFS:OPC cement and the 3:1 PFA:OPC cement. However, with these systems it was only possible to obtain good quality micrographs after 90 and 180 days hydration because of the delayed set. The low loading of ZnCl$_2$ was not as much of a problem as the $SnCl_2$ and it was possible to identify the presence of zinc at this level as its EDS peak was apart from other constituents of the cement which meant there was no overlap, as there had been for tin. At the 5% loading, the only system with which it was possible to produce SEM samples was the 9:1 BFS:OPC system. Although the results were limited, they gave a good indication of what was occurring and, combined with the $SnCl_2$ results, it is possible to suggest explanations.

Plates 16 and 17 show 9:1 BFS:OPC + 1% $ZnCl_2$ after 90 and 180 days hydration, respectively. The microstructure was very similar to that seen previously with the angular slag grains (A) and the hydrating cement phase binding together the slag grains, thereby reducing porosity. There were also particles which looked like anhydrous cement particles but which had darker areas within the grain (B). As with the tin samples, it was decided that these features would be the first to be analysed as they were different to what had been observed in the neat cement. Figure 4.5.8 shows an EDS trace of a darker area within the feature from a system which had hydrated for 90 days. It can be seen that there was a significant amount of calcium, silicon and chlorine with lower amounts of aluminium, magnesium, iron and zinc. Figure 4.5.9 is an EDS trace of the lighter area within one of these features. The EDS analysis was dominated by calcium, aluminium, and iron. This would suggest that it was possibly an unhydrated ferrite phase such as C_4AF.

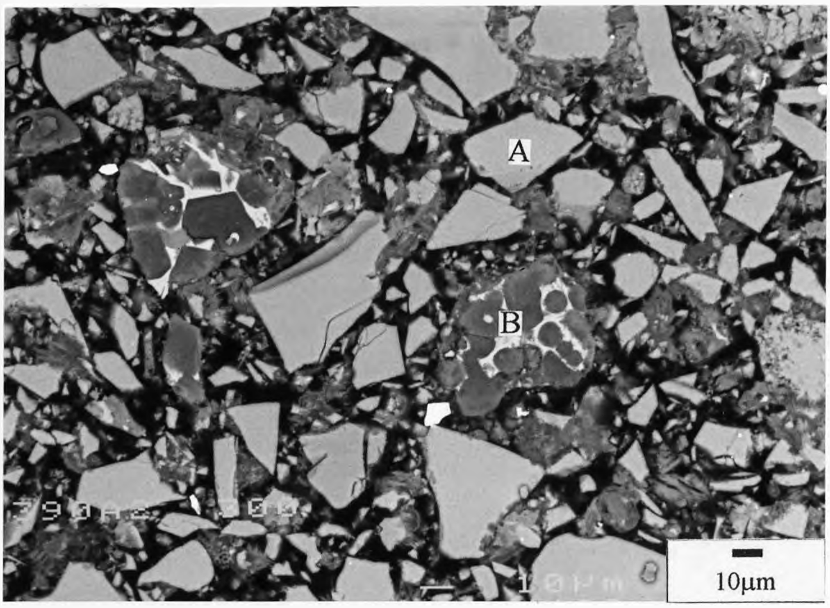

Plate 16 BEI of 9:1 BFS:OPC + 1% $ZnCl_2$ Hydrated for 90 Days

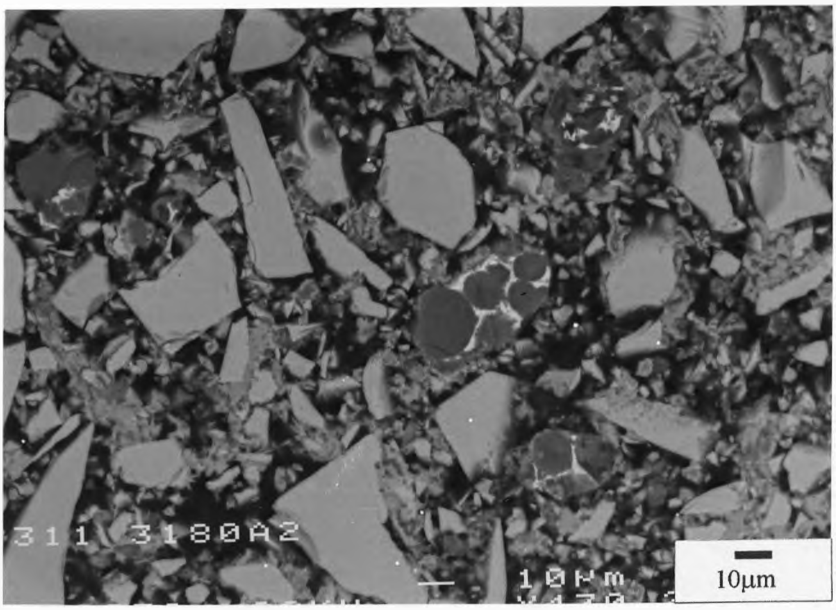

Plate 17 BEI of 9:1 BFS:OPC + 1% $ZnCl_2$ Hydrated for 180 Days

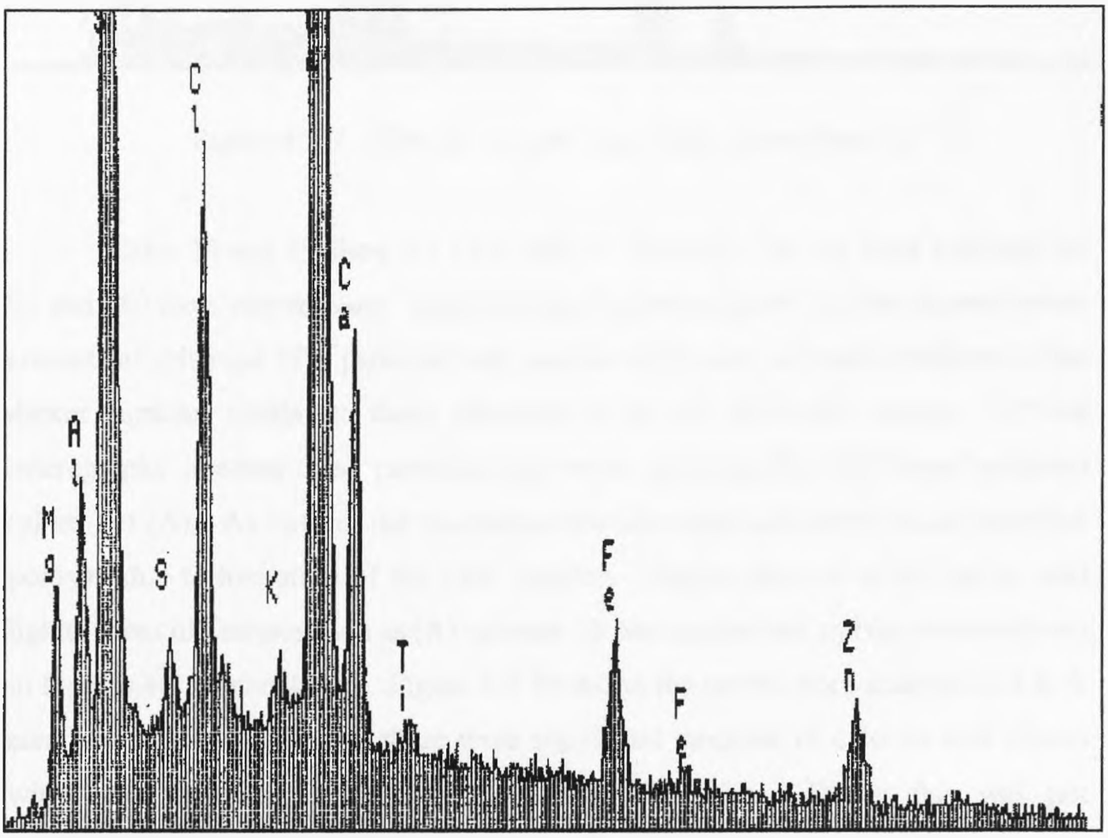

Figure 4.5.8 EDS of a Dark Area Taken from Plate 16

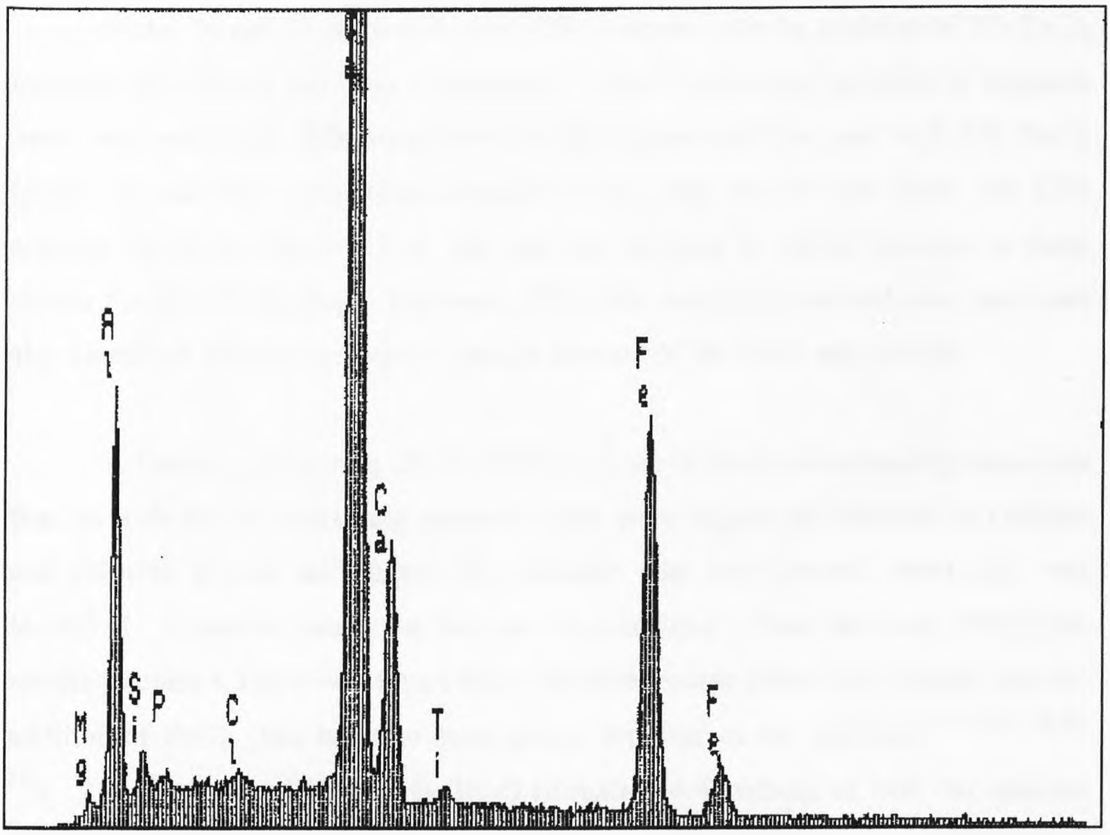

Figure 4.5.9 EDS of a Light Area Taken from Plate 16

Plates 18 and 19 show 3:1 PFA:OPC + 1% $ZnCl_2$ having been hydrated for 90 and 180 days, respectively. After 90 days hydration (plate 18) the microstructure consists of spherical PFA particles with pockets of cement and some evidence of the darker particles similar to those observed in the 9:1 BFS:OPC system. Of the micrographs selected these particles were more obvious after 180 days hydration (plate 19) (A). As before, the microstructure also appeared more dense with less porosity due to hydration of the OPC fraction. Again, analysis of the darker and lighter areas of features such as (A) on plate 19 was carried out and the results shown in Figures 4.5.10 and 4.5.11. Figure 4.5.10 shows the results from analysis of a dark area and it can be seen that there were significant amounts of calcium and silicon with lesser amounts of chlorine, aluminium and zinc. Whilst this was not unexpected, there was a difference between the fly ash and the slag systems in that there was significantly less iron and no magnesium in the PFA cement. Therefore, when the lighter area was analysed (Figure 4.5.11) it was not a surprise to find that it appeared to be a calcium silicate phase as opposed to the ferrite phase observed in the slag cement.

Plates 20 and 21 show a 9:1 BFS:OPC cement with the addition of 5% $ZnCl_2$ hydrated for 28 and 180 days respectively. These have been included to illustrate there was very little difference between this system and the one with 1% $ZnCl_2$ (plates 16 and 17). The microstructures were very similar and, from the EDS analysis shown in Figure 4.5.12, the zinc was situated in similar features to those shown for the 1% loading. The main difference was that a second zinc peak was also identified due to there being a greater amount of the metal salt present.

A feature common to all the EDS analyses of the zinc-containing areas was that, as with the tin-containing systems, there were significant amounts of calcium and chlorine present and, again, the chlorine was only present when zinc was identified. A similar reason for this can be postulated. From the x-ray diffraction results (section 4.3.4) it was found that a calcium zincate phase was formed with the addition of $ZnCl_2$ (this has also been widely reported in the literature[36,41,43,44,46,49-51]). The phase was $CaZn_2(OH)_6.2H_2O$ (Equation 4.4) which, as with the calcium hydroxo stannate formed in the tin systems, would account for the presence of calcium. Also, again in the same way as the $SnCl_2$ systems, Friedel's salt ($Ca_3Al_2O_6.CaCl_2.10H_2O$) was formed but only in conjunction with the calcium zincate.

In summary, the addition of $ZnCl_2$ to the two composite cements shown here appeared to have similar effects on the microstructure to the $SnCl_2$. The main differences were that, from the EDS analysis, it was apparent that there was a significant amount of silicon present in the zinc-containing phases which was not the case with the tin systems. Also, in the 9:1 BFS:OPC system the zinc appeared to be associated with a ferrite phase whereas, in the PFA system it was a calcium silicate phase, similar to the tin systems.

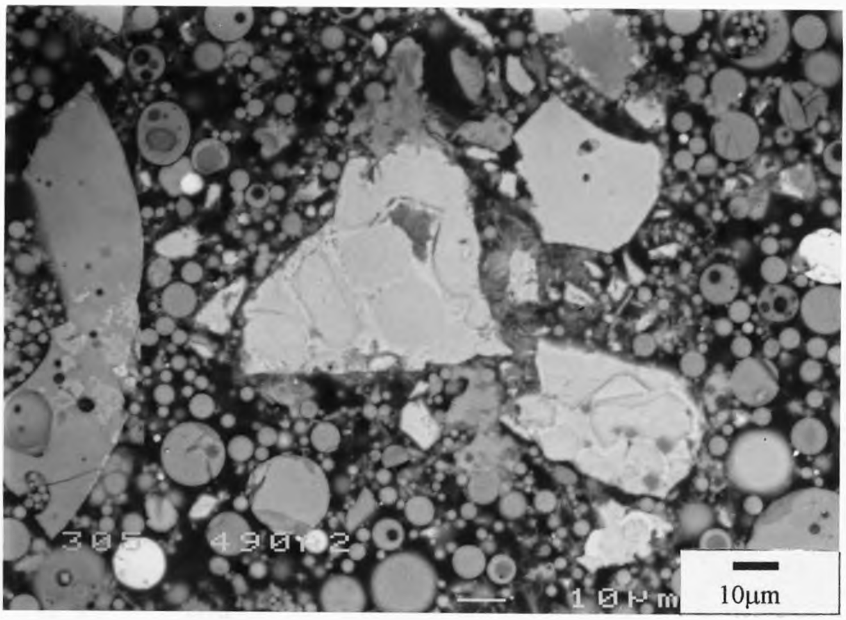

Plate 18 BEI of 3:1 PFA:OPC + 1% $ZnCl_2$ Hydrated for 90 Days

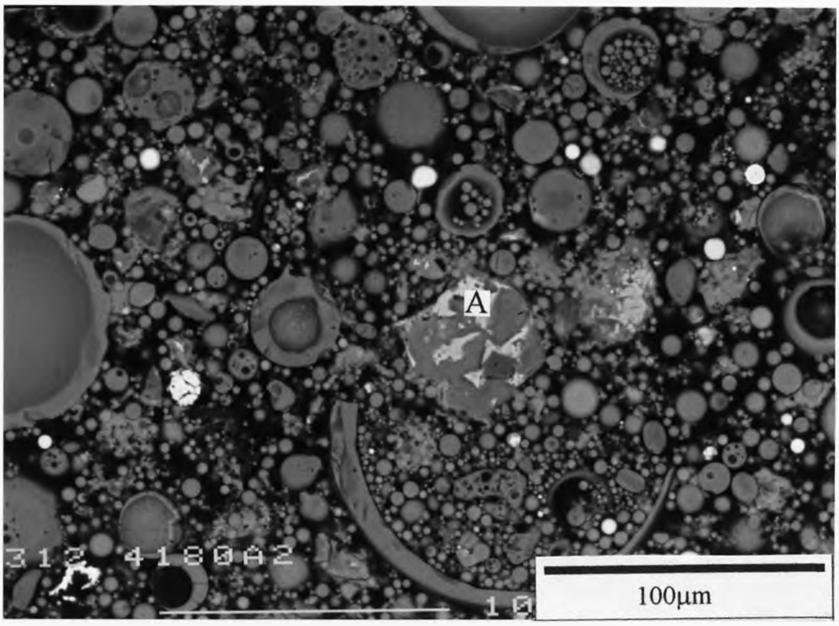

Plate 19 BEI of 3:1 PFA:OPC + 1% $ZnCl_2$ Hydrated for 180 Days

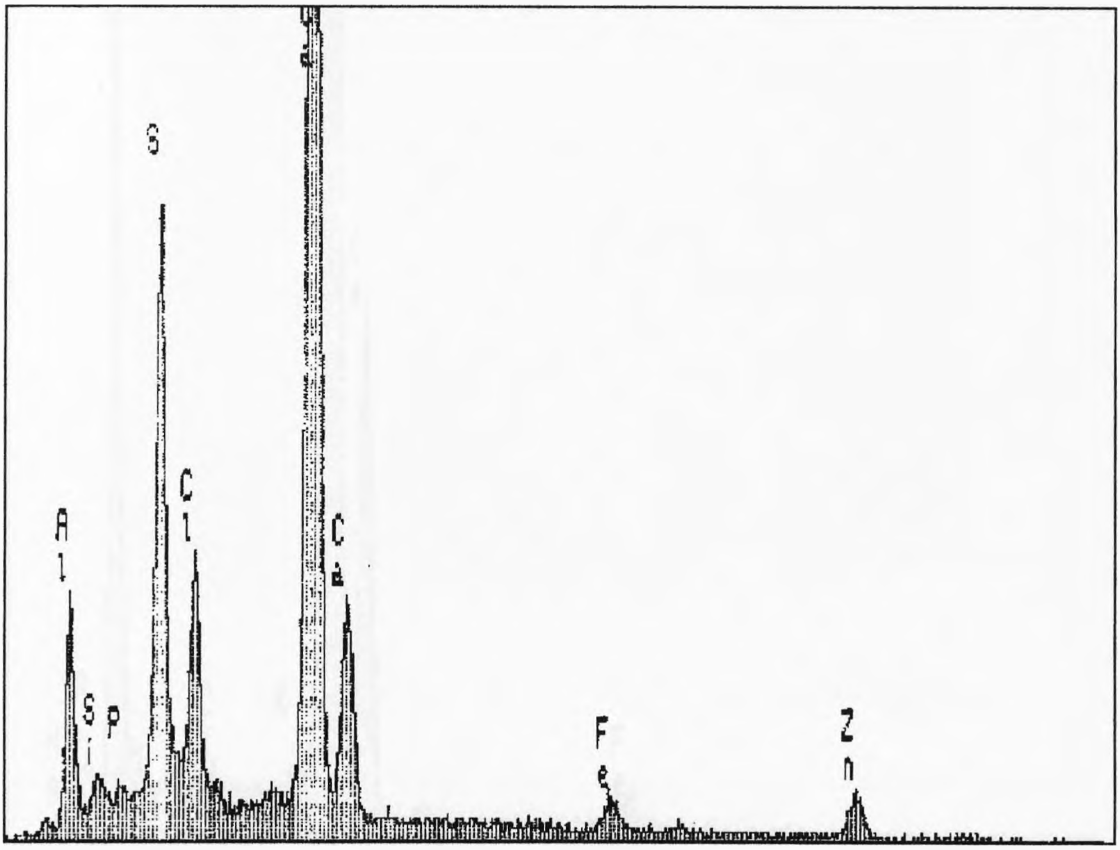

Figure 4.5.10 EDS of a Dark Area Taken from Plate 18

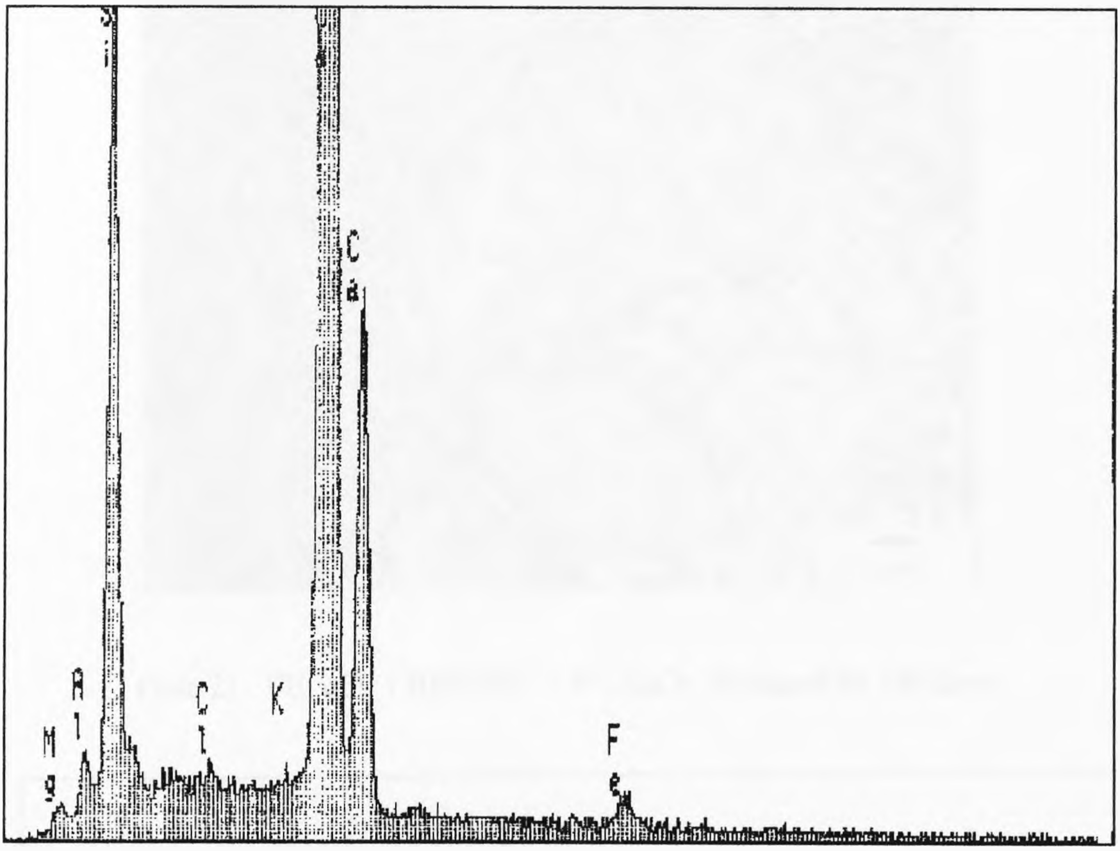

Figure 4.5.11 EDS of a Light Area Taken from Plate 18

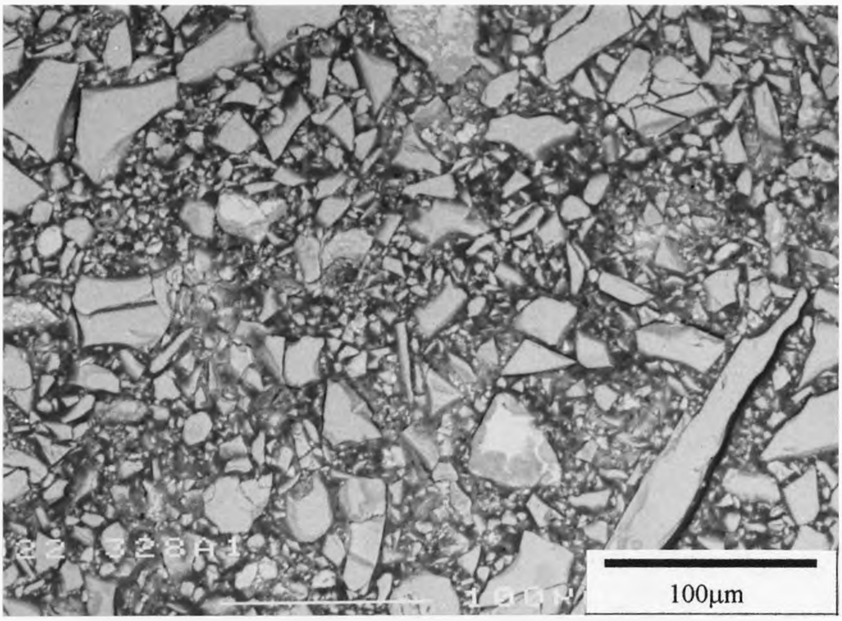

Plate 20 BEI of 9:1 BFS:OPC + 5% $ZnCl_2$ Hydrated for 28 Days

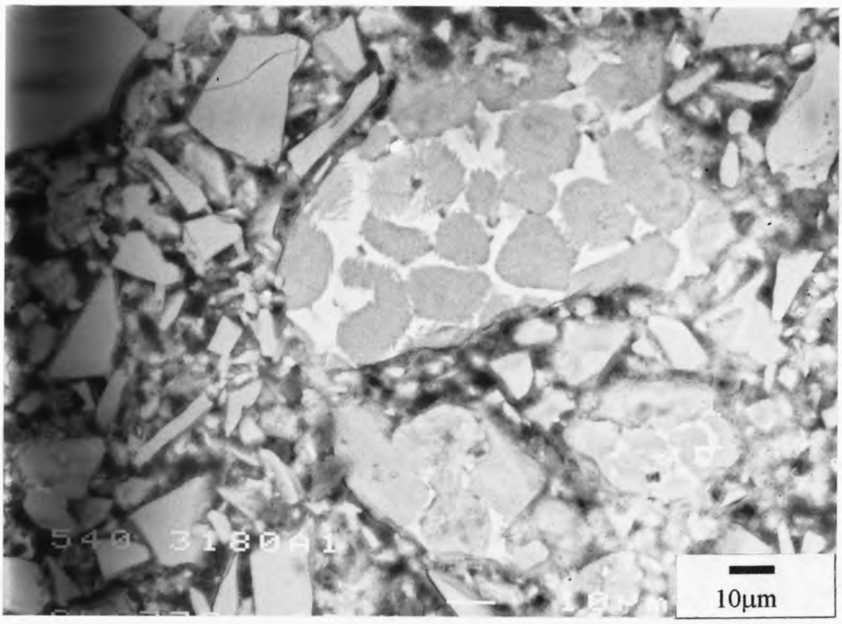

Plate 21 BEI of 9:1 BFS:OPC + 5% $ZnCl_2$ Hydrated for 180 Days

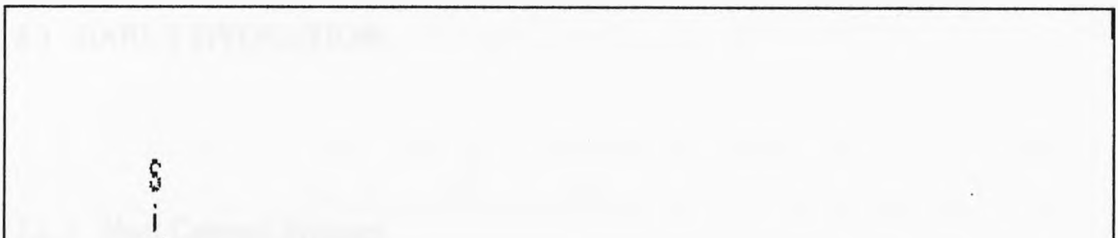

Figure 4.5.12 EDS of a Dark Area Taken from Plate 21

CHAPTER FIVE

5. DISCUSSION

The results from the experimental work of this project, presented in Chapter 4, are discussed in more detail and reference made to relevant results reported in the literature. The initial work involving pH measurements and determination of setting times are correlated with the calorimetry results. By considering the x-ray diffraction and scanning electron microscopy results together an overall view of the effects of inorganic metal salts on the hydration products of Portland and composite cements is given.

5.1 EARLY HYDRATION

5.1.1 Neat Cement Systems

The results for the neat cement systems showed that there was a significant difference between the 100% OPC cement and the three composite cements in terms of the amount of heat generated. The heat output of the composite systems were similar although there were some differences between these, even between the two slag systems. As a generalisation, the trend in terms of the amount of heat output of the cements, after 72 hours hydration, in descending order was:

OPC > 3:1 BFS:OPC > 9:1 BFS:OPC > 3:1 PFA:OPC

This is an area that has been widely studied and reported[16,17,19,29,55,68-70] because it is often beneficial to reduce the heat evolution in a cement so as to decrease the occurrence of thermal stresses which could induce cracking of the cement. There is general agreement that the addition of mineral admixtures to a cement paste has the effect of lowering the heat evolution over the first few days. A model hydration curve for a Portland cement is given in Figure 5.1[53].

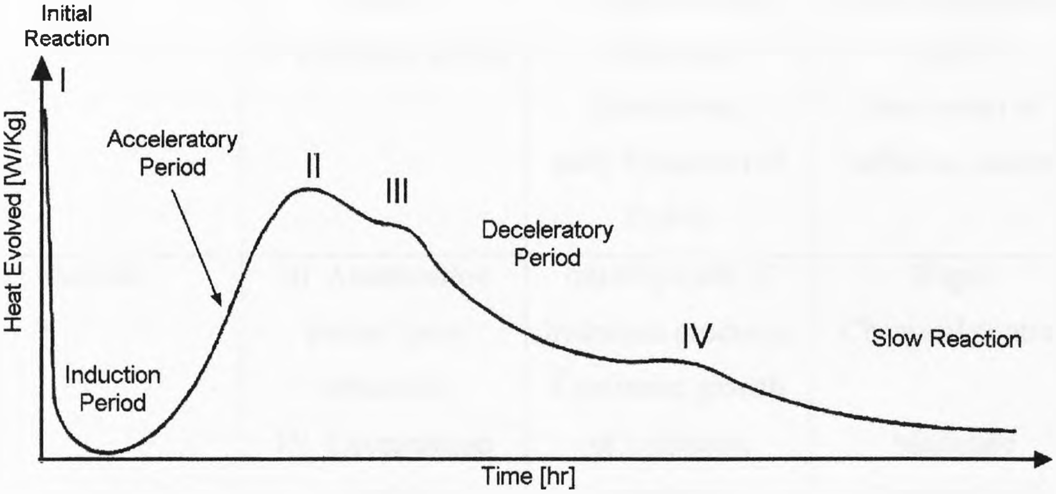

Figure 5.1 Model Hydration Curve for and OPC Paste

It can be seen that it has been split into four regions about which there is some disagreement. Peak I is the initial reaction of the cement powder and early stage reactions[1] which is followed by an induction (or dormant) period when there is very little heat evolved and the stiffness of the paste increases.[54] After this there is an acceleratory period when it is thought that setting occurs. Peak II occurs immediately after this acceleratory section and is generally believed to be due to the hydration of C_3S and the formation of calcium hydroxide. Peaks III and IV are less well defined and occur during the deceleratory and slow reaction periods.[1] Peak III is sometimes well defined or may appear as a shoulder to peak II, and there is disagreement as to the cause of this peak. It could be due to the transformation of AFt to AFm or the renewed formation of AFt or, in the case of slag cements, it has been attributed to the hydration of the slag fraction[16]. It has also been said to be due to the hydration of C_4AF[71], but there appear to be no definite reactions associated with its occurrence. Peak IV is sometimes associated with the hydration of the ferrite phase although this is by no means established. Jawed, Skalny and Young[7] identified five stages in a model curve and summarised the processes in the following table:

Period	Reaction Stage	Chemical Processes	Overall Kinetic Behaviour
Early	I. Pre-induction period II. Induction period	Initial hydrolysis; release of ions Continued dissolution; early formation of C-S-H	Very rapid Chemical control Slow Nucleation or diffusion control
Middle	III. Acceleration period (post induction) IV. Deceleration period	Initial growth of hydration products; Continued growth of hydration products; development of microstructure	Rapid Chemical control Moderate Chemical and diffusion control
Late	V. Diffusion period (steady-state period)	Gradual densification of microstructure	Very slow Diffusion control

Table 5.1 Stages of hydration of C_3S [7]

The neat OPC curve shown in the results follows the model very closely and could be said to be a classic hydration curve for Portland cement. The composite cements did not only produce a lower heat output, but the curves were a different shape. This was most pronounced in the 3:1 BFS:OPC and 9:1 BFS:OPC systems where a definite shoulder to peak II was observed. As mentioned previously, this has been attributed to the hydration of the slag fraction and has also been referred to as peak X[16] or peak S[53,55] (as it will be referred to here). It was clear that with increasing amount of slag replacement, peak II became smaller and peak S more evident and possibly slightly accelerated. Also, peak II in both slag systems occurred at approximately the same time as in the 100% OPC system but with decreased heat output. According to Richardson et al[16] the occurrence of peak II at the same time with increased loading of slag has general agreement but, as with peak S in general, there is disagreement as to the effects of increasing the slag fraction.

Wilding and McHugh[72] and Lee[73] (who attributed the peak to the replacement of AFt by AFm) noticed a gradual sharpening and acceleration of the peak with increased loading. However, Wu et al[17] considered the time to peak S to remain the same for all loadings, although the study only considered loadings to 60% replacement. In contrast to this, Cook and Cao[74], in considering the third peak to be attributable to the onset of C_4AF hydration, reported a retardation with increased loading of blast furnace slag. It can be seen from this that it is very difficult to find consistent results for an explanation of the third peak but the results of this study appear to agree with those suggesting that there was a sharpening of peak S and a possible shift to the left with increasing slag replacement.

Of all the systems, the 3:1 PFA:OPC system appeared to be the most retarded as the peak had shifted to the left and the peak height was intermediate between those of the two slag cements. This retardation, in comparison to both Portland and slag cements, has been widely documented[16,29,75,76] although there is disagreement in the literature as to whether the fly ash retards or accelerates the set. However, the majority of workers report a retarding effect on the C_3S and C_3A hydration and agree that the reason for this is due to the condition of the fly ash surfaces. Fajun et al[29] explain that these surfaces act as a calcium sink. Calcium in solution is removed by the ample amount of aluminium associated with the fly ash because an AFt phase forms preferentially on the surface of the fly ash. This depresses the Ca^{2+} ion concentration in solution which retards the formation of a calcium rich layer on the surface of the clinker materials. Until the formation of the additional AFt phase is slowed the clinker layer cannot form which results in a longer induction period as the formation of calcium hydroxide and C-S-H is delayed.[75] the results from this study would agree with the fact that pulverised fuel ash causes a retardation in set.

Also, the temperature at which the calorimetry was conducted has an effect on the hydration of the cement in all systems. It was illustrated that, at 21°C, the hydration of the cement was retarded in comparison to that at 35°C. This has also been well documented and is important to bear in mind because it means that the calorimetry work carried out for this project at 35°C cannot be directly related to other techniques which were all carried out at a lower temperature. All reported work[53,76] has stated that, as temperature increases, the rate of hydration also increases alongside an increased amount of heat evolved. This trend is followed for all cement systems and was confirmed here.

Another factor which has to be considered when comparing the 100% Portland cement with composite cement systems is the amount of water used. For this work a water:cement powder (w:cp) ratio of 0.35 was used for all the cement systems which means that there was an increased w:c ratio for the composite cements compared to the OPC. The difference would be especially great for the 9:1 BFS:OPC cement as there was so little Portland cement present. The actual w:c ratios are given in Chapter 3.

5.1.2 Cements Containing Inorganic Metal Salts

The effects that metal salts have on the hydration properties of the cement systems differ depending on the nature of the metal added. However, the effect of a specific metal salt is the same regardless of the type of cement used although the degree to which the addition affects the hydration differs. Therefore, the discussion will be split up into the effects caused by metal salts as opposed to discussion by cement type.

It is widely known that the effect which chlorides have upon the set of cement depends on the nature of the cation associated with it[1,40] and it is thought that the solubility of any hydroxides formed determines whether or not there will be acceleration or retardation.[41] That is, the alkali metal salts which form soluble hydroxides will be accelerators and those which are less soluble will cause retardation. Adding $ZnCl_2$ caused massive retardation of set in all cements and this effect increased with increasing concentration of metal salt in the same way as observed in the preliminary mixes. This is most clearly illustrated by the values of Q_{max}, t_{max} and the total heat values shown in Tables 4.2.1 - 4.2.8. Q_{max} is the maximum rate of heat output (Wkg^{-1}) and t_{max} is the time at which this occurs. A large value for t_{max} and a small value of Q_{max} indicate a retardation of set. The addition of $ZnCl_2$ to all the cement systems caused retardation in comparison to the neat cement. With a loading of 0.1% $ZnCl_2$ the value of Q_{max} was between one third and one fifth of the neat cement value, depending on the type of cement used, which was coupled with a value for t_{max} which was between four and sixteen times the neat cement value. The greatest effect was seen with the 9:1 BFS:OPC system where the Q_{max} value was one fifth of the neat cement value and tmax sixteen times bigger. The effect on the PFA-containing cement were similar to the effects seen with the Portland cement. There were no values of Q_{max} or t_{max} for the 1% loading as the system was so retarded there were no peaks within 72 hours.

The total heat values (Tables 4.2.2, 4.2.4, 4.2.6 & 4.2.8) show a greater difference between the cements than the Q_{max}/t_{max} values. After 3 hours hydration, the neat Portland cement system had a greater heat output than that containing 0.1% $ZnCl_2$ but after 70 hours they were approximately the same. At the 1% loading, the value after 70 hours hydration was approximately one third of neat and 0.1% addition cements. Conversely, the 3:1 PFA:OPC systems showed the opposite trend. After 3 hours hydration the cement with the 1% loading had evolved more heat than the other two systems with the neat cement having evolved the most. However, this changed rapidly and after 70 hours the trend was the same as for Portland cement. The slag cements showed a lower heat output of the zinc-containing systems from the beginning and, as would be expected the greatest difference was seen with the 9:1 BFS:OPC system. This shows that, although the zinc retards the set of all the systems, the overall heat evolved can be very similar to that of the neat cement. Figure 4.2.4 shows that not only does the cement containing 0.1% $ZnCl_2$ show classic retardation but the peak shape has changed in comparison to the neat cement. It can be seen that there is the appearance of a shoulder to peak II which would not be expected in an OPC system. The two slag cements are too retarded to note any difference, although, Figure 4.2.10 shows the 75% slag cement hydrating for 150 hours and peak S seems to have disappeared although it is not clear. The PFA system shows no change in the shape of the curve. These observations correlate well with calorimetry studies carried out by Hills et al[77] where it was shown that the addition of zinc hydroxide to a Portland cement caused retardation of set, a decrease in the value for Q_{max} and shoulders on the main peak were resolved.

The results of the $Zn(NO_3)_2$ additions were different to those seen for the chloride addition in that in the OPC and PFA cements the retarding effect was less severe than for the chloride and, in the Portland cement, the shape of the peak remained the same. However, the total heat evolved after 70 hours was less than for either the neat cement or the zinc chloride containing cement. The addition of the nitrate to the slag cements appears to have caused greater retardation than with the chloride and, in the case of the 90% slag cement, the total heat output indicates that hydration ceased altogether. These effects appear to be more random than with the chloride and, as the same molar amounts of zinc were added in both cases, it appears that the anion is causing the different effects.

The effect of tin was investigated as a comparison to that of zinc and, also, as a comparison of the two oxidation states of the metal. Therefore, the effects of Sn(II) and Sn(IV) chlorides will be discussed separately and in conjunction with each other. The effect of the $SnCl_2$ addition was not as pronounced as that of the zinc. In comparison to the effects of the zinc, there was much less change in a lot of the cement systems but some retardation with the 1% loading. This was illustrated in the Portland cement where Q_{max} was similar at both 0.1% and 1% addition levels and the values of t_{max} for the neat cement and the 0.1% loading were also similar, although the effect of adding 1% $SnCl_2$ was to double this value. However, the total heat values showed an accelerating effect with increasing tin content after three hours hydration, but very little difference after 70 hours. Similarly, the 3:1 BFS:OPC system showed values of Q_{max} similar to each other although the 1% addition was slightly less, but the values of t_{max} were different which indicated that there was some slight retardation with the 1% loading. This was confirmed with the very early total heat data where the values for the tin-containing cements were approximately half that of the neat cement but, as with the Portland cement, the values were all very similar after 70 hours hydration. The 9:1 BFS:OPC showed classic retardation of set with increasing loading of $SnCl_2$, that is decreasing values of Q_{max} and increasing t_{max} with increased loading. The PFA cement showed a different effect again in both the Q_{max} and total heat data. The trend for the values of Q_{max} were 0.1% loading > neat cement > 1.0% loading with the t_{max} values being equal for the neat cement and the 0.1% addition, but the 1% loading was slightly higher. There was no trend in the total heat results but the overall effect after 70 hours hydration was the same as the Q_{max} values with the 0.1% addition evolving the greatest amount of heat. Therefore, it can be seen that the trends for the Sn(II) addition were not as clear as for the zinc addition but it can be said that the 1% addition caused some slight retardation of the set in all cement systems. The peak shapes were similar to the neat cements apart from the slag cements. The 3:1 BFS:OPC system showed no change at the 0.1% loading level but, at 1% the peak was more spread out and the shoulder appeared to be on the left of the peak. It is possible that this was peak S which had become bigger than peak II as this was the effect observed in the 9:1 BFS:OPC cement with 0.1% addition. At 1% loading, the peak in the 90% slag cement became smooth and there was no peak S visible.

The addition of $SnCl_4$ to the cement systems had mixed effects in a similar way to those of $SnCl_2$. The total heat results for all systems showed a similar trend in that, after three hours hydration, the tin-containing systems had evolved more heat than the respective neat cements but after 70 hours the systems with 1% loadings of $SnCl_4$ showed values less than either the neat cement or the 0.1% addition cements. The values of Q_{max} were either all very similar (3:1 BFS:OPC and 3:1 PFA:OPC cements) or the 1% addition cement was slightly less than the other two systems suggesting some retardation. The values of t_{max} for the 9:1 BFS:OPC cement followed this trend (although the value for the 0.1% addition was greater than the 1% addition) but the other cements showed values which did not correspond to this trend. The OPC and 3:1 BFS:OPC cements both had the 1% loading reaching Q_{max} in less time than the neat or 0.1% addition cements whose values were similar) which would suggest an acceleration of set. The results for the 3:1 PFA:OPC cement also suggested an acceleration due to the addition of $SnCl_4$ as the 1% addition time was less than the 0.1% addition which, in turn, was less than the neat cement. These results illustrate the necessity of considering more than one property at a time as, from the Q_{max} values it would be assumed that there was retardation with addition of $SnCl_4$, but acceleration would be concluded from the t_{max} results. The total heat results help to clarify the correct assumption from these two sets of results as it was shown that there was some acceleration of set in the first few hours but this levelled off and, after 70 hours there were similar amounts of heat evolved for all systems. If the results are studied together it can be seen that Q_{max} occurred within 10 hours and, as there was evidence for early acceleration of set, it would follow that tmax would indicate accelerated set. Therefore, it can be assumed that the set would be accelerated due to increased evolution of heat during the first few hours but that overall the effect on the amount of heat generated would be minimal. The peak shapes, as with the $SnCl_2$, were not greatly affected. The main difference again came with the 9:1 BFS:OPC cement where the 0.1% addition caused peak S to be greater in magnitude than peak II, whilst there was a complete absence of peak S with the 1% addition.

It can be seen from the results that the effects of adding $SnCl_2$ and $SnCl_4$ were not as pronounced as the addition of $ZnCl_2$ on any of the cement systems but there were various subtle effects. In summary, adding $SnCl_2$ caused a slight retardation in the set of the cement as the loading increased, while the $SnCl_4$ caused a slight acceleration at early hydration times, but overall the effects were minimal and the amount of heat evolved over 70 hours was not significantly different to that observed in the neat cements. The acceleration caused by the increasing addition of $SnCl_4$ could be due to the increased amount of heat generated at very early hydration times which were shown in the preliminary mix results. The temperature increase was not as great as for the $AlCl_3$ addition but, at 1% the difference between the slurry temperature and the cement temperature was around 10-15°C, whereas for the tin(II) and the zinc systems this difference was only 1-5°C with the greatest difference being in the tin-containing systems.

Another suggestion for the difference between the tin and zinc additions was the pH of the systems. At 1% loading the pH for $ZnCl_2$ was about 7, whereas that for $Zn(NO_3)_2$ was about 4. In contrast, the values for the tin slurries were 2 ($SnCl_2$) and 1 ($SnCl_4$) and both of the zinc systems showed substantial retardation of set. The pH of the slurries was measured for both 5% and 1% loadings of all the metal salts. It was observed that, with the exception of As_2O_3, all the slurries for the 5% loadings were acidic with values ranging from 1 to 4 ($As_2O_3 = 7$). The results of the 1% loadings were more mixed and in general, less acidic than the 5% slurries. pH is important for the containment of metals. This is because a high pH is required for the containment as most metal hydroxides have minimum solubilities in the range 7.5 to 11[34] but, as the minimum solubilities of the hydroxides vary, the pH can only be a guide as to what may occur with a specific system. Whilst a study of the effect of pH was not directly undertaken in this project, it was decided that knowledge of the pH of the slurries may help to explain some of the phenomena observed. A cement is an alkaline environment due to the phases present within the system. Therefore, in most instances, there was an interaction between an acid and a base when the cement powders were added to the slurries which means that the environment was being changed from that of a standard cement system (Portland or composite).

The effect of the oxidation state of the tin did not appear to be particularly significant as, although the tin(IV) showed some acceleration and tin(II) some retardation, neither effect was particularly large and, in a lot of the cement systems, not significantly different from the neat cements. A reason for the lack of difference between the two tin additions could be that the $SnCl_2$ oxidises when it is added to the mix water to form the slurry. This oxidation can be seen in equation 5.1[57]:

$$6SnCl_2 + 2H_2O + O_2 = 2SnCl_4 + 4Sn(OH)Cl \qquad \text{Equation 5.1}$$

The oxidation arises from the oxygen available in the water and when $SnCl_2.2H_2O$ is dissolved in water and acid solution is formed (as mentioned previously) which, unless metallic tin is added, will form $SnCl_4$ and stannous oxychloride. This could account for the relatively small differences observed in the setting behaviour of the cements containing the two tin compounds, since the addition of tin(II) chloride leads to the formation of tin(IV) chloride in solution.

The addition of $AlCl_3$ to the cement systems appeared to have a mixed effect which was probably due to the amount of heat generated when the slurry was added to the cement powders. In the slag cements the addition of 1% $AlCl_3$ appeared to kill the set of the cement. This was apparent from the total heat data because the amount of heat generated after 70 hours was minimal. The heat generated after 3 hours could be attributed to the heat of wetting and, therefore corresponded to peak I.

However, there was no peak II because the cement set was poisoned. In contrast, at the 0.1% loading the set was retarded but not significantly. In the Portland cement system the effect appeared to be increased retardation with increasing salt addition, although, the effects were not significant and the overall amount of heat generated was similar for all systems. In the pulverised fuel ash cement the effect was to accelerate the set of the cement quite significantly but, again with regards to the total heat evolved, this had stabilised after 70 hours hydration.

In contrast to the aluminium additions, incorporating arsenic into the cement systems had virtually no effect on the setting behaviour or on the amount of heat evolved both at early and longer hydration times.

In summary, the effects of metal salts on the early hydration of cements varied between cement systems, composition of salt and also, in some cases, between the amount of salt added. Therefore, it can be said that it was not possible to predict the outcome of adding a particular salt to a particular cement but there was a general trend of an increase in the amount of retardation with increasing salt addition. These conclusions correlate with the findings of the preliminary mixes which were carried out before any other experimental work to try to gauge the effects of the salts on the cements and, also to assess which of the suggested systems would form a cement paste. The temperature of the slurry and the cement paste were measured because it had become apparent from some earlier work that the temperature of the system could rise dramatically and it was thought to be important to ascertain if there were any trends with the rises in temperature. For example, to find out if an individual metal salt caused a large temperature difference in all cements or whether it was cement specific. As a generalisation, it was found that there were differences between the temperature of the systems incorporating same salt at different loadings and that certain salts caused greater temperature differences than others regardless of the cement system. In the neat cements the difference between the water temperature and the mix temperature were negligible and were still around room temperature for all the cement systems. However, on addition of the metal salts the difference in temperatures became apparent. The addition of $ZnCl_2$ had the effect of raising the slurry temperature, but only at the 5% loading. In all cement systems with the addition of 1% and 0.1% $ZnCl_2$ the temperatures of both the slurry and the cement paste were not raised significantly above room temperature. However, at 5% loading the slurry temperature increased substantially (to approximately 40°C) in all systems and, in the OPC and 3:1 BFS:OPC systems, the cement paste temperature was raised to between 50 and 60°C.

$SnCl_2$ and $SnCl_4$ additions had a slight effect on temperature which varied between cement system and was, again, most pronounced with the 5% addition but it was not significant. The As_2O_3 addition caused very little change in the temperature of any of the cement systems at any of the loadings. The biggest change was brought about by the $AlCl_3$ salt where, in all but the 3:1 PFA:OPC system ($\approx$ 70C), the cement paste temperature at the 5% loading was around 100°C. This was surprising because the slurry temperature was around 40°C in all cements which was similar to the zinc systems. One explanation for this substantial temperature difference could be that, because of the way in which the loadings were calculated, the amount of $AlCl_3$ added to each system was significantly greater than any other salt. This is illustrated in Table 3.2.2 when considering the mole additions made. It can be seen that, at the 5% loading, there is nearly one mole of $AlCl_3$ added compared to 0.4 moles of zinc and 0.2 moles of tin. The temperature of the cement paste affected which systems could be used because, when the temperature was increased substantially, there was insufficient water left to form a paste. The increased temperature and a lowering of the pH, due to a greater concentration of chloride ion, would also account for the varied effects observed from the calorimetry results.

The setting times for the cement systems were important as, in an industrial context, there is a limit on how long the cement can be left before storage. Therefore, a limit of seven days was put on the cements to reach final set as this was the time for the waste encapsulation process at Sellafield. The results from the preliminary mixes showed that the results varied significantly between types of metal salt and cement system. However, the main trend was that the greater the amount of metal salt addition, the longer the time taken to set, with the exception of systems incorporating As_2O_3 in which the effect of increasing the loading was to decrease the setting time. Also, all systems had set within 24 hours. The preliminary mixes were quite crude but did serve the purpose of giving some idea of the systems it would be practical to attempt to scale up for the main body of the work and what to expect from the early hydration of the various cement systems.

The calorimetry work reported in the literature appears not to have covered the effects of specific metal salts on the early hydration of cements, so it has been difficult to compare the results obtained. However, as the hydration of the systems was followed for longer periods, the confidence in the results increased as the results of the long term hydration confirmed these findings of the early hydration studies.

5.2 LONG TERM HYDRATION

The results from the x-ray diffraction investigations followed the hydration from early ages (3 days) through to 180 days. The aim was to identify standard and non-standard hydration phases in all the cement systems at all ages and compare the neat cements with the salt-containing systems. It was for this study that the number of systems was decreased so that a more thorough study of the systems involving $ZnCl_2$, $SnCl_2$ (both at 5% and 1% loadings) and $SnCl_4$ (at 1% loading only) could be undertaken.

5.2.1 Neat Cement Systems

The results from the neat cement systems showed that there was a substantial difference between the cement types. The main phases identified in the OPC system were calcium hydroxide, calcium carbonate and ettringite (Figure 4.3.1) with the addition of quartz and mullite in the ash cement (Figure 4.3.2) and gehlenite in the slag cements (Figures 4.3.3 and 4.3.4). The most significant difference between the OPC and the composite cements was the amount of calcium hydroxide present. That is, in the composite cements there was a drastically reduced amount present at all ages (Figures 4.4.5–4.3.8) which was to be expected due to the decreased amount of Portland cement present in the composite cement systems and because of the pozzolanic reaction in the presence of PFA. The occurrence of a pozzolanic reaction with slag replacement has been documented in the literature[18,30,68,78], although the reaction occurs to a lesser extent than in the fly ash cements.

The identification of the main phases was confirmed from the differential thermal analysis results. Figures 4.4.1(OPC) and 4.4.4(3:1 BFS:OPC) show the presence of calcium hydroxide (around 480°C) and C-S-H with some ettringite at around 120°C. It was not possible to detect C-S-H with x-ray diffraction as the phase is amorphous. There was also a DTA peak at around 170°C in the OPC cement. This could have been due to an AFm phase which had not been detected by the x-ray diffraction because it was poorly crystalline.[1] Another interesting feature was that, with increasing time the presence of ettringite was not detected in the composite cements, although it was still present in the OPC. Also, it appeared that the amount of calcium carbonate present was greater in the composite cements than in the Portland cement at all ages.

5.2.2 Tin-Containing Systems

The results from the neat systems were as expected for the cements and conditions employed for this work. However, once the metal salts had been added, the hydration phases identified by powder x-ray diffraction were modified. This was clearly illustrated in the case of the addition of 5% $SnCl_2$ to OPC at all ages (Figures 4.3.9-4.3.12). The standard hydration phases were present but there was also the presence of two different peaks which were identified as Friedel's salt and $CaSn(OH)_6$ (calcium hydroxo stannate). The appearance of these non-standard phases also caused a change in some of the standard phases present, the main one being a significant decrease in the amount of calcium hydroxide present when compared to the neat cement. It should also be noted that the oxidation state of the tin in the calcium hydroxo stannate phase was +4 which meant that oxidation had occurred which was explained earlier in Equation 5.1. This oxidation helped to postulate an equation for the formation of the two non-standard hydration phases present in the tin-containing cement as follows:

$$SnCl_4 + 2Ca_3Al_2O_6 + 3Ca(OH)_2 + 20\ H_2O \downarrow 2Ca_3Al_2O_6.CaCl_2.10\ H_2O + CaSn(OH)_6 \quad \text{Equation 5.2}$$

(Friedel's Salt) (Phase X)

It can be seen that combining the tin chloride with the cement (tricalcium aluminate and calcium hydroxide specifically) the two phases which were not present in the neat cements were formed, i.e. Friedel's salt and calcium hydroxo stannate. It can be seen that the formation of the non-standard phases consumes the calcium, leaving less available for the continued formation of calcium hydroxide, and consequently accounting for the significant decrease in the amount identified in the presence of these phases. These phases were clearly present at all ages in the OPC system and were also identified in all of the composite cement systems (Figures 4.3.13-4.3.18) but at different amounts and with differing effects on the standard hydration phases. In all cases, the main effect was to reduce the amount of calcium hydroxide present in the system which meant that, in some cases, there was no calcium hydroxide present at all.

At early ages there was little or no identification of either phase (see Figures 4.3.13, 4.3.15 & 4.3.16). In the 9:1 BFS:OPC and 3:1 PFA:OPC systems the calcium hydroxo stannate phase was clearly evident after 28 days hydration but, even after hydrating for 90 days, there was no clear evidence for Friedel's salt. It was not clear why this should have occurred but it could be possible that, because there was less Portland cement present in the composite systems than in the OPC system, there was less C_3A and calcium hydroxide present for the formation of both Friedel's salt and calcium hydroxo stannate. However, if this was the case then the 3:1 BFS:OPC cement should have demonstrated similar effects and this was clearly not the case as there was clear evidence for the formation of both non-standard phases. Therefore, there had to be another contributing factor to the effect. It has been well documented that, to proceed, the pozzolanic reaction consumes the calcium hydroxide produced from the reacting Portland cement which could account for the lack of Friedel's salt present in these cements. Also, from the x-ray diffraction results, it was observed that, after 180 days hydration, the amount of calcium hydroxo stannate was beginning to decrease, which suggests that the pozzolanic reaction consumes the calcium hydroxo stannate phase once all the calcium hydroxide has been exhausted. It was suggested earlier that a pozzolanic reaction with slag could be occurring, although it only becomes obvious with the 90% replacement level.

The results obtained from the DTA study also confirmed the existence of the non-standard hydration phases observed with the addition of 5% $SnCl_2$ (see Figures 4.4.2-4.4.3, 4.4.5-4.4.6 & 4.4.8). In all the systems there was evidence for the calcium hydroxo stannate phase at around 330°C. In some systems this endotherm appears as a doublet (OPC and 3:1 BFS:OPC cements) and in others as a single peak (9:1 BFS:OPC and 3:1 PFA:OPC). In the OPC and 75% slag cements there was also a peak at around 150°C which, when combined with the x-ray diffraction results, was thought to be due to Friedel's salt. The endotherm temperature quoted by Birnin-Yauri et al[61] was 120°C but this was for a laboratory produced Friedel's salt and, allowing for differences due to reactions occurring to form the phase identified in this work, the higher value found here was not significantly higher. Also, this endotherm peak did not occur in the 9:1 BFS:OPC and 3:1 PFA:OPC cements which correlates well with the lack of Friedel's salt identified from x-ray diffraction and helps to clarify that the endotherm does relate to the Friedel's salt.

The results of the cements with 1% addition of $SnCl_2$ were not as conclusive as with 5% added. This was to be expected as, at 1%, the levels were at the limits of detection of the equipment and, also, there was not as much of the metal salt added so there was less for the reactions to occur and form the non-standard hydration phases. However, there were some very small peaks of calcium hydroxo stannate visible in some of the systems and it was also possible to identify Friedel's salt. The work carried out at the 5% replacement level helped to clarify that the identification of these weak peaks was correct. It also showed that it was necessary to place as much of the metal salt in the cements as possible so that identification of phases was made easier because, without the phase identification from the 5% systems, it would not have been possible to confidently assign the peaks at 1%.

The x-ray diffraction results of the $SnCl_4$ systems were similar to the results obtained with the 1% $SnCl_2$ additions as it was possible to add only 1% of the $SnCl_4$. This was because the amount of heat generated prohibited any greater amount being incorporated as it did not allow sufficient water to form a paste. It would follow that, as the tin(II) was oxidised to tin(IV), the hydration products should be very similar to those when $SnCl_4$ was added, so it would be expected that calcium hydroxo stannate and Friedel's salt would be formed. However, as with the 1% $SnCl_2$ systems, the amount of salt added was restrictive in terms of both the sensitivity of the equipment and the amount of salt available for the reactions to occur. The results obtained showed evidence of Friedel's salt and some evidence of $CaSn(OH)_6$ but, as with $SnCl_2$, the peaks overlapped with other peaks and were, therefore, not exclusively calcium hydroxo stannate. The 1% additions of both of the tin salts served to help to clarify the results observed with the 5% additions but would have been of little use on their own as the peak intensities were insufficient to draw any firm conclusions.

5.2.3 Zinc-Containing Systems

The results of the addition of $ZnCl_2$ to the cement systems were not as conclusive as the tin salt results. This was because there was a limit to the number of cement systems which could be studied due to the retarding effect of the zinc being so great. However, the research reported in the literature for zinc additions was much more extensive than for the tin systems which meant that it would be easier to identify any non-standard hydration phases which may have formed. There is agreement in the literature that, seemingly regardless of the anion involved, the addition of a zinc salt to a cement will result in the formation of the calcium zincate phase, ($CaZn_2(OH)_6.2H_2O$)[36,41,43,44,46,49-51] which was identified in the work carried out. However, with the 5% addition (which was only in the 9:1 BFS:OPC cement) the evidence for the existence of the calcium zincate increased with time up to 180 days (Figures 4.3.31-4.3.33). The main hydration products appeared to be gehlenite, calcium zincate and Friedel's salt. The continued presence of the gehlenite in such quantities and the lack of calcium carbonate until late hydration times would suggest a retardation of hydration which was not unexpected due to the significant early retardation observed from the calorimetry results. The definite identification of Friedel's salt suggested that a similar process to that described for the formation of calcium hydroxo stannate was employed. Therefore, a similar equation could be suggested to explain the formation of these non-standard hydration phases:

$$\begin{array}{c} 2ZnCl_2 + 2Ca_3Al_2O_6 + 3Ca(OH)_2 + 22\ H_2O \\ \downarrow \\ 2Ca_3Al_2O_6.CaCl_2.10\ H_2O + CaZn_2(OH)_6.2H_2O \\ \text{(Friedel's Salt)} \qquad\qquad \text{(Phase Z)} \end{array} \qquad \text{Equation 5.3}$$

At 1% loading in the 9:1 BFS:OPC cement (Figures 4.3.34 & 4.3.35) the main differences were that the calcium carbonate formed at earlier ages than with the 5% and there was no evidence of formation of Friedel's salt. However, as with the 5% loading the identification of phase Z was more evident as the cement aged although the peaks were not as strong due to the lower amount of salt incorporated originally.

In the 3:1 PFA:OPC cement (Figures 4.3.36-4.3.38) the effects were slightly different. The early age hydration appeared to have been retarded and there was no evidence for the formation of calcium zincate or Friedel's salt. After 28 days hydration, there was a significant peak corresponding to $CaZn_2(OH)_6.2H_2O$ but still no Friedel's salt and after 180 days hydration the evidence for calcium zincate had all but disappeared which mirrored the effects seen in this system with the $SnCl_2$ and $SnCl_4$ salts. It was suggested for these systems that the disappearance of the non-standard phase was due to the lack of calcium hydroxide present which meant that the new phase was being consumed for the pozzolanic reaction and it was possible that something similar had occurred in this system. It would seem that, although the zinc salt caused greater retardation then either of the tin salts, the chemistry which was occurring was closely related in all cases.

The effects of zinc salts of all types have been relatively extensively reported in the literature and there appears to be agreement that the addition of zinc retards the set and hydration of the cement and the reason for this retardation is also a source of agreement. It has been suggested that zinc retards the hydration and setting of cement by precipitating an amorphous layer of zinc hydroxide at the surface of the anhydrous clinker grains. This zinc hydroxide then reacts with the calcium hydroxide to form the calcium zincate.[41,49] This phenomenon was described in more detail using lead as the metal. The hydroxide precipitates are deposited mainly as a colloidal gelatinous form and this colloidal membrane formation is typical of precipitation processes which occur between two solutions at high degrees of supersaturation. Therefore, the retarding capacity includes any kind of metal cations which give highly insoluble hydroxy compounds in alkaline solution (copper, zinc and tin). As the solubilities of these compounds are very low it should not take high concentrations to cause significant effects – only enough to give a coherent coating around the grains.[49] Thomas et al[49] pointed out that as hydration is not completely stopped by the precipitation there must be some diffusional processes through the coating which remained active to supply water to the cement reactants. The permeability of the coating will depend on both its colloidal structure and chemical composition so that any change could cause it to be less effective after the initial retardation. They suggest that the conversion of zinc hydroxide to calcium zincate could be an example of such a process. This would correlate with the finding from the x-ray diffraction results in which there was substantial retardation at early hydration ages (as also seen in the calorimetry results) but, at later ages the hydration appears to proceed and, alongside this, evidence for calcium zincate is identified. This process also gives conviction to the osmotic membrane model for cement hydration mentioned in Chapter 2.[11-13]

Ivey et al[79] have also shown zinc to retard OPC and OPC/PFA mixtures by locating a layer of amorphous gel on particles. This occurs alongside the formation of ettringite which results in a drastic increase in pore volume and the proportion of pores with large radii. Retarding species form insoluble salts and tend to precipitate as dense coatings on hydrating phases which results in a loss of permeability and, therefore, forms a diffusion barrier to water which slows the rate of hydration. The x-ray diffraction results for the PFA cement also agree with this finding as there was evidence for the formation of ettringite which was absent in the 9:1 BFS:OPC system. However, the ettringite disappeared as the formation of calcium zincate appeared. This formation of ettringite was also apparent with both the tin salts. If there was ettringite present in the neat cement then it was apparent at longer hydration times with the tin additions and, especially at the 1% loadings, there was formation in the tin-containing systems even if there was none in the neat cements.

5.2.4 Summary

The results obtained from the calorimetry investigation show that there was substantial retardation of set and early hydration with the zinc additions, and clear retardation, but at a lower magnitude, with the tin additions. The x-ray diffraction results of the zinc systems confirmed the early retardation and then showed that some hydration began to occur at later ages. This correlated with the reports in the literature which suggested that zinc hydroxide was precipitated on the hydrating grains and formed a barrier to diffusion. The zinc hydroxide then reacted with the calcium hydroxide to form calcium zincate which enabled hydration to continue. The reaction with calcium hydroxide would also account for the lack of the latter phase in the cements containing the metal salts.

5.2.5 Microstructural Investigation

The microstructures that developed in the four cement systems used for this project were significantly different even in the neat cements. Plates 1 and 2 (in section 4.5) show a typical Portland cement with the large anhydrous particles visible after three days hydration but evidence of hydration rims and much less anhydrous material after 180 days hydration. These micrographs illustrated the hydration of this type of cement and were similar to that which has been reported in the literature.[1,66,80] Diamond and Bonen[81] supply a description of the different aspects of the microstructure. A similar micrograph to that seen in Plate 3 was described as having two distinct sections to it – the large anhydrous particles (termed 'phenograins') embedded in a porous matrix of finer material (groundmass). It was also observed that the phenograins consisted of more than one class of material and could be cement particles which have remained unhydrated or which have partly or completely hydrated in situ or agglomerates of calcium hydroxide. The groundmass was distinguished from the phenograins by the individual particles of which it is constructed being smaller in size and by the fact that these particles were embedded in interconnected pore space of approximately the same size as the groundmass particles. The solid part of the ground mass was identified as C-S-H, calcium hydroxide and smaller amounts of ettringite and other phases.

Another way of describing the products of hydrating cement is inner and outer product (IP and OP respectively) and these terms that are more widely used. Definitions[1] of these terms are not particularly conclusive. Inner product is the in situ hydration product which has formed during hydration. That is, as hydration proceeds the clinker phases are replaced by hydration products which have formed in situ and which are initially observed as hydration rims around the unhydrated material. This is progressively replaced until no significant quantity remains. The term inner product can be criticised because the apparent outlines of the cement grains may lie within the true ones and, therefore, 'late product' may be a better term. The outer product relates to the matrix in which all other regions appear to be embedded. However, again Taylor[1] does not think this term satisfactory and suggests 'undesignated product' as being preferable. It can be seen that there is not agreement as to the terms to be used. What is clear is that the products these terms are attempting to describe are common to all and can be clearly seen in the micrographs shown in Chapter 4.

The blast furnace slag cements have microstructures dominated by the angular slag particles, interspersed with areas of hydrating Portland cement and a very porous matrix (Plates 3-5). The microstructures of the two slag cements were similar as the amount of slag present in the two systems was not vastly different (75% and 90%) but the slag grains in the 9:1 BFS:OPC cement were larger and appeared to have hydrated less than those in the corresponding 3:1 BFS:OPC cement after 90 days hydration. Previously reported micrographs were not common but the consensus was that the slag grains were large and angular[1] and calcium hydroxide grows around the slag grains[66]. This phenomenon was observed clearly in both the systems after 90 days hydration. In contrast to the angular slag grains observed, the microstructure of the pulverised fuel ash cement was dominated by spherical particles, again interspersed with Portland cement product and with a very porous matrix. Published micrographs of fly ash cements reported very similar results to those observed in this study.[22,66,67,82] The hollow spheres which are visible are known as cenospheres and the smaller spheres occurring inside larger ones – plenospheres.[1] EDS traces (Figures 1 and 2) from these two composite cements also help to illustrate the differences between the slag and the fly ash. The slag grain shows a composition of calcium, silicon and aluminium with some lesser amounts of magnesium and sulphur. This was as expected from the chemical analysis shown in Chapter 3.

The pulverised fly ash particle was significantly different from this in that there was very little calcium, less silicon and aluminium, but significant amounts of potassium and iron. The EDS reported by Xu et al[82] shows a similar trace with respect to the aluminium and silicon although with less potassium. However, that reported by Tenoutasse et al[67] shows a similar trace for the elements involved. The differences can be expected because the composition of fly ash varies significantly between supplies. Again, the neat cements confirm what has been reported in the literature and, therefore, serve as a good comparison for the metal salt containing systems.

Microstructural evidence of cements containing metal salts has not been widely reported and it has, therefore, been difficult to compare the results found in this project with any others. The overall microstructure of all the cement systems containing either $ZnCl_2$ (at 5% and 1% loadings) or $SnCl_2$ (at 5% only) were apparently unchanged. That is, the angular slag grains and spherical cenospheres still dominated the slag cements and pulverised fuel ash cements, respectively, and the OPC consisted of larger anhydrous grains within a matrix of finer material. However, there were differences. In the OPC cement, the tin-containing system showed bright areas within the matrix of the cement which were apparent at both early and later hydration times. With EDS analysis it became clear that the bright areas were a calcium-containing phase which illustrated the presence of tin (Figure 4.5.3). It was also apparent that there was chlorine present which was not the case with the neat cement systems.

The 3:1 and 9:1 BFS:OPC systems (Plates 9-11) exhibited bright areas which were different to those observed in the Portland cement in that they were 'slotted in' between the slag grains. In the 3:1 BFS:OPC system these areas appeared to be of a similar shape to the cement areas seen in the neat cement system. However, in the 90% slag cement they were very angular and a similar shape to the slag grains. The EDS analysis of the bright area (Figure 4.5.4) shows similar results to that of the OPC system in that there was a significant calcium peak with substantially less silicon and there was also significant evidence of tin. The relatively small amount of aluminium detected suggested that the tin was not connected with the slag grain but was incorporated into the cement phase. This was confirmed with EDS results of analysis performed on a slag grain from a tin-containing system (Figure 4.5.5) which revealed a composition identical to that from the neat cement. Another interesting feature from the tin-containing system was the identification of chlorine which, as with the OPC system, was not in evidence in the neat cement.

The pulverised fuel ash system produced similar results to the slag cements in that there were bright areas between the PFA particles which were tin and chlorine containing and the particles themselves were unchanged when compared to the corresponding neat cement. It was also interesting to note that as the hydration proceeded the tin-containing areas helped to connect the spherical particles which, in turn, helped to reduce the porosity of the matrix. This would be a positive result for the incorporation of a waste because, the less porous the microstructure, the better the retaining powers of the material. The composite cements appeared to behave in a similar way in that the tin was deposited between the particles and was never associated with the mineral additions. The EDS analyses showed that the tin was associated with a very strong calcium peak which would correlate with the identification of calcium hydroxo stannate ($CaSn(OH)_6$) from the x-ray diffraction studies. The presence of a chlorine peak in all the cements when tin was identified also gives credence to the presence of Friedel's salt ($Ca_3Al_2O_6.CaCl_2.10H_2O$) which would also help to account for the large calcium peak.

The zinc-containing systems exhibited similar features to the tin systems in that there were particles between the slag or ash grains which were not the same as those of the cement phases observed in the neat cements. These were not as bright as the tin-containing areas but it transpired that they contained the zinc (Figure 4.5.8) along with significant amounts of calcium, silicon, aluminium and chlorine (9:1 BFS:OPC cement). EDS analysis of the lighter area of these features showed what appeared to be an unhydrated ferrite phase. In contrast to this, the PFA cement gave similar results for the zinc containing area but the lighter area appeared to be a calcium silicate phase (Figures 4.5.10 & 4.5.11). As with the tin-containing system, the large calcium peak identified alongside the zinc suggested that the calcium zincate phase (as identified by x-ray diffraction) was formed and, also, the chlorine peak again correlates with the presence of Friedel's salt in systems containing the metal salt. The difference in the lighter areas between the slag and ash cements could be due to the substantial retardation of the system when zinc is added (as seen in the calorimetry results) as this could result in the long term hydration being substantially retarded which would mean the ferrite phase had not hydrated. This would not necessarily be the case with the PFA because the retardation was not as great in this system and, also, there was more Portland cement present. However, the microstructural study into the zinc-containing systems was limited because of the difficulty of sample preparation which means that there was not enough information to draw definite conclusions. In summary, the EDS results confirm the findings from the x-ray diffraction study for the identification of the non-standard phases formed on addition of tin and zinc chlorides. Also, it was clear that the metal was incorporated into the cement hydrates present in the systems.

CHAPTER SIX

6. CONCLUSIONS

6.1 Neat Cement Hydration

The hydration behaviour of the neat cement systems differed from one another. The heat of hydration was less for the composite cement systems than for the Portland cement, which was expected. This is an important property when considering storage of wastes because it is important to minimise the heat output of the cement so as to reduce the risk of cracking which, if it occurred, would increase the rate of leaching of the waste from the cement monolith. However, for the purposes of scientific study this meant that it was not possible to correlate the results of one type of cement directly with another.

The x-ray diffraction, scanning electron microscopy and EDS results confirmed literature results on the hydration phases formed and the microstructure of Portland and composite cements. This was useful because it meant that any changes noted with the addition of metal salts were due to the salt and not to the cement itself.

6.2 The Effect of Zinc Chloride Additions

Zinc chloride, even at 0.1% loading, retarded the set of all cement systems although the extent to which this occurred depended on which cement system was being used. The longer term hydration was also retarded and this was indicated from the x-ray diffraction results in that there were substantial amounts of gehlenite present even after 28 days hydration. The retardation can be linked with the formation of calcium zincate ($CaZn_2(OH)_6.2H_2O$) which was identified by x-ray diffraction. The zinc may retard the hydration and setting of cement by precipitation of an amorphous layer of zinc hydroxide on the hydrating cement grains. The zinc hydroxide then reacts with calcium hydroxide to form calcium zincate. This would also account for the absence of any calcium hydroxide in the zinc-containing systems (although there was relatively little in the neat composite cements). Evidence for the formation of Friedel's salt was also confirmed by x-ray diffraction and it was postulated that both Friedel's salt and the calcium zincate were formed from the tricalcium aluminate and calcium hydroxide phases of the hydrating cement. From electron microscopy and EDS studies it was found that the zinc was dispersed in the cement phases of the composite cements as opposed to any of the mineral addition sites. Also, whenever zinc was detected in the microstructure there was always evidence for chlorine which was not the case in areas with no zinc content. This correlates well with the x-ray diffraction results which show the formation of Friedel's salt alongside the calcium zincate. This also led to an equation being postulated for the formation of these non-standard hydration products:

$$\begin{array}{c} 2ZnCl_2 + 2Ca_3Al_2O_6 + 3Ca(OH)_2 + 22\ H_2O \\ \downarrow \\ 2Ca_3Al_2O_6.CaCl_2.10\ H_2O + CaZn_2(OH)_6.2H_2O \\ \text{(Friedel's Salt)} \qquad\qquad \text{(Phase Z)} \end{array} \qquad \text{Equation 6.1}$$

Zinc nitrate also had a retarding effect on the set of the cement but the effect was not as great as with zinc chloride. This indicates that the retardation behaviour was affected by the anion as well as the cation, as zinc nitrate would form calcium zincate in the same way as the chloride. The effects of the anion on the set and hydration of the cement merit further investigation which was not possible during this project due to time constraints.

6.3 The Effect of Tin Chloride Additions

Tin(II) chloride showed an overall effect of retarding the set of the cement although the effect was much less than that of zinc chloride. It was not obvious whether the long term hydration was affected but it would appear from the limited microscopy studies and the x-ray diffraction investigation that it wasn't. As with the zinc chloride, the tin chloride formed an insoluble hydroxy compound which resulted in the subsequent formation of calcium hydroxo stannate – an analogous compound to calcium zincate. The compound was identified using x-ray diffraction and differential thermal analysis and, therefore, it would seem logical that the tin would cause retardation by the same mechanism as the zinc salt. Again, an equation was suggested to explain this formation of Friedel's salt and calcium hydroxo stannate:

$$\begin{array}{c} SnCl_4 + 2Ca_3Al_2O_6 + 3Ca(OH)_2 + 20\ H_2O \\ \downarrow \\ 2Ca_3Al_2O_6.CaCl_2.10\ H_2O + CaSn(OH)_6 \\ \text{(Friedel's Salt)} \qquad\qquad \text{(Phase X)} \end{array} \qquad \text{Equation 6.2}$$

The addition of tin(IV) resulted in a slight acceleration of set in all cements even though it might be expected that its effect would be the same as that of the tin(II) due to its oxidation to tin(IV) in the mix water. However, one reason for the difference is the increase in temperature of the paste with the addition of $SnCl_4$. It was shown, by running the calorimeter at 35°C and 21°C, that increasing the temperature at which the cements hydrate results in an acceleration of the set of the cement. Therefore, it would follow that, if the paste temperature increased because of the addition of a salt, there would be some acceleration of set. It was illustrated that $CaSn(OH)_6$ and Friedel's salt were formed with addition of this salt which clarifies the results obtained from the addition of $SnCl_2$.

6.4 The Effects of Aluminium Chloride and Arsenic Trioxide Additions

The only results presented from these systems were obtained with conduction calorimetry because of the need to streamline the part of the project concerned with long term hydration studies. The aluminium had a mixed effect depending on the cement into which it had been incorporated. In the slag cements the aluminium appeared to retard the set at 0.1% loading and kill it at the 1% loading. This was probably due to the excessive amount of heat generated as the loading increased when the slurry was mixed with the cement powders which caused the water to volatilise and, consequently, leave a dry paste. In OPC, the effect was increased retardation with increasing salt loading and in the PFA cement, the aluminium caused an acceleration of set. Without other techniques to gain more information it is difficult to comment on these observed effects. However, one explanation could be that the amount of aluminium present in the cement powders could contribute to the effect. That is, if the aluminium causes the retardation effect then it would be expected that the greatest effect would be seen with the slag cements as the raw material contained a substantial amount of aluminium oxide. It would be prudent to continue this part of the study along the same route as the zinc and tin salts so as to be able to better understand the effects it appears to be exhibiting.

The arsenic oxide brought about the least effect on any of the cement systems investigated. From the calorimetry results it was found that As_2O_3 had virtually no effect on the setting behaviour or on the amount of heat evolved in any of the cements at any loading. Again, it would be imprudent to draw conclusions based on the results of just one technique, but it is worth further investigation because, as it appears that the arsenic had very little effect, the prospects for incorporation in cements seem to be good.

6.5 Summary

Overall, this project has illustrated that it is not easy to predict the effects of different metal salts on different composite cements as there are so many variables. However, there were some interesting trends and, when the results from the techniques used for this project are combined with other techniques, such as leach tests, the combined information provides a good indication of what may be expected. However, using only the results obtained from this project, it is possible to suggest which cement systems were the best for the incorporation of the zinc and tin chlorides. As the zinc chloride retarded the set of the cement so greatly, it is this factor which would govern a decision. Therefore, the 100% OPC cement would be the best for the incorporation of the zinc chloride as it was the least affected by the retardation and reached a set within seven days. However, the aim of the project was to incorporate the salts into composite cements, so the next best option would be the 3:1 PFA:OPC cement as this was not as greatly affected by the retardation and, from the SEM results, both the fuel ash and the slag cements behaved in a similar way at the longer hydration times.

The tin chloride additions cause significantly less retardation than the zinc chloride so the issue of the set was not a problem. Therefore, it was important to consider the amount of heat generated by the systems as this was one of the reasons for incorporating the salts in composite cements due to their ability to decrease the heat of hydration. With regards to the microstructure, any of the composite cements would have been satisfactory as they all behaved in a very similar way. That is, the calcium hydroxo stannate was incorporated into the cement phase and not the mineral addition and, also, the effect of the tin-containing phase was to decrease the amount of porosity in the matrix. However, this was most apparent in the 3:1 PFA:OPC system, which was also the system that set within a reasonable time scale and produced the least amount of heat. Therefore, from these criteria, the best cement for incorporation of either of the tin chloride salts would be the 3:1 PFA:OPC cement. It is clear that, from the results obtained during this project, the pulverised fuel ash cement would appear to be the most suitable composite cement system for the purposes of incorporating zinc chloride, tin(II) and tin(IV) chloride.

CHAPTER SEVEN

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