

Influence of Cement Composition and Curing Regimes on the Susceptibility of Heat-Cured Cementitious Systems to Delayed Ettringite Formation

by

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Certificate of Original Authorship

I, *Yogesh Kumar Ramu* declare that this thesis, is submitted in fulfilment of the requirements for the award of Doctor of Philosophy in the School of Civil and Environmental Engineering, Faculty of Engineering and Information Technology at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise reference or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

This document has not been submitted for qualifications at any other academic institution.

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This thesis is dedicated to my family

*"Though things diverse from divers sages' lips we learn,
'Tis wisdom's part in each the true thing to discern "*

Thiruvalluvar

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Abstract

Delayed ettringite formation (DEF) occurs in precast concrete elements and mass concrete structures where curing temperature and/or high heat of hydration delays the formation of ettringite; which instead forms at the later stage of hydration. The late crystallisation of ettringite may cause localised cracks, as it occurs within the confined spaces of the hardened concrete matrix. The presence of such cracks may reduce the service life of the structure. Previous research indicates that curing concrete above 70°C, cement sulphate, alkali, and aluminate content as vital factors contributing to deleterious DEF. However, linking deterioration of concrete with a mere presence of DEF needs further investigation.

In this research, two Australian general-purpose cements with different alumina contents have been used to prepare a matrix of cementitious systems with varying sulphate and alkali levels. The effect of different heat curing regimes on these cementitious systems had been investigated. Mortar prisms length and mass changes had been recorded for 600 days. Various characterisation techniques such as X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), pore solution analysis, scanning electron microscopy (SEM) image and elemental analysis were used to understand the phase development of hydration products, microstructure and ettringite deposition location. Electrochemical impedance spectroscopy (EIS) had been used to study implications of heat curing in microstructure and its relevance to DEF.

For systems using the as received GP cements, with no elevation of the sulphate and alkali contents, no expansion was observed in heat-cured mortars, although DEF was noted in TGA and XRD analysis of parallel cured cement pastes. Similar results were obtained for the sulphate or alkali modified cements. Significant expansion and mass gain, however,

was observed in cementitious systems containing 4% SO_3 and 1% $\text{Na}_2\text{O}_{\text{eq}}$ when cured at 80-90°C for 8-12 hours. The XRD analysis of the parallel cured cement pastes reveal that the quantity of DEF was higher in expanding mortars than the non-expansive ones. Further, localised DEF was observed in the microstructure in the interfacial transition zone (ITZ). The resistivity for expanding mortars was observed to be significantly lower than the non-expanding mortars, indicating microstructural changes associated with the precipitation of DEF resulting in increased number conduction pathways.

The efficacy of fly ash (FA) in mitigating DEF was also tested by incorporating 25% FA in the mortar mixes which gave maximum expansion; mortars containing 4% SO_3 and 1% $\text{Na}_2\text{O}_{\text{eq}}$. Results demonstrated that FA was effective in mitigating expansive DEF.

The outcomes of this investigation suggest that precast concretes manufactured using Australian GP cements cured below 80°C are unlikely to be subject to DEF. Concrete mixes that contain GP cements and FA are even less likely to be subject to expansive DEF.

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List of Abbreviations

ACI	American Concrete Institute
AFm	calcium aluminate monosulphate phases ($\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-mono}$)
AFt	calcium aluminate trisulphate phases ($\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-tri}$)
AS	Australian Standards
ASR	alkali-silica Reaction
ASTM	American Society for Testing and Materials
ATIC- SP	Australian Technical Infrastructure Committee- standard procedure
BSE	back scattered electron
C-A-S-H	calcium-alumino-silicate-hydrate
CCFA	class C fly ash
CFFA	class F fly ash
CH	calcium hydroxide or portlandite
C-S-H	calcium-silicate-hydrate
DEF	delayed ettringite formation
EDS/EDX	energy-dispersive X-ray spectroscopy
EEF	early ettringite formation
EIS	electrochemical impedance spectroscopy
Et	ettringite
FA	fly ash
FTIR	Fourier transform infrared spectroscopy
Hc	hem carbonate
Hg	hydrogarnet
ICP-OES	inductively coupled plasma - optical emission spectroscopy
IP	inner product (C-S-H)
IPA	isopropanol
ITZ	Interfacial Transition Zone
Mc	monocarbonate
Ms	monosulphate
NDT	Non-Destructive Testing
OP	outer product (C-S-H)

qXRD	quantitative X-Ray diffraction
Qz	quartz
RH	relative humidity
SEF	secondary ettringite formation
SEM	scanned electron microscopy
(SO₃/Al₂O₃)_m	cement molar ratio of SO ₃ to Al ₂ O ₃
TGA	thermogravimetric analysis
w/b	water to binder ratio by mass
w/c	water to cement ratio by mass
XRD	X-ray diffraction
XRF	X-ray fluorescence

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Chapter 1 Introduction

Concrete is the most widely used construction material in the world (Aïtcin 2000; Megid & Khayat 2018) due to its low cost and versatility (Kumar Mehta 1999). The versatility of concrete is due to in-situ forming, which requires relatively low-skilled labour (Bhattacharjee 2010). However, in-situ concreting is not always the most productive means of construction. Particularly in infrastructure projects such as the construction of bridges, railroads and tunnels, in-situ concreting can impede the existing traffic flow and hinder project completion time (Tomek 2017). These limitations can be overcome by manufacturing large structural ‘precast concrete’ elements such as girders, sleepers or wall linings at an offsite location and rapidly assembling them on-site. The first use of precast concrete dates back to 1897; the methods and technologies to produce precast concrete in an offsite manufacturing units have improved over subsequent decades (Elliot & Hamid 2017).

Reducing the production cycle time is an economic necessity in precast concrete manufacturing units (Wang et al. 2019). Production cycle times can be reduced by attaining sufficient concrete strength to allow the release of prestress in one-day (Day 1992; EL-Zein 1973). To accelerate strength attainment, precast concrete manufacturers employ different methods such as steam curing, autoclaving, microwave heating and electrical heating of reinforcement (Ramezani pour, Khazali & Vosoughi 2013). Among these, the most commonly practised method is steam curing at atmospheric pressure (Erdem, Turanli & Erdogan 2003; Wang, Li & Zhang 2014). However, the durability of steam-cured concretes is often questioned due to the possible occurrence of delayed ettringite formation (DEF).

DEF is a later stage ettringite precipitation which occurs in steam-cured precast concrete (Heinz, Ludwig & Nasr 1982) and rarely in mass cast-in-place concrete elements (Divet & Pavoine 2002). High steam curing temperatures (above 70°C) in precast concrete production inhibit the formation of or decompose the primary ettringite (H. F W Taylor, Famy & Scrivener 2001). Ettringite may precipitate in confined spaces in the hardened concrete and potentially cause localised cracks (Shao et al. 1997), thereby reducing the service life of the precast concrete structure.

This problem was first recognised in European precast railway sleepers in the early 1980s. The premature deterioration of prefabricated concrete structures due to DEF has been subsequently reported in many countries, including the USA, Australia and South Africa (Fu & Beaudoin 1996). However, the excellent laboratory work on the recrystallisation of calcium sulphotoaluminate hydrate (ettringite) with varying cement sulphate in concrete was studied by Lerch (1945) almost four decades earlier than the first reported field case. The occurrence of on-field DEF cases after 1980 may be attributed to the radical changes in modern-day cement composition, primarily those associated with sulphate content (Hime 1996b).

In Australia, DEF was first reported by Shayan & Quick in 1992 after the investigation of a set of deteriorated precast railway sleepers. Although, the primary deterioration mechanism was not DEF, DEF nevertheless was reported to contribute to durability loss along with alkali-silica reaction (ASR). Despite Australia being one of the earlier countries to report an infield DEF case, no laboratory work has been conducted to understand the potential for Australian cements to cause DEF. High sulphate (above 4%) and alkali (about 1%) contents in cement are often quoted in literature as parameters that are likely to cause DEF (Collepari 2003; Day 1992). To reduce the risk of DEF, Australian standard AS 3972-2010 restricts overall cement sulphate to 3.5% and ATIC

SP-43 specifies that cement alkali levels not exceed 0.60%. However, contemporary experimental evidence is needed to understand the level of DEF risk when steam-cured precast concrete is made with commercially available Australian cements. Understanding cements with different aluminate, sulphate and alkali levels with respect to DEF is also essential, as the use of imported clinkers in Australian cement production increases by 7%/year (and Australian clinker production reduces by 3%/year) (*Cement Industry Federation Report 2017*).

To add more complexity, steam-curing specifications issued, by various road authorities in the Australian States, lack clarity. For instance, the Queensland Department of Transport and Main Roads concrete specification (MRTS 70) limits the concrete core temperature to 75°C, while allowing steam curing temperatures up to 70°C. It is not practically feasible to restrain a core concrete temperature below 75°C with 70°C steam curing, especially in massive concrete elements. The multiplicity of recommendations across the Australian jurisdictions creates uncertainty regarding the durability of precast concrete due to the potential susceptibility of DEF when the concrete temperature exceeds 75°C. This research aims to investigate different cementitious systems by exposing them to various heat curing regimes to understand the possible occurrence of deleterious DEF and its consequences. Further, the role of fly ash (FA) in mitigating deleterious DEF is also investigated.

1.1 Research objectives

The main aim of this research project is to investigate the DEF susceptibility of general-purpose cement systems that are subjected to different heat-curing regimes by examining physical, microchemical and microstructural properties.

The three principal objectives of this research work are to investigate the role of:

1. cement composition on the occurrence of DEF,
2. heat-curing regime on the occurrence of DEF, and
3. fly ash in mitigating deleterious DEF in cementitious systems.

1.2 Thesis outline

This thesis consists of 10 chapters, including the current introduction chapter. A brief outline of the chapters is as follows.

The background of ettringite mineral and its stability conditions, factors influencing DEF, DEF mechanism and consequences are presented in Chapter 2. Chapter 3 provides details of the important physical properties and chemical compositions of materials used in this research, particularly the composition of cement and fly ash. In Chapter 4, the experimental phases scheduled to study the identified DEF factors are provided along with detailed experimental methods. Chapter 5 describes the influence of cement alumina, sulphate, alkali content, fly ash and curing temperature in early age hydration characteristics of various cementitious systems. In Chapter 6, results from the effect of different heat curing regimes on two Australian commercial GP cement systems on DEF are presented. In Chapter 7, cements discussed in Chapter 6 are chemically modified and subjected to different heat curing regimes. The results of possible DEF occurrence and its impacts are presented. In selected mixes from Chapter 7, the effect of increasing the heat curing duration and reduction in pre-cure time on DEF is studied, and the results are presented in Chapter 8. In Chapter 9, the results of mitigating DEF by incorporating fly ash are discussed. Chapter 10 provides a summary and the conclusions of this study and recommendations for future studies.

Chapter 2 Literature review

This literature review focuses on studying ettringite as a mineral, DEF problems in precast concrete, field cases describes DEF and steam curing codes of practice followed by precast concrete producers.

2.1 Ettringite – as a mineral

Ettringite is a calcium sulphoaluminate hydrate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$), discovered as a naturally occurring, colourless mineral by Lehmann (1874) in the village Ettringen, Germany. The first captured X-ray photograph of ettringite (Bannister, Hey.M.H & Bernal.J.D 1935), showing a regular arrangement of vertical and horizontal spots is given in Figure 2.1.

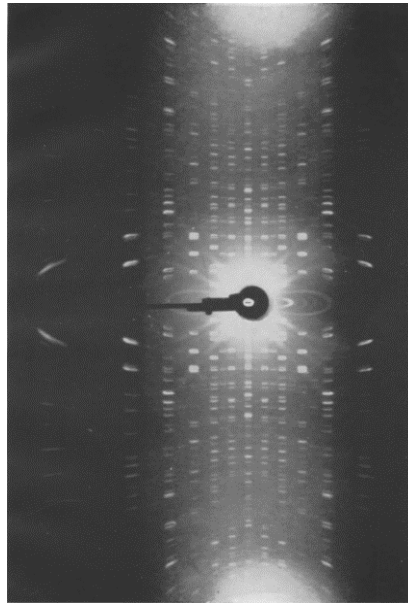


Figure 2.1 X-Ray photograph of Ettringite (Bannister, Hey.M.H & Bernal.J.D 1935)

The chains of Ca^{2+} and $\text{Al}[(\text{OH})_6]^{3-}$ form the basis of the ettringite structure while $[\text{SO}_4]^{2-}$ and H_2O molecules are present in between these chains, as represented in Figure 2.2.a. (Moore & Taylor 1970). $[\text{Ca}_6\text{Al}_2(\text{OH})_{12}.24\text{H}_2\text{O}]^{6+}$ forms columns of ettringite (represented by circles below). Inside these columns is $[3(\text{SO})_4.2\text{H}_2\text{O}]^{6-}$, which forms

channels throughout the ettringite structure (Figure 2.2.b) (Baquerizo, Matschei & Scrivener 2016; Cody et al. 2004).

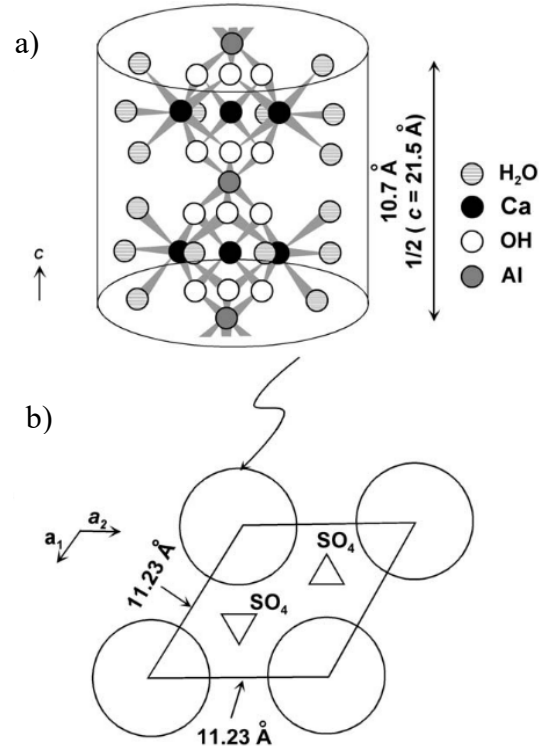


Figure 2.2 a) Simplified crystal structure of ettringite (Cody et al. 2004) based on Moore & Taylor (1970) b) View on a-b plane

The ettringite structure may undergo modifications when exposed to certain conditions, and this may alter the stability of both ettringite and the material in which it is contained. The stability of ettringite in various situations is discussed in the following section.

2.2 Stability of ettringite

The stability of ettringite has been widely researched as it has practical implications for the properties of materials in which it may be found. Since the naturally occurring ettringite mineral is always impure (Clark et al. 2008), for laboratory studies researchers usually used synthesised ettringite. The various ways to synthesise ettringite in the laboratory have been described in detail elsewhere (Shimada & Young 2004; Terai et al. 2007). As the ettringite structure contains between 26 and 32 water molecules, structural

modification usually relies on altering the precise number of water molecules. The stability of ettringite is affected by temperature, pressure, and alkalinity (Glasser 2002). Each of these factors is briefly discussed below.

2.2.1 Temperature

At atmospheric pressure and ordinary humidity, ettringite may start to lose water molecules at temperatures as low as 50°C (Jiménez & Prieto 2015) to 53°C (Deb et al. 2003). Around 60°C, ettringite loses three water molecules from its structure (Shimada & Young 2001). As a consequence, X-ray diffraction (XRD) peak broadening (Ghorab & Kishar 1985) and disorderliness in Raman spectrum sulphate band (S-O) are observed (Deb et al. 2003). However, the crystallinity of ettringite is retained. In the temperature range of 60-70°C, ettringite crystallinity may decrease with the removal of up to 12 water molecules (Shimada & Young 2001; Zhou & F.P. Glasser 2001). The core structure of ettringite is affected even after losing 10-13 water molecules and remains stable as meta-ettringite (Baquerizo, Matschei & Scrivener 2016; Zhou & F.P. Glasser 2001). Above 70°C, ettringite loses approximately 20 water molecules, becomes completely X-ray amorphous and suffers variation to the core structure (Shimada & Young 2001). Complete decomposition of ettringite due to dehydration occurs in a temperature range of 111°C (Satava & Veprek 1975) to 120°C (Taylor 1997b). Monosulphate phases, bassanite (Hall et al. 1996) and gypsum (Zhou & F.P. Glasser 2001) form as a result of this decomposition.

2.2.2 Pressure

The possibility of destabilising ettringite without dehydration was studied by Clark et al. (2008). Ettringite started to lose crystallinity from 1.2 GPa. The complete disappearance

of ettringite XRD peak was observed at 3.7 GPa. The amorphisation of ettringite due to applied pressure is reversible with a return to atmospheric pressure.

2.2.3 Alkalinity

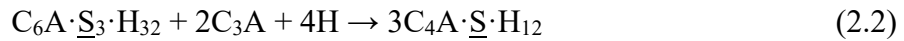
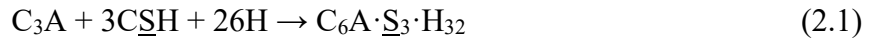
Increase in pH (about 11.5 to 12.5) causes defects in the crystal structure of ettringite by removing aluminium from the ettringite columns (shown in Figure 2.2) and results in about ten times shorter column length (Hampson & Bailey 1982). Further, it also changes the typical morphology of ettringite, i.e., hexagonal prismatic needles to shorter rounded shape crystal (Hampson & Bailey 1983). Ettringite was completely unstable above pH 13.0 ettringite (Hewlett & Liska 2019). Ettringite decomposition is caused not only by increasing pH; acidification to below pH 10.7 was found to decompose ettringite to gypsum and the monosulphate phase (Gabrisová, Havlica & Sahu 1991). Hence, ettringite is only stable in crystalline form in a pH range of 10.7 to 11.5 (Ghorab & Kishar 1985; Hampson & Bailey 1983; Havlica & Sahu 1992). Interestingly, another aluminium trisulphate phase known as thaumasite, which is similar to ettringite, is stable at high pH conditions around 13.0 (Jallad, Santhanam & Cohen 2003), demonstrating the significant impact of small differences in the crystal structure on properties of hydrates and minerals.

2.2.4 Inference

Based on the above information, ettringite appears to be a fragile mineral that is very sensitive to the changes in temperature, pH, and pressure. The properties of materials that contain ettringite may also be affected as a result. The interest of this project lies in understanding the impact of changes occurring in ettringite on cementitious systems at different times. Section 2.3 discusses ettringite as a hydrate in the cementitious system.

2.3 Ettringite – as a hydrate in the cementitious system

Ettringite is one among the various cement hydration products, observed as needle-like hexagonal prismatic crystals. The properties of ettringite may not be the same as the synthetic ettringite discussed in Section 2.2 Stability of ettringite due to the heterogeneous nature of the cementitious system. Hydration of C_3A gives two calcium aluminate trisulphate (Al_2O_3 - Fe_2O_3 -tri; AF_t) hydrate phases such as ettringite and thaumasite (Scrivener, Snellings & Lothenbach 2016). Thaumasite precipitation is favoured only in a low-temperature environment (below $15^\circ C$) (Bensted 2003), so the major and most common AF_t phase in the cementitious system is ettringite (Taylor 1997b). Ettringite precipitates upon the addition of water to cement, as a result of tricalcium aluminate (C_3A) hydration in the presence of gypsum. Ettringite precipitation that occurs before concrete loses its plasticity is termed early ettringite formation (EEF). The EEF reaction is shown here in equation 2.1.



EEF occurs homogeneously throughout the concrete and helps to regulate the setting time (Glasser 1996). Further, it provides shrinkage compensation and early-age tensile strength to the concrete (*Portland Cement Association 2001*).

Ettringite precipitation continues to occur as long as sulphates are available in the pore solution. Sulphate depletion typically occurs after 24 hours of hydration and the ettringite formed goes on to react with aluminates, giving calcium aluminate monosulphate phases (Al_2O_3 - Fe_2O_3 -mono; AF_m) as given in equation 2.2 and as shown in Figure 2.3. Hence, unlike the synthetic ettringite discussed in section 2.2 Stability of ettringite, ettringite in the highly heterogeneous cementitious system does not require an external force for

destabilisation. However, not all of the ettringite disintegrates, and some remains in the cementitious system.

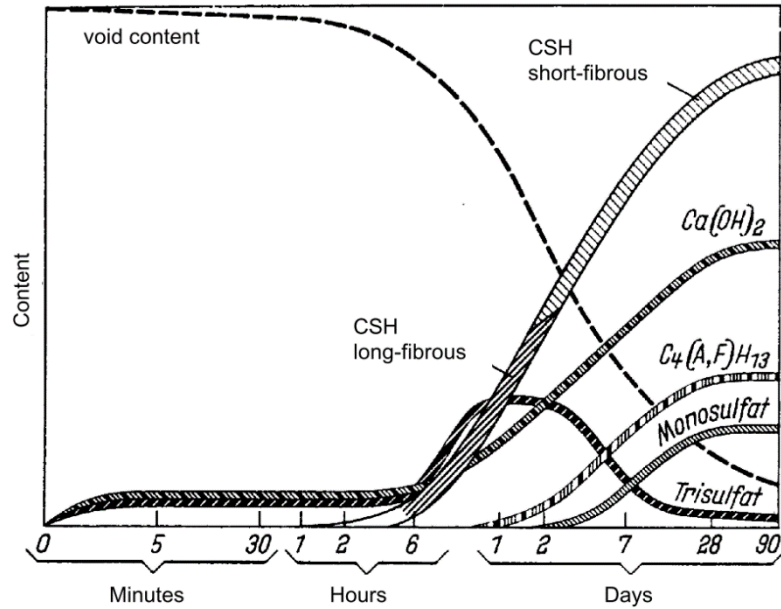


Figure 2.3 Schematic representation of the formation of different cement hydrates (Locher, FW et al. 1976)

2.4 Delayed Ettringite Formation

The beneficial ettringite precipitation that occurs under normal hydration conditions (Section 2.3 Ettringite – as a hydrate in the cementitious system) can turn deleterious depending on the state of concrete when crystallisation occurs. Ettringite crystallisation occurring after the concrete has attained rigidity, i.e., during the service life, is heterogeneous and expansive in nature. As such, it may cause cracks when crystallisation occurs in a confined environment, potentially leading to durability issues (Colleparidi 2003). Ettringite precipitation during later age hydration in concrete is termed as later age ettringite formation. Later age ettringite precipitation is broadly classified into two categories, secondary ettringite formation (SEF) and delayed ettringite formation (DEF).

Severe drying in concrete (in-situ or precast) can result in decomposition of primary ettringite into gypsum and monosulphates. Upon wetting, recrystallisation of ettringite

might occur, and this is termed SEF (Fu & Beaudoin 1996). DEF, on the other hand, occurs due to the decomposition or inhibition of primary ettringite in monosulphates when concrete is subjected to steam curing at elevated temperature (Mehta 1972) and crystallises back into hardened concrete (Collepardi 2003). SEF and DEF are often used interchangeably in the literature, for instance in the literature analysis by Day (1992), and occasionally pseudo-differentiation is provided, for instance in an opinion article by Hime (1996). Hence caution must be used when interpreting the literature. The differentiation of SEF and DEF provided by Fu & Beaudoin (1996) appears to be logical. As the research study interested in understanding DEF, the literature review will henceforth focus only on DEF.

2.4.1 Definition

DEF is a heat-induced internal sulphate attack (Scrivener & Skalny 2005) that decomposes the early ettringite (Divet & Pavoine 2002) to other forms of alumina sulphate phases, which may then recrystallise as ettringite at a later stage in hardened concrete (H. F W Taylor, Famy & Scrivener 2001)

2.4.2 Mechanism of DEF

Elevated temperature curing impacts the normal hydration of concrete. A representation of ettringite instability at high temperature and alkalinity is presented in Figure 2.4. The increase in curing temperature favours increased alkali dissolution in the pore solution. The rise in temperature and alkalinity of the solvent increases the solubility of sulphates (Glasser 1996). The presence of alkalis in the cementitious matrix prevents the crystallisation of ettringite (Pavoine, Brunetaud & Divet 2012), leading to the adsorption of sulphates in calcium silica hydrate (C-S-H) (Divet & Randriambolo 1998) and thus the formation of monosulphate phases is favoured.

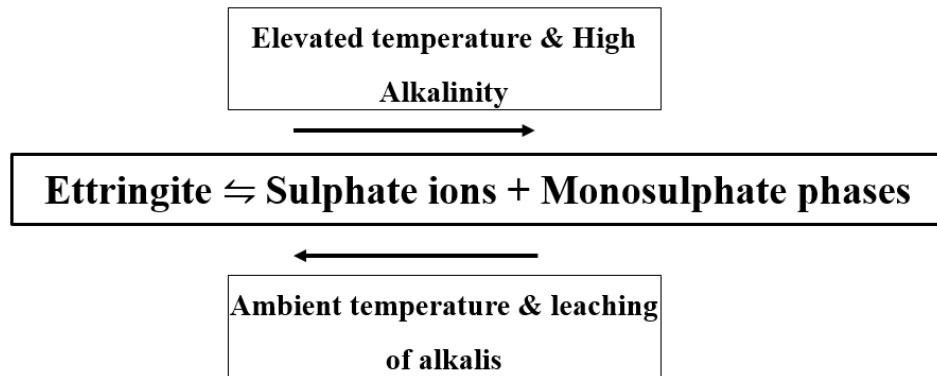


Figure 2.4 Representation of ettringite's instability over high temperature and alkalinity

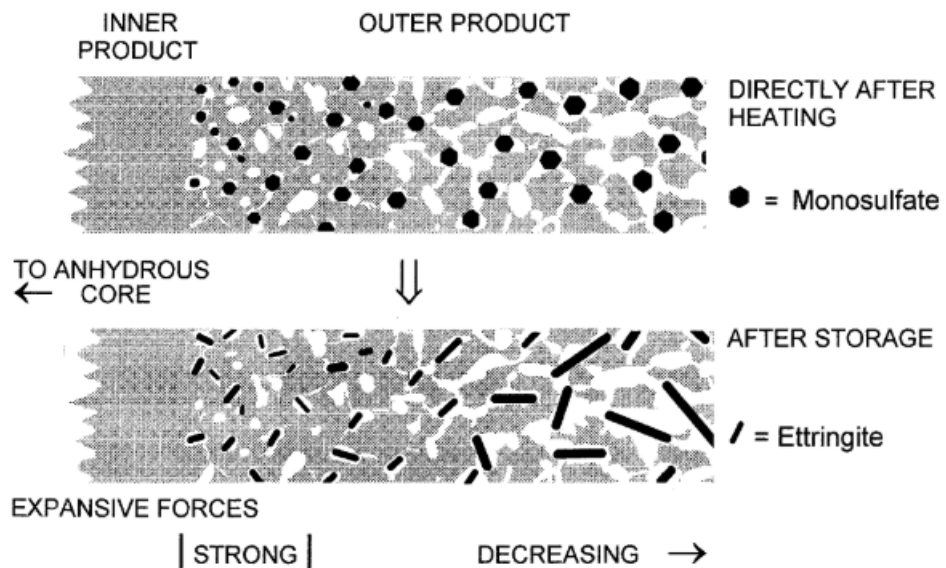


Figure 2.5 Schematic diagram of DEF expansion mechanism (H. F W Taylor, Famy & Scrivener 2001)

After returning to ambient temperature, desorption of sulphates from C-S-H and leaching of alkalis (if direct contact of the concrete member with water exists) favours the precipitation of ettringite through the reactions between sulphates and monosulphate phases in the hardened concrete resulting in DEF (H. F W Taylor, Famy & Scrivener 2001). Thus, the monosulphate phases formed after heat curing serve as a nucleation site for future ettringite precipitation, as illustrated in Figure 2.5. As DEF occurs in the

hardened cementitious system and given that ettringite is a high volume-occupying hydrate, the process may result in cracking.

2.5 Factors influencing DEF

The main factors contributing to DEF can be classified into three broad categories

- (1) Precast concrete manufacturing parameters
- (2) Cement composition factors
- (3) Exposure conditions

2.5.1 Precast concrete production parameters

(i) Effect of elevated temperature curing

As discussed in Section 2.2.1 Temperature, ettringite undergoes changes in crystal structure when exposed to high temperature. In concrete, curing at high temperatures can lead to complete decomposition of ettringite into monosulphate and sulphates (Ramlochan, Thomas & Hooton 2003). The resulting free sulphates in the pore solution penetrate preferentially into the C-S-H phase, as discussed in Section 2.4.2 Mechanism of DEF. The resultant mixture is termed as Phase X (Lerch, Ashton & Bogue 1929; Kalousek & Adams 1951). At later stages, sulphates are released from Phase X and react with aluminates to precipitate ettringite in the hardened concrete matrix, usually resulting in expansion. DEF often precipitates in the interfacial transition zone (ITZ) (Yang et al. 1999) and affects the integrity of the concrete; thus leading to increased permeability and associated problems with durability.

Although the mechanism appears to be clear, the problem lies in determining the safe threshold curing temperature for the production of precast concrete. The safe curing temperature is often derived from the temperature at which ettringite crystal structure

starts to undergo a change in pure phase, as discussed in Section 2.2.1 Temperature, which is in the range of 60°C (Shimada & Young 2001) to 70°C (Collepari 2003; Lawrence 1995; H F W Taylor, Famy & Scrivener 2001). However, in situ concrete may reach 80°C without steam curing due to self-heat of hydration (Thomas 2013b), thus creating ambiguity regarding the safe temperature limit.

(ii) Effect of pre-cure time

Pre-cure or pre-storage time is the time interval between the casting of concrete members and the onset of elevated temperature curing. If the pre-cure time is too short (less than the setting time of concrete), EEF formation is inhibited, resulting in more free sulphates to penetrate C-S-H (Yang 1996). As already discussed, sulphates adsorbed to C-S-H are desorbed at a later stage to form the basis for DEF. Further, the reduction in pre-cure time impacts the vital physical properties of concrete such as compressive strength (Erdem, Turanli & Erdogan 2003), which could indirectly contribute to an increase in DEF risk. Yang (1996) experimentally shown that a reduction in pre-cure time increases the DEF expansion.

2.5.2 Cement composition factors

Chemical composition is a vital factor influencing DEF. Cement contains all the reactants needed to form ettringite; upon hydration, ettringite formation is inevitable. Hence, the individual reactants proportion in cement can certainly have an impact on DEF. This section discusses the effects of cement sulphate, sulphate to aluminate molar ratio and alkalis on DEF.

(i) Effect of sulphates

There are two sources of sulphate in cement: sulphate can originate either from clinker or gypsum. Clinker sulphate is introduced from the raw materials of cement, so the

percentage of clinker sulphate in cement varies significantly. On the other hand, about 5% gypsum is usually added in cement as a set regulator. The sulphate contribution from gypsum is about 2.3-2.5%. Gypsum sulphate is readily available for hydration reactions, whereas clinker sulphates are not. This is due to the difference in dissolution capacity between clinker and gypsum sulphates. Clinker sulphates are usually released at a later hydration stage, which favours DEF (Mielenz et al. 1995). However, statements regarding slow solubility and release of clinker sulphate have been found to be contradicting. An overall cement sulphate (combined gypsum and clinker sulphate) content of approximately 4 to 6% may increase the chance of DEF (Scrivener & Skalny 2005).

Tosun (2006) showed that in heat-cured specimens, expansion increased proportionally increased with an increase in sulphates. This trend also applies to cements with a varying surface area. On the other hand, Kelham (1996) showed that beyond a pessimum level of SO_3 , the ultimate expansion decreased. Hence, there is inconsistency in relating sulphate content and DEF expansion despite many years of research.

Further, in one very peculiar case, oxidation of pyrites in aggregates released sulphates at a later stage of hydration contributing to service life reduction due to DEF (Lee et al. 2005). This suggests, controlling sulphate content in cements does not guarantee DEF free concrete. Hence to accommodate surprise elements, the laboratory research works should include testing higher sulphate content cementitious systems to understand the role of it in DEF.

(ii) Effect of sulphate to aluminate molar ratio

Literature analysis of Zhang, Olek & Diamond (2002) shows maximum DEF expansion occurs when the cement sulphate to alumina molar ratio $(\text{SO}_3 / \text{Al}_2\text{O}_3)_m$ is near to one. When $(\text{SO}_3/\text{Al}_2\text{O}_3)_m$ is close to one, more ettringite forms in the system, leading to high

expansion. However, beyond this pessimum level $(\text{SO}_3 / \text{Al}_2\text{O}_3)_m \sim 1$ magnitude of expansion was reduced. This may be due to more free sulphates available in system and lack of aluminates to react with sulphates. However, considering the ettringite composition, ideally $(\text{SO}_3/\text{Al}_2\text{O}_3)_m$ should have been ~ 3 to get the same result. Also, contrary to this Escadeillas et al. (2007) showed that cements with different alkali levels with same $(\text{SO}_3/\text{Al}_2\text{O}_3)_m \sim 1.2$ expanded differently. Hence the validation $(\text{SO}_3 / \text{Al}_2\text{O}_3)_m \sim 1$ resulting in maximum DEF expansion needs further investigation.

(iii) Effect of alkalis

Potassium and sodium oxides are the sources of alkalis in cement. The presence of alkalis in the pore solution increases with increasing curing temperature. Alkalis increase the solubility of sulphates, hence preventing early ettringite formation (Thomas, Hooton & Ramlochan 2010). Dissolved sulphate may be adsorbed onto the C-S-H. At a later stage, sulphates are desorbed from C-S-H and react with monosulphates to form DEF.

Fukuda et al. (2010) added potassium sulphate (K_2SO_4) in amounts ranging from 0.5 to 4%, in addition to the native cement alkalis, and the influence this had on expansion was studied on mortar bars. The increase in alkali content resulted in further and faster expansion. Addition of 4% K_2SO_4 resulted in the disintegration of the mortar specimen. Since the presence of alkalis hinders the stability of ettringite (Stark & Bollmann 2000), leaching of alkalis from the cementitious system is essential for ettringite precipitation. Odler & Chen (1995) and Yan & Qin (2001) observed that storing mortar bars in water favoured leaching of alkalis and a higher quantity of ettringite was produced, compared to bars stored in a humid air (above 90% humidity) atmosphere.

Leaching of alkalis is accelerated when storage water is renewed at regular intervals (Leklou, Aubert & Escadeillas 2013). Desorption of sulphate ions from C-S-H was found

to be triggered when alkalis are leached from the cementitious matrix (Divet & Randriambolo 1998). Aubert & Escadeillas (2013) found an increase in curing water alkali content (both potassium and sodium) correlated well with the expansion of specimens. Hence, the leaching of alkalis is a favourable condition for DEF. Leaching of even all alkalis from fully water-submerged laboratory specimens is possible, (Lindgård, Thomas, et al. 2013) though it would be unlikely to occur infield concrete structures. Bérubé et al. (2002), found that leaching of alkalis in real structures is restricted to only the near-surface layer of concrete. In that case, consumption of alkalis due to ASR may play a more vital role in promoting DEF (Diamond 2001) in field concrete structures than the leaching of alkalis.

2.5.3 Exposure conditions

In Section 2.5.2 (iii) Effect of alkalis, the differences between heat-cured specimens stored in water or humid air conditions were introduced. The reasons for the higher expansion in water-stored heat-cured specimens are provided in this section.

Samples stored in humid air and saturated lime water environments tend to form ettringite crystals of similar sizes. However, differences arise in the colloidal ettringite formed in the saturated lime water environment. Colloidal ettringite (1 μm length and 0.25 μm wide) has a high specific surface area and so can attract more water molecules, leading to expansion (Mehta 1973).

This enables the tiny ettringite crystals to precipitate even in very confined spaces such as the interfacial transition zone (ITZ) of concrete. DEF occurrence in ITZ affects the integrity of the concrete microstructure and impacts the permeability of concrete, as discussed previously.

2.6 Differentiating expansive DEF and non-expansive DEF.

From Section 2.5, it appears DEF may occur in all heat-cured specimens, however not all result in expansion or in other words deleterious. Hence to differentiate expansive DEF with non-expansive DEF, many works of literature have been referred to find the least DEF expansion and mass gain resulted in some form of deterioration in laboratory specimen or concrete structure. Among the referred articles, research work by Pavoine, Divet & Fenouillet (2006) shows at cracks appeared in a concrete structure at an expansion $\sim 0.2\%$ due to DEF. Similarly, expansive DEF has characteristics mass gain above 2% (Zhang, Olek & Diamond 2002a).

2.7 DEF mitigation by mineral addition/SCMs

2.7.1 Effect of limestone addition

Studies on the impact on DEF when cement is blended with limestone yield inconsistent results. Even 15% of added limestone did not reduce the DEF expansion in a study by Kelham (1996). Similar expansion obtained when limestone was added as fine aggregate (instead of sand), however at a much slower rate compared to the mix which contained sand (Kelham 2002).

Conversely, Duszak (2002) showed that 15% limestone addition reduced DEF expansion and 30% addition completely eliminated it in a similar fashion to FA. XRD phase analysis in mixes with 15% limestone showed that the monosulphate peak appeared in the early stages but was not detectable after 200 days, while the ettringite peak remained strong. To conclude, the impact of limestone on DEF mitigation is not clear from the literature as the results are inconsistent and minimal differences have been found in ettringite reformation behaviour in cement with or without limestone.

2.7.2 Effect of Fly ash addition

FA use in heat-cured mortars reduces DEF expansion behaviour (Amde, Azzam & Livingston 2005; Amine, Leklou & Amiri 2016; Fukuda et al. 2010; Kelham 2002; Silva et al. 2010a). The efficiency of DEF mitigation depends on the class of FA used; low calcium Class F Fly Ash (CFFA) was found to be more effective than Class C Fly Ash (CCFA) in DEF mitigation (Fu 1996). The expansion was much lower for CFFA mortars than CCFA. Tishmack, Olek & Diamond (1999) predicted that the presence of more soluble calcium aluminate glass available in CCFA favours ettringite formation and that this might explain the expansion behaviour. Further, no drop in dynamic elastic modulus was observed in FA-substituted heat-cured mortars, unlike the DEF-affected plain cement mortars. (Amine, Leklou & Amiri 2016; Leklou, Nguyen & Mounanga 2017a). Steam cured cementitious systems with FA incorporated exhibited good microstructure in terms of ITZ. The ettringite band observed in the ITZ of plain cement mortars was absent in FA-substituted mortars, resulting in expansion reduction and other improved properties such as modulus of elasticity and strength (Leklou, Nguyen & Mounanga 2017a).

FA contributes aluminates that reduce the cement sulphate to alumina molar ratio. This reduction favours the formation of other alumina-ferrite phases such as monosulphate (Ms), hemicarboaluminate (Hc) and monocarboaluminate (Mc), rather than ettringite (Tishmack, Olek & Diamond 1999). This may be the fundamental reason for DEF mitigation by FA. The increased precipitation of monosulphate reduces the sulphate ion concentration in the pore solution and reduces the adsorption on C-S-H (Leklou, Nguyen & Mounanga 2017a). Furthermore, portlandite consumption by amorphous silica from FA to form more C-S-H (Tishmack, Olek & Diamond 1999) has the potential to reduce the pore size in FA-blended cement systems. This reduces permeability and hinders the diffusion of sulphate ions (Hughes 1985), thus contributing to DEF mitigation.

2.8 Gaps in the literature

Expansion in heat-cured concrete, mortar and paste specimens has generally been observed. However, the relationship between expansion and microstructural was not consistent in the literature. The general trend of ettringite band in ITZ, cracks and voids in heat-cured cementitious systems warrants some scepticism. Some research suggests expansion occurs first and ettringite later precipitates preferentially in ITZ or cracks created during expansion. Therefore, despite many years of DEF research, there is no clear consensus on the correlation between microstructural changes and expansion. The cement sulphate and alkali content impacting the DEF is not clear as some studies suggest pessimum effect.

Early age hydration characteristics of DEF-prone cementitious systems and heat curing conditions are not studied along with crystallisation changes in cement hydrates. Changes in the heat evolution characteristics of cementitious systems could aid in the understanding of DEF. This could also be used to develop simple test methods to identify the DEF susceptibility of a particular cementitious system or heat curing condition.

Mitigation of DEF with fly ash has been widely studied, and the results are consistent. However, DEF mitigation with limestone addition is not consistent. Since much of the commercially used cement is blended with limestone, further research is needed to understand its role in long-term concrete hydration and DEF mitigation. Further, FA was incorporated in the mix as a partial substitution for cement, thus has only been studied in relation to the dilution effect of FA in DEF mitigation. No studies currently exist that examine the addition of FA without reducing the cement content of a mix.

This research work aimed to address the existing gaps in the literature.

Chapter 3 Materials

This chapter introduces the different materials used in this research. The relevant physical and chemical characteristics of the materials are studied and discussed in detail.

3.1 Cements

Two Australian general-purpose Portland cements complying with AS 3972:2010 have been used in this research. Cements produced in the same batch were used throughout this research, to keep variability low. Cements were packed in plastic bags and stored in sealed buckets. The cements were chosen based on the DEF literature review (refer to Chapter 2) to have significantly different alumina content. Cement 1 is a grey colour GP cement, widely used for structural concretes in Australia. Cement 2 is a white colour GP cement mainly designed for non-structural applications. Further, Cement 2 has a weaker resistance to external sulphate attack according to the manufacturer, which makes this cement an ideal choice for DEF laboratory studies.

According to the corresponding manufacturer-supplied data, the specific surface areas of Cement 1 and Cement 2 are $395 \text{ m}^2/\text{kg}$ and $420 \text{ m}^2/\text{kg}$, respectively. The critical difference between the cements is in mineral addition and tricalcium aluminate (C_3A) content. Cement 1 contains 7.5% limestone as a mineral addition, whereas Cement 2 has no added limestone. The mass loss at around 500°C to 720°C in the thermal gravimetric analysis (TGA) corresponds to decarboxylation of calcium carbonate (CaCO_3), which is much higher for Cement 1 than Cement 2. This mass loss is indicative of the addition of ground limestone to Cement 1 (Figure 3.1). The chemical composition of cements was estimated using Philips PW2400 XRF spectrometer with SuperQ software. The results are presented in Table 3.1.

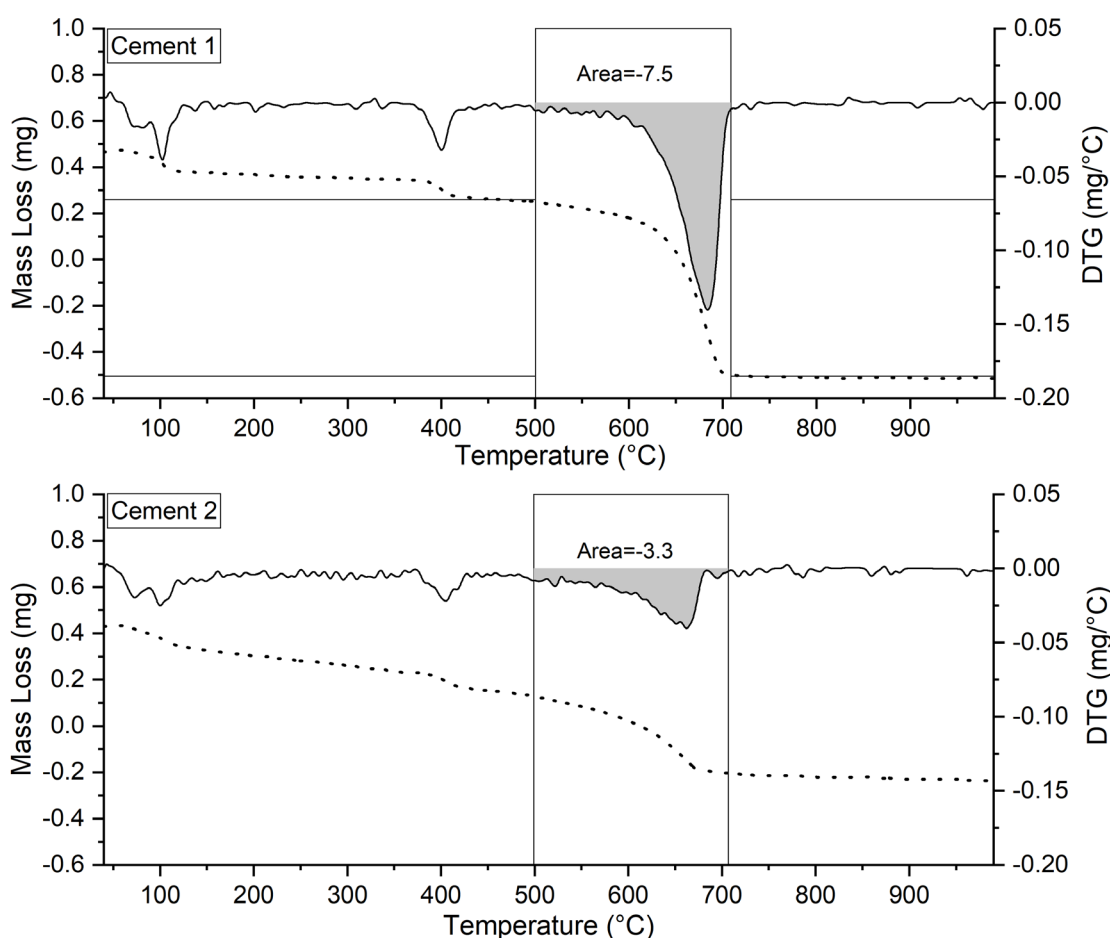


Figure 3.1 TGA patterns of cements

Australian standard AS 3972-2010 restricts overall cement sulphate to 3.5%. Australian Technical Infrastructure Committee's specification ATIC SP-43 specifies that the alkali content of cement (as sodium oxide equivalent) not exceed 0.60%. Referring to Table 3.1, both cements have sulphate and alkali content within the specified limits of Australian standards and specifications. The Fe_2O_3 content of Cement 2 is less than one percent (0.26%), which is responsible for the white colour. The clinker phase composition of these cements was estimated using principles arrived at from a modified Boques' calculation suggested by Taylor (1989). The results are given here in Table 3.2.

Referring to Table 3.2, The C_3A content of Cement 2 (11.2%) is significantly higher than Cement 1 (7.4%) suggesting aluminate content of Cement 1 is much less than Cement 1.

However, both cements have similar Al_2O_3 contents (Cement 1 has 0.4% more Al_2O_3) (Table 3.1); the difference in C_3A content is attributed to the Fe_2O_3 contents as the available Al_2O_3 is distributed between the C_3A and the C_4AF phases, hence the Al_2O_3 content in Cement 2 forms predominantly C_3A , whereas, in the case of Cement 1, Al_2O_3 content is distributed between the C_3A and C_4AF . The C_3A content in Cement 1 (7.4%) is therefore lower than in the Cement 2 (11.2%) despite similar Al_2O_3 content.

Table 3.1 Oxide composition of raw materials

Oxide %	Cement 1	Cement 2	Fly ash	Fine sand	Coarse sand
CaO	64.18	65.70	3.88	0.04	0.20
SiO_2	19.67	22.82	55.46	95.7	95.06
Al_2O_3	4.78	4.38	24.42	1.27	1.79
Fe_2O_3	3.10	0.26	6.91	0.46	0.70
Mn_3O_4	0.12	0.02	0.04	0.01	0.01
MgO	0.91	0.68	1.22	0.05	0.15
TiO_2	0.22	0.26	1.05	0.21	0.11
Na_2O	0.23	0.16	0.77	0.19	0.34
K_2O	0.41	0.29	0.88	0.32	0.51
P_2O_5	0.06	0.07	1.14	0.01	0.02
SO_3	2.37	3.07	0.19	BLD	0.38
Cr_2O_3	BLD	BLD	0.02	0.01	0.03
ZrO_2	BLD	BLD	0.04	0.02	0.01
SrO	BLD	BLD	0.07	BLD	BLD
ZnO	BLD	BLD	0.01	BLD	BLD
CuO	BLD	BLD	0.02	BLD	0.01
NiO	BLD	BLD	0.02	BLD	BLD
BaO	BLD	BLD	0.03	BLD	BLD
PbO	BLD	BLD	BLD	BLD	BLD
L.O.I.*	4.09	2.20	2.52	0.61	0.49
Total	100.14	99.91	98.69	98.90	99.80
$\text{Na}_2\text{O}_{\text{eq}}$ **	0.50	0.35	NA	NA	NA

* Loss on Ignition ** Calculated from Na_2O and K_2O . BLD – Below level of detection

Table 3.2 Modified Bogue's phase composition of cements

Compound	Cement 1	Cement 2
C ₃ S%	49.9	56.3
C ₂ S%	18.3	22.9
C ₃ A%	7.4	11.2
C ₄ AF%	9.4	0.8

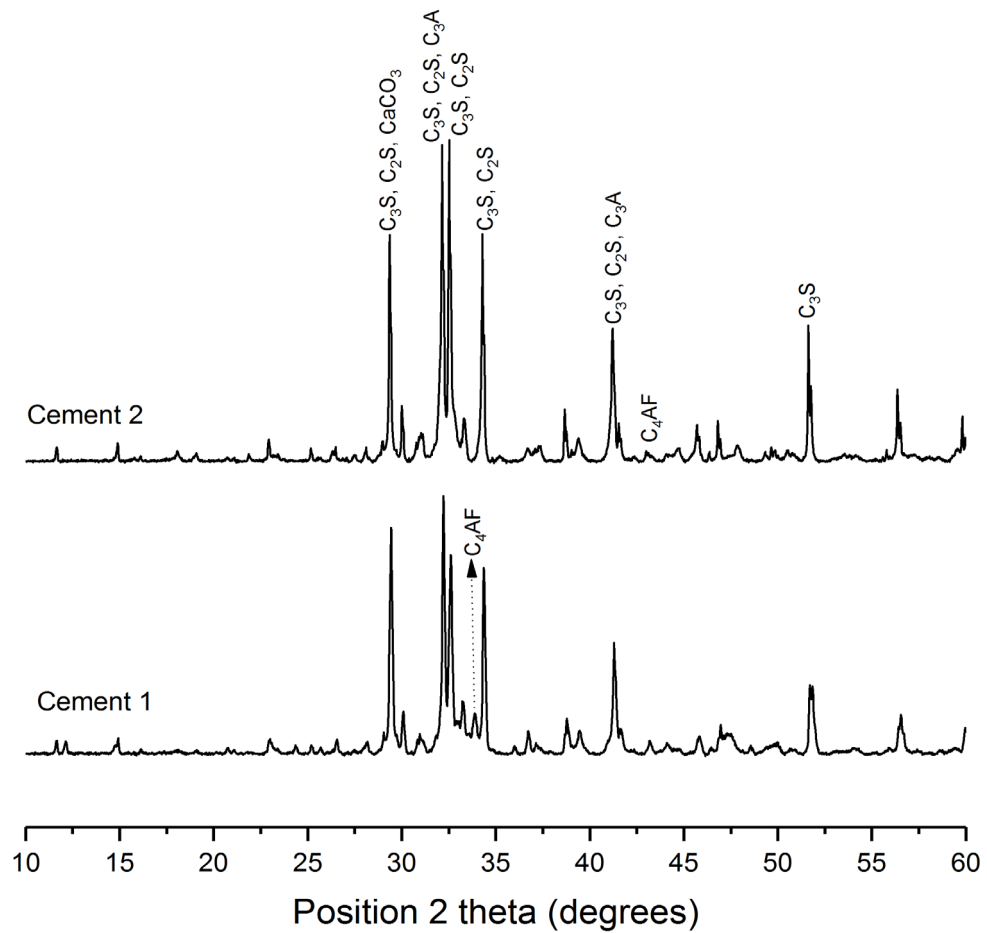


Figure 3.2 XRD patterns of cements used in this research

The absence of ferrite phase in Cement 2 is noted in the XRD patterns in Figure 3.2 and the phase composition calculation in Table 3.2. Further, isothermal calorimetry was conducted to understand how these phase compositions affect the hydration characteristics of cements. Results (Figure 3.3) show that Cement 2 hydrates faster than Cement 1. The main hydration peak corresponding to C₃S hydration reaches its peak at

around 4 hours in Cement 2, which is 2 hours earlier than in Cement 1. The heat evolved from the hydration was also higher for Cement 2 than Cement 1. This higher heat of evolution could be due to a combination of the absence of limestone mineral addition, higher C_3A and C_3S content and higher specific surface area in Cement 2. The accelerated hydration of Cement 2 also implies the setting time would be significantly less than that of Cement 1. Initial setting time is vital for precast concrete production as it dictates the pre-cure time.

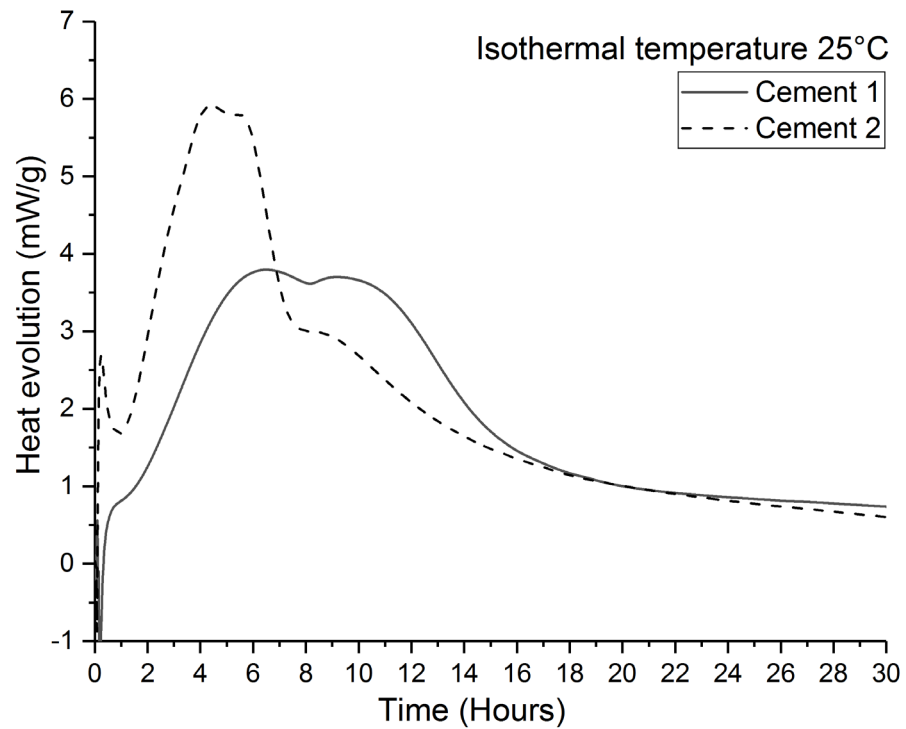


Figure 3.3 Hydration characteristics of two cements

3.2 Fly Ash (FA)

Processed FA, conforming to AS/NZS 3582.1:2016, is used in this research project. From Table 3.1 the chemical composition of FA reveals a low CaO content (3.88%). FA conforms to Grade 1 classification according to AS/NZS 3582.1:2016 (equivalent to ASTM C618 class F fly ash) as it has 86.7% pozzolanic compounds (the sum of silica, alumina, and iron oxides is above 70%). The amorphous silica hump is visible in the XRD

pattern shown in Figure 3.4, again confirming the pozzolanic nature of FA, though some crystalline silica peaks as quartz (Q) and mullite (Mu) are also observed.

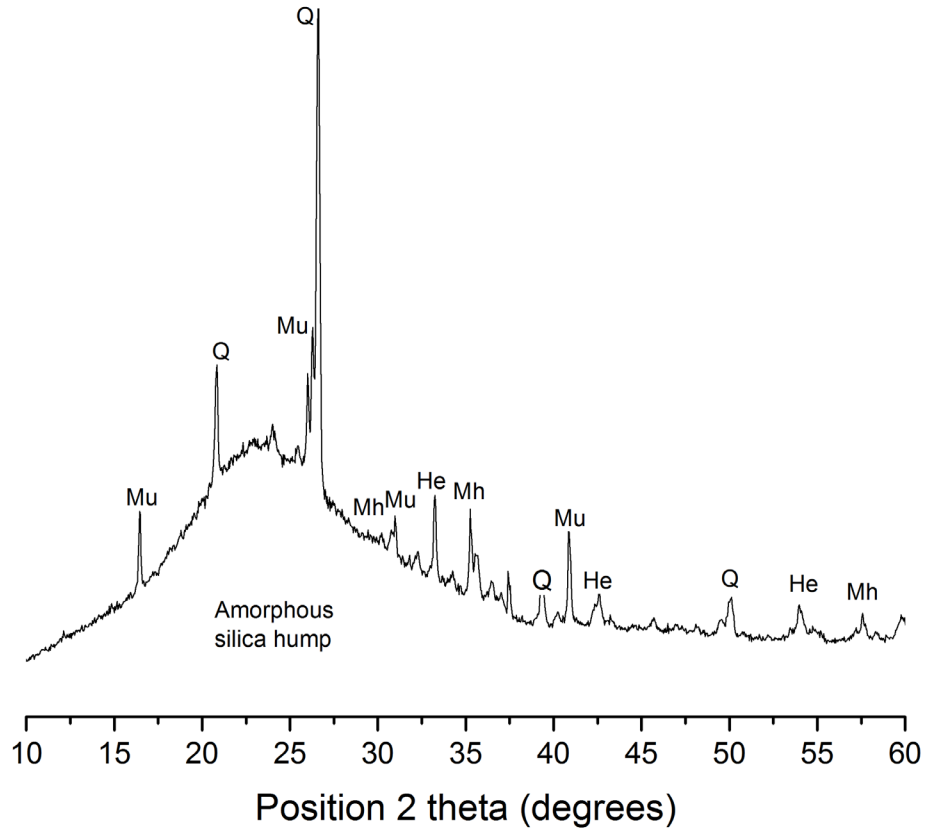


Figure 3.4 XRD pattern of fly ash used in this research

3.3 Aggregates

Pink Lilly coarse sand and Kinka Beach fine sand are used in this research. XRD patterns of the sands confirm the abundance of crystalline silica peaks (shown in Figure 3.5). The oxide compositions of both sands are given Table 3.1. This confirms that both types of sand do not contain any significant sulphates, eliminating late sulphate release from aggregates as a factor that may contribute to DEF. However, the alkali contents in the sands are significant. Petrographic studies were done to understand the reactivity of the aggregates and the results are summarised in Table 3.3. Results confirm that both the sands contain unstrained crystalline silica which is non-reactive.

Table 3.3 Mineral composition of sand

Mineral		Coarse sand	Fine sand
		(%)	
Unstrained quartz		61	74
Strained quartz		10	9
Feldspar		5	5
Chert		1	-
Quartz epidote rock		1	-
Lithic clasts of	strained quartzite	2	2
	granite	10	-
	sandstone	2	-
	cherty meta-pelite	2	-
	meta-pelite	1	-
	acid volcanic rock	5	8
	arenite	-	2

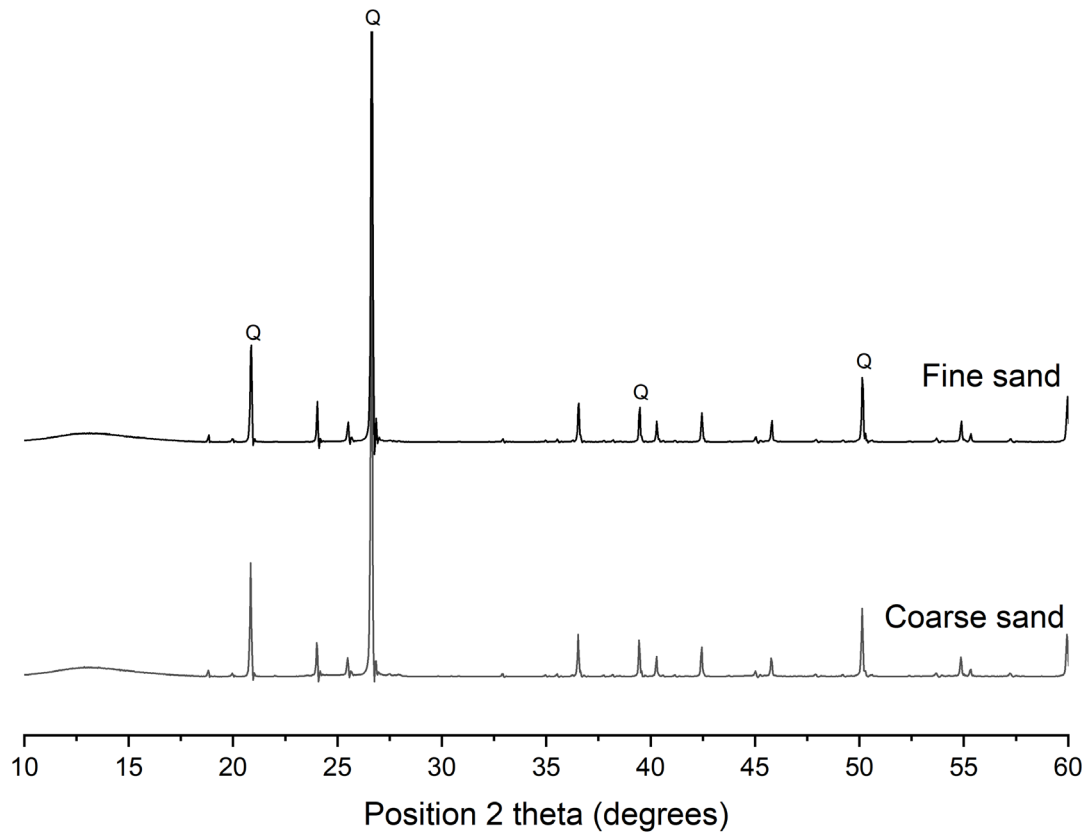


Figure 3.5 XRD patterns of coarse and fine sands used in this research

However, the significant strained quartz and feldspar content could have the potential to cause a mild or slow deleterious alkali-silica reaction (ASR). Hence, expansion results

should be carefully considered, and microstructural characterisation is required to identify and differentiate DEF effects from ASR.

3.4 Other materials

Analytical grade gypsum and sodium hydroxide of minimum 98.5% purity were used to alter the chemical composition of the cements. Laboratory-made distilled water was used throughout the research for preparing cement paste and mortar specimens.

Chapter 4 Experimental design and methods

This chapter outlines the experimental phases, cement and mortar mixes, methods of sample preparation, various experimental methods and characterisation techniques used in this research work.

4.1 Experimental design

The experiments were carried out in 5 phases after grouping the identified research variables from the literature review. Phase 1 covers the study of hydration behaviour differences in various systems at two different temperatures. Phase 2 focuses on understanding the impact of heat curing factors such as temperature, pre-cure time and curing duration on standard commercial cement systems with respect to DEF. Phase 3 studies the susceptibility of cement mortars to DEF after chemical modification by increasing the sulphate and alkali contents and altering the exposure conditions. Phase 4 concentrates on understanding the influence of heat curing duration and pre-cure time on the susceptibility of standard and chemically modified cement systems to DEF. Phase 5 tests the efficacy of fly ash incorporation on heat-cured chemically modified cement systems in mitigating DEF.

4.1.1 Phase 1: Hydration characteristics of heat-cured cement systems

It was understood from the literature review that the primary factors influencing DEF are heat-curing temperature, sulphate content and alkali content in the cementitious system. Further, these factors can influence the early stage hydration of cement clinker phases. In this study, cements were chemically modified in two ways: one, by raising sulphates to 4% without changing the alkali content, and then by increasing sulphates to 4% along increasing alkalis to 1%. With an isothermal calorimeter, a detailed study on hydration characteristics of standard commercial cements and chemically modified cements under

two different temperatures 25°C and 55°C (refer to section 4.2.1 Isothermal calorimetric studies for experimental method) was carried out. Further, the impact of incorporation of fly ash in the cement systems was also studied. Refer to Table 4.1 for a detailed description of mixes.

Table 4.1 Cement paste mixes for hydration characteristics studies

Sl No	Cement	SO ₃ (%)	Na ₂ O _{eq} (%)	Fly ash (%)	Isothermal condition (°C)	Mix ID*
1	Cement 1	2.4	0.5	0.0	25	C1-25°C
2	Cement 1	4.0	0.5	0.0	25	C1-S4-25°C
3	Cement 1	4.0	1.0	0.0	25	C1-S4N1-25°C
4	Cement 1	2.4	0.5	25.0	25	C1-FR-25°C
5	Cement 1	4.0	1.0	25.0	25	C1-S4N1-F-25°C
6	Cement 1	2.4	0.5	0.0	55	C1-55°C
7	Cement 1	4.0	0.5	0.0	55	C1-S4-55°C
8	Cement 1	4.0	1.0	0.0	55	C1-S4N1-55°C
9	Cement 1	2.4	0.5	25.0	55	C1-FR-55°C
10	Cement 1	4.0	1.0	25.0	55	C1-S4N1-F-55°C
11	Cement 2	3.0	0.3	0.0	25	C2-25°C
12	Cement 2	4.0	0.3	0.0	25	C2-S4-25°C
13	Cement 2	4.0	1.0	0.0	25	C2-S4N1-25°C
14	Cement 2	3.0	0.3	25.0	25	C2-FR-25°C
15	Cement 2	4.0	1.0	25.0	25	C2-S4N1-F-25°C
16	Cement 2	3.0	0.3	0.0	55	C2-55°C
17	Cement 2	4.0	0.3	0.0	55	C2-S4-55°C
18	Cement 2	4.0	1.0	0.0	55	C2-S4N1-55°C
19	Cement 2	3.0	0.3	25.0	55	C2-FR-55°C
20	Cement 2	4.0	1.0	25.0	55	C2-S4N1-F-55°C

* Nomenclature: C1, 2 stands for cement 1 & 2. S, N stands for sulphate and sodium equivalent, respectively; the following numeric value represents the overall content (of S or N) in the cement. FR stands for 25% fly ash incorporation as partial replacement of cement. If an ID does not have any special alphabets (say S, N or F) means the mix uses cement in 'as-received' condition. *The numerical with °C represents the curing temperature. For example, the mix C2-S4N1-FR-55°C means the mix prepared is with Cement 2, which has 4% sulphate and 1% sodium equivalent in it and 25% of cement was replaced with fly ash. The curing temperature of the mix was 55°C.*

4.1.2 Phase 2: Impact of heat curing in standard GP cement systems

Phase 2 involves studying the impact of various heat curing factors on standard (commercial, as received) GP cement systems, to understand whether DEF occurs. Since Cement 1 is widely used in Australia to make structural precast concrete and has significant commercial importance, mortar mixes with Cement 1 were cured at temperatures 23, 50, 60, 70, 80 and 90°C to understand the influence of a range of curing temperatures on DEF-related expansion and other implications. In the case of Cement 2 mixes, the testing program includes only three different curing temperatures: 23, 80 and 90°C. When heat curing, the duration of exposure to high temperature varied from 8 to 12 hours and the time prior to initiating heat curing varied from (pre-cure time) 4 to 0 hours. Table 4.2 provides a detailed description of the mixes. The linear expansion and mass changes of all mortar prisms were monitored for 600 days. For selected mixes, cement pastes were also prepared and characterised using XRD, TGA and FTIR techniques. Further, the pore solution extracts from cement pastes were studied. These studies enable an understanding of the chemistry associated with the linear expansion behaviour of the mortars. To understand microstructural changes and the impact on long term durability characteristics, mortar prisms (from selected mixes) were studied with SEM and electrochemical impedance spectroscopy. Sections 4.2.2 Mortar prisms linear expansion and mass change studies 4.2.6 Electrochemical impedance spectroscopy analysis a detailed description of these experimental methods.

4.1.3 Phase 3: Impact of heat-curing in chemically modified cement systems

In this phase, both Cement 1 & 2 were chemically modified with sulphates and alkalis. First, cement sulphates (SO_3) were increased from its original (C1 2.3% & C2 3.07%) level to 4, 5 and 6% without changing the alkali content. Mortars and pastes prepared with these sulphate-modified cements were cured at two different temperatures: 23°C and

90°C. Table 4.3 provides details of these sulphate-modified cement mixes. The alkali content was then increased its original level (C1 0.5% & C2 0.35%) to 1.0 and 1.5% without altering the initial sulphate level. Mortars prepared with these alkali-modified cements were cured at two different temperatures: 23°C and 90°C. Table 4.4 provides details of the alkali- modified cement mixes. Further, both sulphates and alkalis were increased to 4% and 1% respectively. Specimens prepared with these cements were cured at a range of temperatures: 23, 50, 60, 70, 80, and 90°C. Table 4.5 provides details of the sulphate and alkali- modified cement mixes. Test procedures were the same as described in Section 4.1.2 Phase 2: Impact of heat curing in standard GP cement systems

4.1.4 Phase 4: Varying heat curing time and pre-curing time in cement systems

Three representative cement systems from the previous phases (e.g., standard GP cements, 4% sulphate cements and 4% sulphate & 1% alkali cements) were investigated in this phase. The specimens prepared with these representative cement systems were subjected to heat curing at 90°C durations of either 8 or 12 hours. Table 4.6 provides details of the mixes. In the next set of experiments, the pre-cure time was reduced from 4 hours to 0 hours. Table 4.7 provides details of the mixes. Test procedures were the same as described in section 4.1.2 Phase 2: Impact of heat curing in standard GP cement systems

4.1.5 Phase 5: Incorporation of fly ash in heat-cured cement systems

The representative systems for this phase of the study was cement with 4% sulphate & 1.0% alkalis. Fly ash was incorporated into the mixes in two ways: firstly, by partial substitution of cement in the mixes by 25% by weight of cement, so that the total cementitious content of the mixes remain constant; and secondly, by addition of 25% fly ash by weight of cement into the mixes, thus increasing the total cementitious content of

the mixes. Table 4.8 provides details of the mixes. Test procedures were the same as described in section 4.1.2 Phase 2: Impact of heat curing in standard GP cement systems

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Table 4.2 Phase 2: Mortar mixes to study the effect of heat curing in standard GP cement systems

S No	Cement	SO ₃ content (%)	Na ₂ O _{eq} content (%)	Pre-heat cure time (Hours)	Ramp time to reach maximum temperature (Hours)	Curing temperature (°C)	Duration of elevated temperature curing (Hours)	Mix ID*
1	Cement 1	2.37	0.49	NA [#]	NA	23	NA	C1-23°C
2	Cement 1	2.37	0.49	4	2	50	8	C1-P4-50°C-8H
3	Cement 1	2.37	0.49	4	2	60	8	C1-P4-60°C-8H
4	Cement 1	2.37	0.49	4	2	70	8	C1-P4-70°C-8H
5	Cement 1	2.37	0.49	4	2	80	8	C1-P4-80°C-8H
6	Cement 1	2.37	0.49	4	2	90	8	C1-P4-90°C-8H
7	Cement 1	2.37	0.49	4	2	90	12	C1-P4-90°C-12H
8	Cement 1	2.37	0.49	0	2	90	12	C1-P0-90°C-12H
7	Cement 2	3.07	0.35	NA	NA	23	NA	C2-23°C
8	Cement 2	3.07	0.35	4	2	80	8	C2-P4-80°C-8H
9	Cement 2	3.07	0.35	4	2	90	8	C2-P4-90°C-8H
10	Cement 2	3.07	0.35	4	2	90	12	C2-P4-90°C-12H
11	Cement 2	3.07	0.35	0	2	90	12	C2-P0-90°C-12H

**Nomenclature: P4 represents the mix was pre-cured for 4 hours before being exposed to heat curing. 8H or 12H represents the duration of heat curing. Other nomenclature is as described for Table 4.1*

[#]Note: NA – Not applicable. In this table, it represents the stages of heat curing that are not applicable for ambient 23°C cured mortars

Table 4.3 Phase 3: Mortars mixes to study the effect of heat curing in chemically modified cements- Variable: Sulphate

S No	Cement	SO₃ content (%)	Na₂O_{eq} content (%)	Pre-heat cure time (Hours)	Ramp time to reach maximum temperature (Hours)	Curing temperature (°C)	Duration of elevated temperature curing (Hours)	Mix ID
1	Cement 1	4.00	0.49	NA	NA	23	NA	C1-S4-23°C
2	Cement 1	4.00	0.49	4	2	90	8	C1-S4-90°C
3	Cement 1	5.00	0.49	NA	NA	23	NA	C1-S5-23°C
4	Cement 1	5.00	0.49	4	2	90	8	C1-S5-90°C
5	Cement 1	6.00	0.49	NA	NA	23	NA	C1-S6-23°C
6	Cement 1	6.00	0.49	4	2	90	8	C1-S6-90°C
7	Cement 2	4.00	0.35	NA	NA	23	NA	C2-S4-23°C
8	Cement 2	4.00	0.35	4	2	90	8	C2-S4-90°C
9	Cement 2	5.00	0.35	NA	NA	23	NA	C2-S5-23°C
10	Cement 2	5.00	0.35	4	2	90	8	C2-S5-90°C
11	Cement 2	6.00	0.35	NA	NA	23	NA	C2-S6-23°C
12	Cement 2	6.00	0.35	4	2	90	8	C2-S6-90°C

Table 4.4 Phase 3: Mortars mixes to study the effect of heat curing in chemically modified cements- Variable: Sodium equivalent

S No	Cement	SO₃ content (%)	Na₂O_{eq} content (%)	Pre-heat cure time (Hours)	Ramp time to reach maximum temperature (Hours)	Curing temperature (°C)	Duration of elevated temperature curing (Hours)	Mix ID
1	Cement 1	2.37	1.00	NA	NA	23	NA	C1-N1-23°C
2	Cement 1	2.37	1.00	4	2	90	8	C1-N1-90°C
3	Cement 1	2.37	1.50	NA	NA	23	NA	C1-N1.5-23°C
4	Cement 1	2.37	1.50	4	2	90	8	C1-N1.5-90°C
5	Cement 2	3.07	1.00	NA	NA	23	NA	C2-N1-23°C
6	Cement 2	3.07	1.00	4	2	90	8	C2-N1-90°C
7	Cement 2	3.07	1.50	NA	NA	23	NA	C2-N1.5-23°C
8	Cement 2	3.07	1.50	4	2	90	8	C2-N1.5-90°C

Table 4.5 Phase 3: Mortars mixes to study the effect of heat curing in chemically modified cements- Variable: Sulphate & Sodium equivalent

S No	Cement	SO ₃ content (%)	Na ₂ O _{eq} content (%)	Pre-heat cure time (Hours)	Ramp time to reach maximum temperature (Hours)	Curing temperature (°C)	Duration of elevated temperature curing (Hours)	Mix ID
1	Cement 1	4.00	1.00	NA	NA	23	NA	C1-S4N1-23°C
2	Cement 1	4.00	1.00	4	2	50	8	C1-S4N1-50°C
3	Cement 1	4.00	1.00	4	2	60	8	C1-S4N1-60°C
4	Cement 1	4.00	1.00	4	2	70	8	C1-S4N1-70°C
5	Cement 1	4.00	1.00	4	2	80	8	C1-S4N1-80°C
6	Cement 1	4.00	1.00	4	2	90	8	C1-S4N1-90°C
7	Cement 2	4.00	1.00	NA	NA	23	NA	C2-S4N1-23°C
8	Cement 2	4.00	1.00	4	2	50	8	C2-S4N1-50°C
9	Cement 2	4.00	1.00	4	2	60	8	C2-S4N1-60°C
10	Cement 2	4.00	1.00	4	2	70	8	C2-S4N1-70°C
11	Cement 2	4.00	1.00	4	2	80	8	C2-S4N1-80°C
12	Cement 2	4.00	1.00	4	2	90	8	C2-S4N1-90°C

Table 4.6 Phase 4: Mixes to study the impact of heat-curing duration in cement systems

S No	Cement	SO₃ content (%)	Na₂O_{eq} content (%)	Pre-heat cure time (Hours)	Ramp time to reach maximum temperature (Hours)	Curing temperature (°C)	Duration of elevated temperature curing (Hours)	Mix ID
1	Cement 1	2.37	0.49	4	2	90	8	C1-90°C-8H
2	Cement 1	2.37	0.49	4	2	90	12	C1-90°C-12H
3	Cement 1	4.00	0.49	4	2	90	8	C1-S4-90°C-8H
4	Cement 1	4.00	0.49	4	2	90	12	C1-S4-90°C-12H
5	Cement 1	4.00	1.00	4	2	90	8	C1-S4N1-90°C-8H
6	Cement 1	4.00	1.00	4	2	90	12	C1-S4N1-90°C-12H
7	Cement 2	3.07	0.35	4	2	90	8	C2-90°C-8H
8	Cement 2	3.07	0.35	4	2	90	12	C2-90°C-12H
9	Cement 2	4.00	0.35	4	2	90	8	C2-S4-90°C-8H
10	Cement 2	4.00	0.35	4	2	90	12	C2-S4-90°C-12H
11	Cement 2	4.00	1.00	4	2	90	8	C2-S4N1-90°C-8H
12	Cement 2	4.00	1.00	4	2	90	12	C2-S4N1-90°C-12H

Table 4.7 Phase 4: Mixes to study the impact of pre-cure time in cement systems

S No	Cement	SO₃ content (%)	Na₂O_{eq} content (%)	Pre-heat cure time (Hours)	Ramp time to reach maximum temperature (Hours)	Curing temperature (°C)	Duration of elevated temperature curing (Hours)	Mix ID
1	Cement 1	2.37	0.49	4	2	90	12	C1-P4-90°C
2	Cement 1	2.37	0.49	0	2	90	12	C1-P0-90°C
3	Cement 1	4.00	0.49	4	2	90	12	C1-S4-P4-90°C
4	Cement 1	4.00	0.49	0	2	90	12	C1-S4-P0-90°C
5	Cement 1	4.00	1.00	4	2	90	12	C1-S4N1-P4-90°C
6	Cement 1	4.00	1.00	0	2	90	12	C1-S4N1-P0-90°C
7	Cement 2	3.07	0.35	4	2	90	12	C2-P4-90°C
8	Cement 2	3.07	0.35	0	2	90	12	C2-P0-90°C
9	Cement 2	4.00	0.35	4	2	90	12	C2-S4-P4-90°C
10	Cement 2	4.00	0.35	0	2	90	12	C2-S4-P0-90°C
11	Cement 2	4.00	1.00	4	2	90	12	C2-S4N1-P4-90°C
12	Cement 2	4.00	1.00	0	2	90	12	C2-S4N1-P0-90°C

Table 4.8 Phase 5: Mortar mixes to study the impact of fly ash incorporation in heat-cured cement systems

S No	Cement	SO ₃ Content (%)	Na ₂ O _{eq} Content (%)	Fly ash (%)	Pre-heat cure time (Hours)	Ramp time to reach maximum temperature (Hours)	Curing temperature (°C)	Duration of elevated temperature curing (Hours)	Mix ID*
1	Cement 1	4.00	1.00	0	4	2	90	12	C1-S4N1-F0
2	Cement 1	4.00	1.00	25 R	4	2	90	12	C1-S4N1-FR
3	Cement 1	4.00	1.00	25 F	4	2	90	12	C1-S4N1-FF
4	Cement 2	4.00	1.00	0	4	2	90	12	C2-S4N1-F0
5	Cement 2	4.00	1.00	25 R	4	2	90	12	C2-S4N1-FR
6	Cement 2	4.00	1.00	25 F	4	2	90	12	C2-S4N1-FF

**Nomenclature: F0-mix contains 0% fly ash in binder; FR- mix contains 25% fly ash to weight of cement as replacement in total binder content; FF- mix contains 25% fly ash to weight of cement increasing total binder content.*

4.2 Experimental methods

4.2.1 Isothermal calorimetric studies

In cement research, isothermal conduction calorimeters are used to study the heat evolution characteristics of cement/mortar hydration at a constant temperature. Heat evolution characteristics include the rate of reaction and total heat produced. A typical isothermal conduction calorimeter consists of heat flow sensors connected to the sample and reference holders (ASTM C1702, 2017). Reference material does not evolve heat and should be of the same specific heat capacity as the test sample. Both heat sensors are connected to the heat-sink, as shown in Figure 4.1. The entire setup is kept inside a thermally insulated box with a thermostat to maintain the internal temperature. The thermal difference between sample and reference material is then measured.

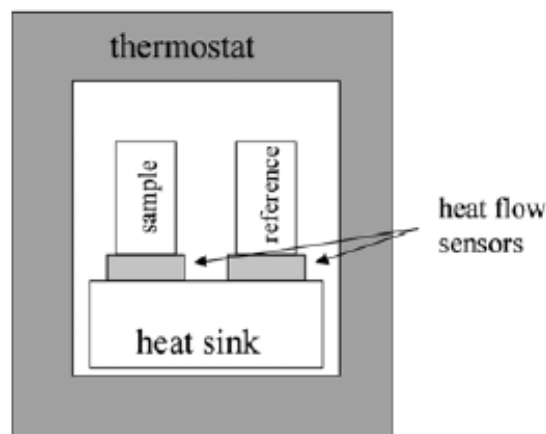


Figure 4.1 Schematic diagram of isothermal conduction calorimeter (ASTM C1702, 2017)

Applications of calorimetric studies in cement and concrete research involve the influence of mineral and chemical additives, supplementary cementitious materials, and gypsum adjustment on cement hydration and temperature rise due to hydration. Figure 4.2 provides a typical heat evolution curve of cement hydration. The initial peak (A) corresponds to the “heat of wetting” that occurs due to early dissolution of ions from

cement into the water. This is then followed by a dormant period (B). The dormant period occurs due to the dissolution of sulphate ions into the pore solution and consequent suppression of the aluminate reaction. This latent period allows the concrete to be transported and placed in formwork during construction. After the dormant period, the reaction of calcium silicates (mainly from C_3S) dominates to form calcium silicate hydrate (C-S-H) until the maximum point (D). This silicate reaction is responsible for the initial setting and early-age strength development. After the silicate reaction (F), sulphate depletion occurs and accelerates the calcium aluminate reaction. The hydration of silicates and aluminates together form the main hydration peak. Post main peak, the hydration reactions continue to happen, however at a much slower rate with little difference in terms of heat evolution.

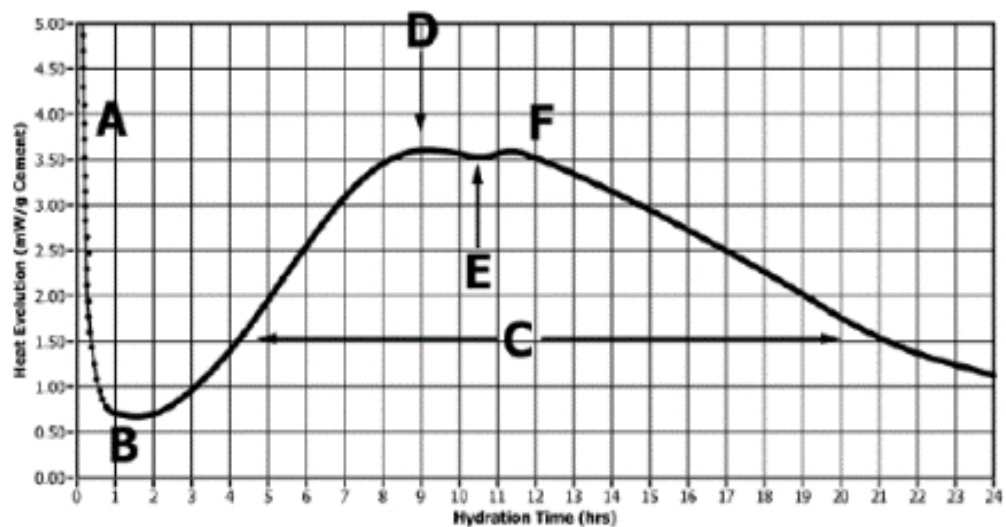


Figure 4.2 Typical heat evolution curve of cement hydration using isothermal calorimeter (ASTM C1679, 2014)

In this research, calorimetric studies are used to understand the impact of sulphate and alkali changes in cement and fly ash addition on the hydration kinetics of clinker phases such as alite, belite, ferrite and aluminate at two different temperatures (25°C & 55°C). Understanding the changes in aluminate phase hydration with sulphates to form ettringite

and other alumino-ferrite hydrates at different curing temperatures is of particular interest in this study.

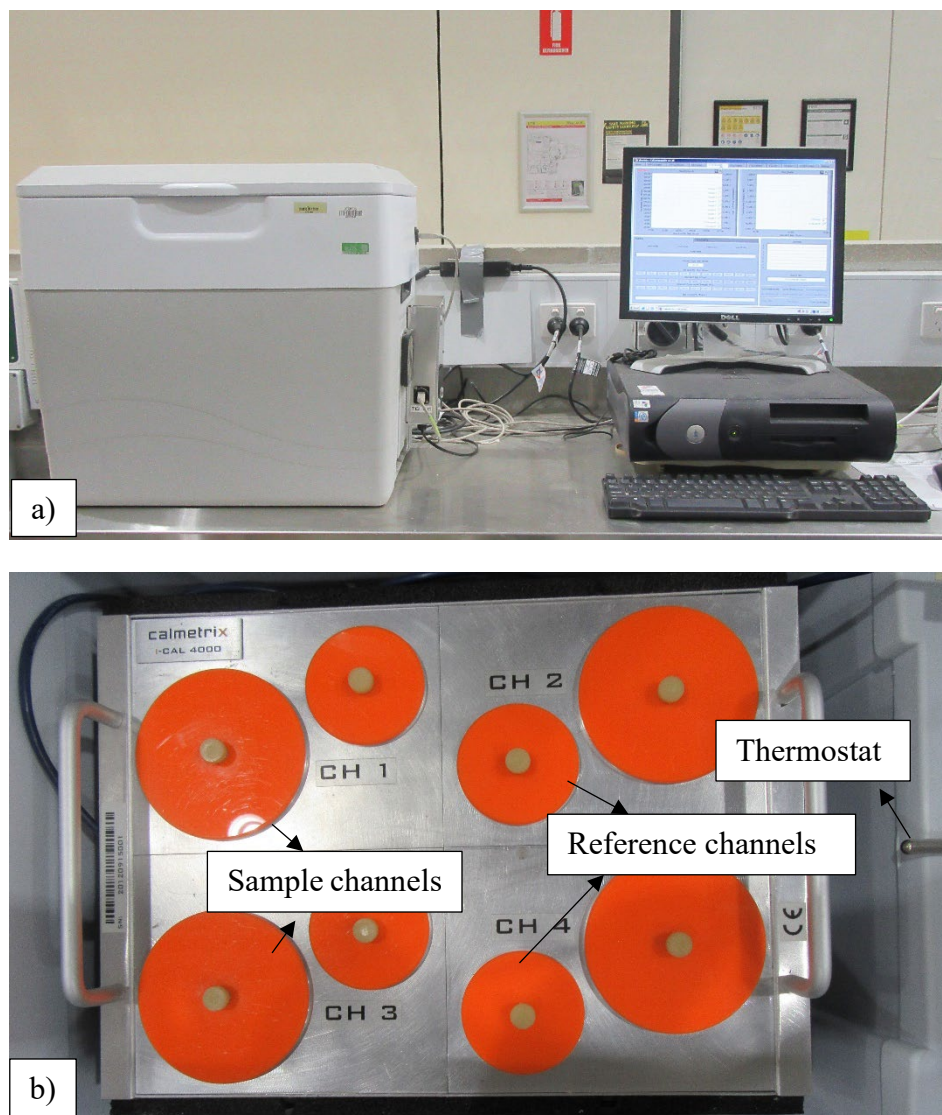


Figure 4.3 a) Calmetrix I-Cal 4000 HPC isothermal calorimeter used in this research b) Four sample channel arrangement with respective reference channels

In this research work, a computer-controlled Calmetrix I-Cal 400 HPC four-channel isothermal calorimeter (Figure 4.3.a) was used. I-Cal 400 HPC is able to run experiments at a temperature range of 5 to 60°C and can record data for up to 96 hours. Metal blocks provided by the manufacturer were used as the reference material. Before every experiment, the calorimeter was allowed to attain thermal equilibrium and then

maintained at this equilibrium for at least 24 hours. Raw materials such as cement, gypsum, fly ash and water (in some mixes, NaOH solution) were batched and stored at 23°C to attain thermal equilibrium before preparing a cement paste. On the day of each experiment, cement pastes were made with distilled water at a water to cement ratio of 0.4, using a hand-held blender by external mixing method. Sample cups were lubricated with silicone spray and the prepared cement pastes were carefully spooned into the cups. For each cement paste mix, four samples weighing 50 grams each were made. Sample cups with closed lids were carefully loaded in the sample cells within five minutes of the addition of water to the cement. The hydration characteristics data was logged for 48 hours using I-Cal logger software. In addition to the calorimetric studies, X-ray diffraction patterns were collected at two different ages of 15 and 48 hours, to understand the hydration curves with respect to early age ettringite and monosulphate formation.

4.2.2 Mortar prisms linear expansion and mass change studies

Linear expansion and mass change studies of mortar prisms are classic test methods in external sulphate attack, DEF and ASR deterioration mechanisms; any hydrate or other product formed within the hardened mortar may lead to relative linear expansion and mass changes.

Mortar prisms were prepared with the mix design of cement: sand: water = 1:2:0.45. The chemical composition of the cements was altered by calcium sulphate and sodium hydroxide addition wherever necessary. Distilled water was used for mixing mortar specimens throughout the study. Mortars were mixed according to the guidance given in AS 2350.12-2006 and cast in steel moulds of size 40 × 40 × 160 mm, in compliance with AS 2350.11-2006. Four specimens per mix were cast: 3 with steel studs at both ends to measure length changes and one without steel studs for other non-destructive testing

(NDT) and scanning electron microscopy (SEM) studies (Sections 4.2.5 Scanning electron microscopy to 4.2.6 Electrochemical impedance spectroscopy analysis).

After casting at ambient temperature, the mortars were cured in a humidity chamber at 23°C and 95% relative humidity for 24 hours. For steam curing, fresh mortar specimens (in steel moulds) were packed in an oven bag (temperature resistant up to 120°C) and placed in a steel tray, as shown in Figure 4.4a. The steel tray contained some water to stimulate steam curing conditions. This setup was then wrapped with aluminium foil (Figure 4.4b), kept in a programmable oven (Thermoline scientific TD-150F) and subjected to the respective elevated temperature curing regimes (Figure 4.5). After 24 hours, prisms were demoulded (Figure 4.4c) and subjected to further curing in saturated lime water. The saturated lime water was not renewed throughout the study.

A digital length comparator was used to monitor the expansion of prisms (Figure 4.4 d.). Readings were taken once a week until the first 90 days and, after that, once a month. The seventh-day reading was taken as the initial length, to avoid misinterpretation of early age dimensional changes as DEF related expansion. Equation (4.1) was used to calculate the percentage of expansion:

$$\% \text{ Expansion} = [L_n - L_i] \times 100 / L_i \quad (4.1)$$

Where,

L_i is the length of a specimen at 7 days

L_n is the length of a specimen at n days

The expansion values given in the results section are an average of 3 specimens.



Figure 4.4 a) Water bath containing mortar prisms in sealed oven bag b) Foil covered enclosed system inside oven c) demoulded samples cured in a humidity chamber (left) and oven (right) d) Specimen linear expansion measurement using digital length comparator

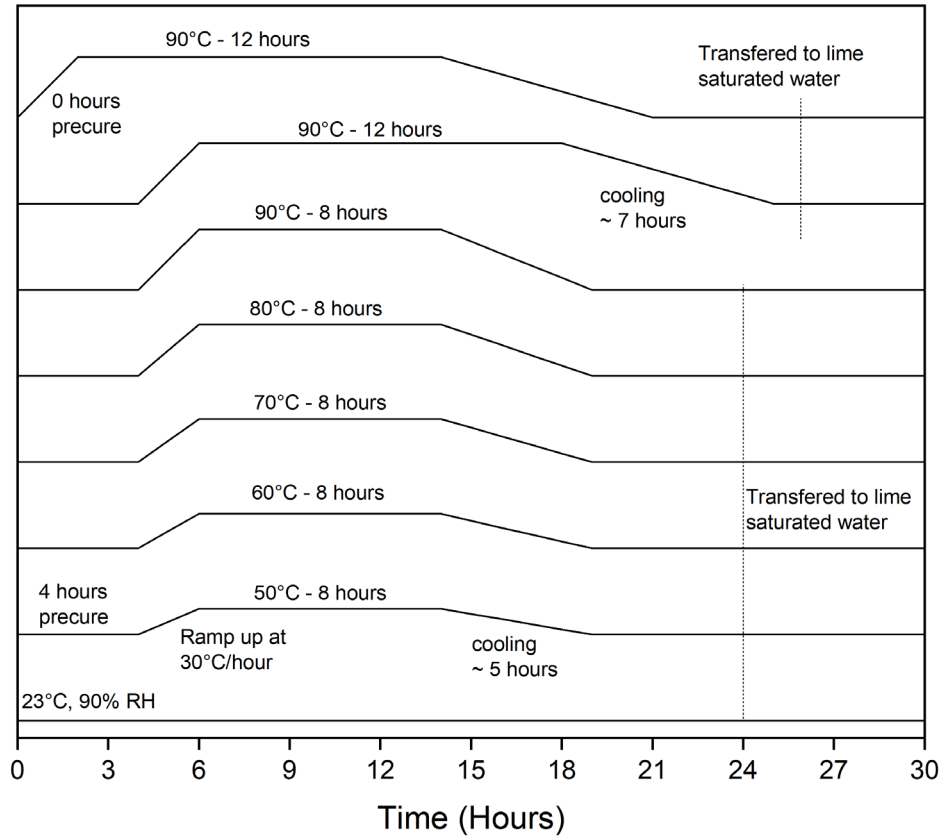


Figure 4.5 Various curing regimes used in this research

Similarly, mass changes were also monitored on $40 \times 40 \times 160$ mm prisms, considering the seventh-day reading as initial weight. Specimens were surface dried before weighing. Equation (4.2) was used to calculate the percentage of mass change.

$$\% \text{ Mass change} = [M_n - M_i] \times 100 / M_i \quad (4.2)$$

Where,

M_i is mass of specimen at 7 days

M_n is mass of specimen at n days

Mass change values given in the results section are an average of 4 specimens, until the 4th specimen was sectioned for other tests.

Linear expansion and mass change results are discussed in Chapters 6 to 9.

4.2.3 Phase development of hydrates: characterisation studies

Various factors such as curing temperature, modification of cement sulphate, alkali levels, difference in aluminates, and fly ash incorporation will affect the phase development of ettringite and other hydrates. Characterisation techniques such as X-ray diffraction (XRD), thermogravimetric analysis (TGA) and Fourier-transform infrared spectroscopy (FTIR) were utilised to understand the phase development of various cement paste systems. A detailed description of cement paste sample preparation and characterisation techniques follows.

4.2.3.1 Cement paste sample preparation

Cement pastes were prepared with a water to cement ratio of 0.4. All raw materials were stored at a constant temperature of 23°C for at least 24 hours before sample preparation. Gypsum, sodium hydroxide and fly ash were added as required (as and when necessary for the particular mix). A hand-held blender was used to mix the raw materials with distilled water until a uniform paste was obtained. The pastes were then transferred to sample vials using a disposable syringe. In case of ambient curing (at 23°C), pastes were filled in a 10 ml (2 per mix) standard vial with a closed lid. The vial was further sealed with laboratory parafilm to avoid carbonation and kept in a humidity chamber at 23°C and 95% relative humidity for 24 hours. In the case of heat curing (90°C for 8-12 hours with 4 hours pre-cure), pastes were filled in a polystyrene mould (to withstand the high temperature) of 25 ml (1 per mix) capacity. The samples were then packed in an oven bag with a steel tray bath and cured in a programmable oven (as identical to the Section 4.2.2 Mortar prisms linear expansion and mass change studies. After the initial curing (typically 24-30 hours) the hardened cement paste specimens were taken out from the vial or mould, marked and transferred to lime saturation water for further curing.

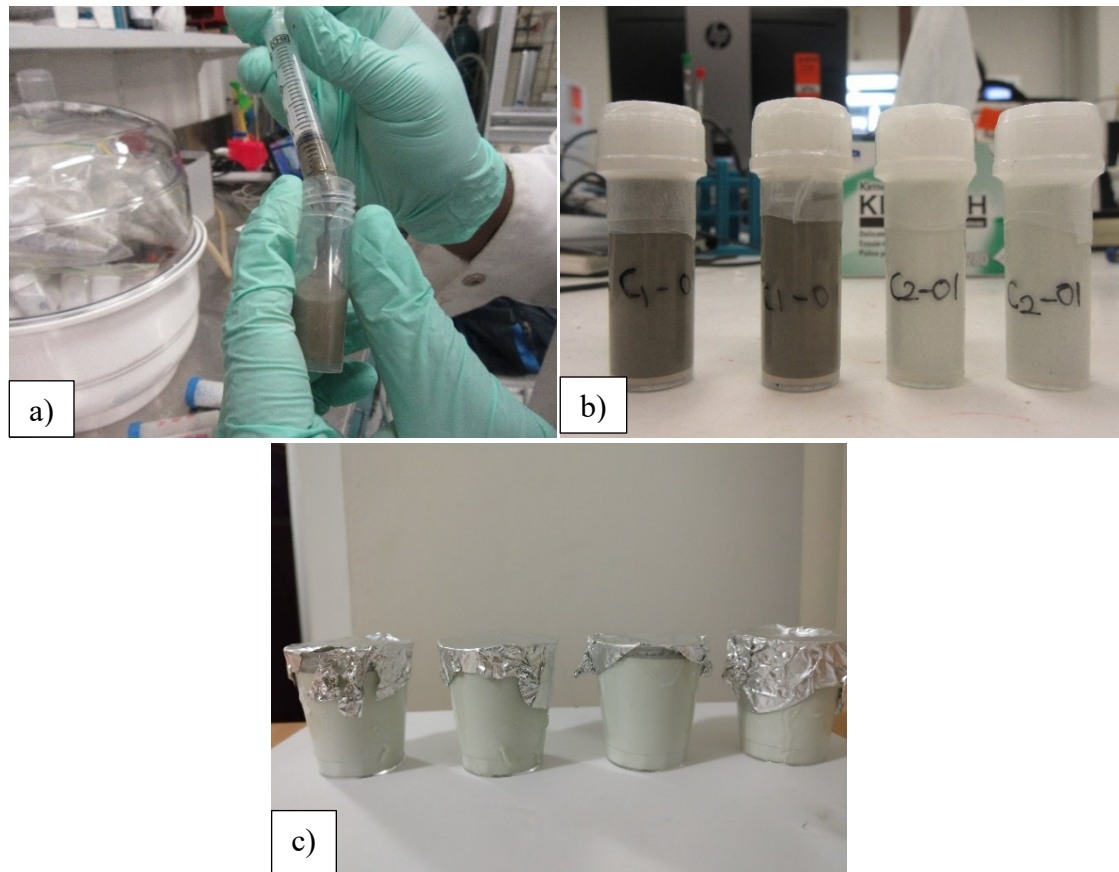


Figure 4.6 Steps involved in cement paste preparation a) injecting the fresh paste into a vial b) Samples in standard 10 ml vials ready for curing at 23°C c) Samples in 25 ml mould covered with aluminium foil prepared for heat curing at 90°C

To study the phase development of hydrates at a particular age, arresting hydration is essential. Stopping hydration ensures that no structural change occurs in hydrates between reaching the desired age and the time of testing. Compared to many hydration stoppage methods, solvent exchange using isopropanol is found to be the least destructive to the microstructure (Zhang & Scherer 2011). Since the primary interest is to study ettringite, this solvent exchange method was adopted to stop hydration. Hydration of cement pastes was arrested at the end of 1, 7, 30, 60, 300, 450 and 600 days by a solvent replacement method. The cement paste specimens were pulverised to a fine powder by grinding in a Rocklabs ring mill for one minute (Figure 4.7). Mechanical grinding to prepare samples is not recommended when the intent is to study hydration products, as it may alter the

phases (Scrivener, Snellings & Lothenbach 2016). However, in this work, after repeating the experiments many times it was seen that all the expected hydration phases were present irrespective of mechanical grinding; this could be attributed to no heat being evolved during the short grinding time (1 min). Further, it was a good compromise considering the number of samples needed to be prepared (28 samples per set) in a day. Crushed cement powder was sieved in 75-micron sieve.

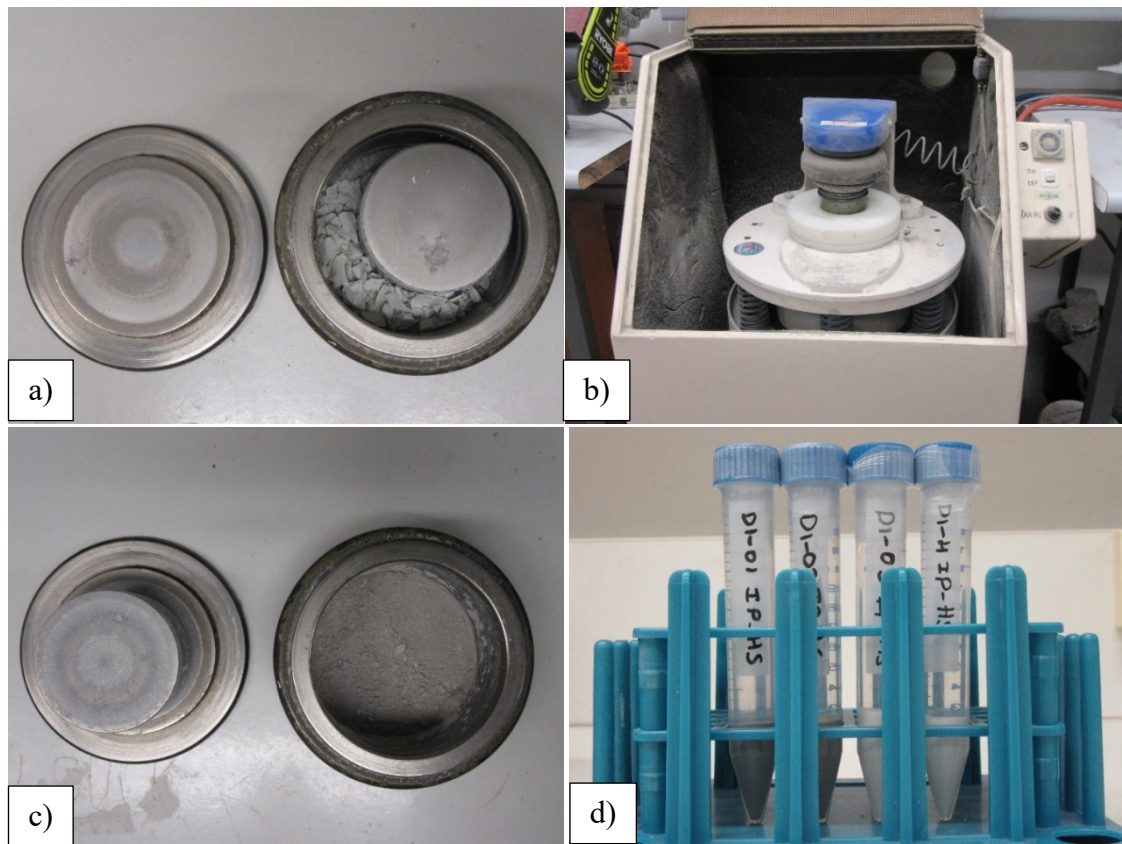


Figure 4.7 a) hydrated cement paste in holder b) grinding in disc mill c) finely ground hydrated cement paste. d) Centrifuge tube containing cement paste immersed in isopropanol

Hydrated cement powder passed through 75 microns was collected and immersed in isopropanol at a ratio of 1:10 for about 1 hour (Figure 4.7.d). The cement paste was then separated from isopropanol by filtering through Whatman 42 filter paper (pore size of 2.5 μm) under vacuum as shown in Figure 4.8. a. The residue was kept in a vacuum oven

(refer to Figure 4.8.b) at 45°C for 1 hour to evaporate any remaining isopropanol from the sample.

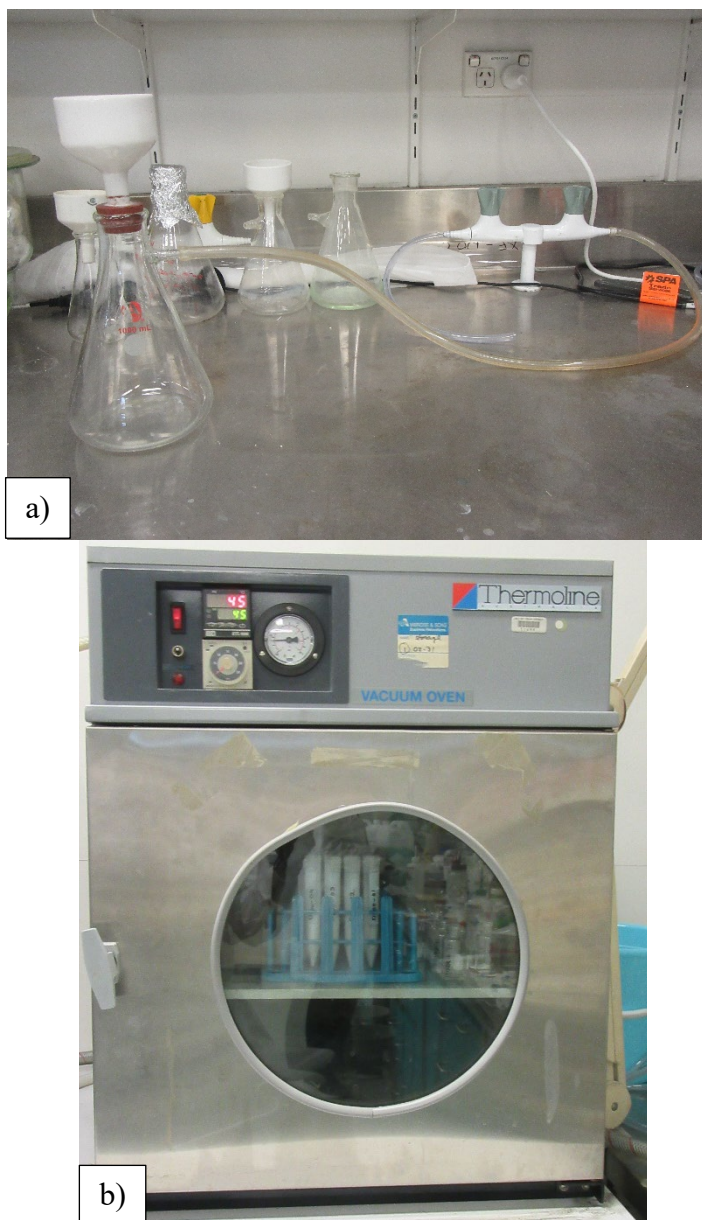


Figure 4.8 a) Vacuum filtration to separate solvent (isopropanol) from cement paste b) cement paste residue under vacuum to remove rest of solvent

The treated samples were stored in airtight centrifuge tubes. The samples were kept in a desiccator with silica gel (as a drying agent) under light vacuum until testing to avoid or minimise the microchemical changes due to moisture and carbonation. However, prolonged storage under vacuum can affect the crystallinity of ettringite (Zhang &

Scherer 2011; Zhou & F. P. Glasser 2001). The prepared samples were therefore tested within three days of preparation. The stored samples were tested for phase changes using XRD, TGA and FTIR.

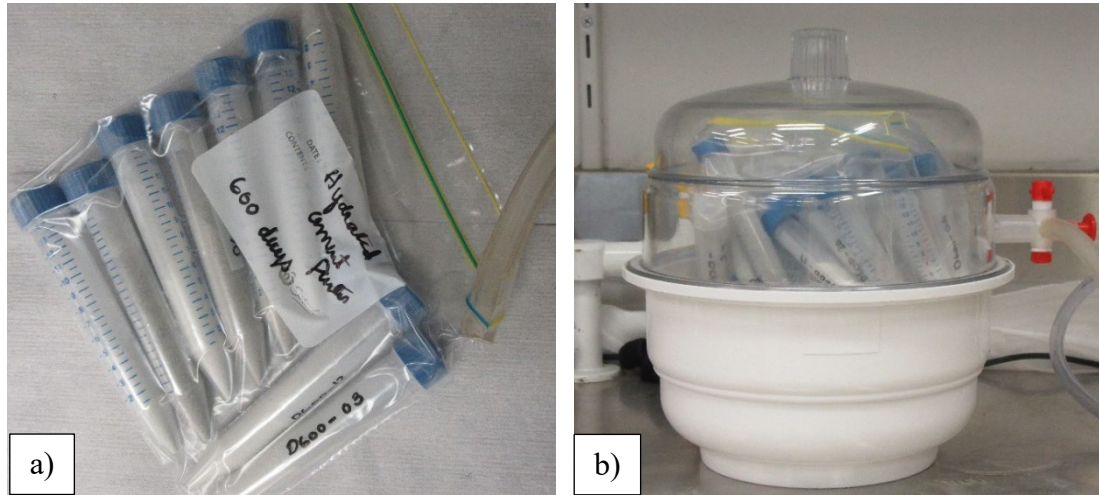


Figure 4.9 a) Vacuum packing of prepared cement paste (after hydration arrest) b) Stored in a desiccator under vacuum

4.2.3.2 X-ray Diffraction (XRD)

Application of XRD in cement and concrete research dates back many years. A well-compiled review on the history and principles of XRD, different techniques for sample preparation and applications in unhydrated cement and cement hydrates can be read elsewhere (Ramachandran & Beaudoin 2001; Scrivener, Snellings & Lothenbach 2016). In this research, XRD was mainly used to study the hydrate ettringite and other aluminoferrite phases. XRD diffraction patterns were collected using a Bruker D8-discover diffractometer (Figure 4.10.a) in Bragg-Brentano geometry configuration with $\text{Cu}_{\text{K}\alpha 1}$ ($\lambda = 1.54060 \text{ \AA}$). The goniometer radius of the instrument was 240 mm. The specimens were irradiated by the application of an electric voltage of 40 kV and 40 mA. Diffraction patterns were collected with two different angular scans with a lynxeye detector. The primary and secondary roller slit angles were 2.5° . The divergence and anti-scatter slits were 20 mm wide. Powdered hydrated cement (prepared as described in

4.2.3.1 Cement paste sample preparation) was front-loaded in sample holders and stacked as shown in Figure 4.10.b. Front loading for XRD may increase the possibility of preferred orientation, however since the XRD patterns in this research were used only for qualitative and semi-quantitative analysis the effect is likely negligible.

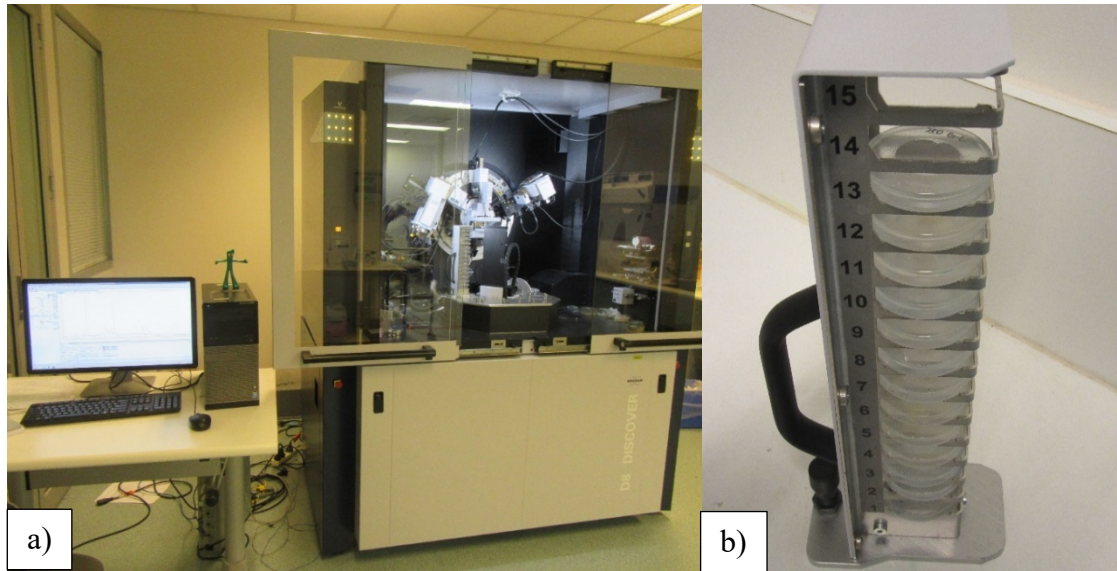


Figure 4.10 a) Bruker D8-discover X-ray diffractometer b) XRD specimens stacked in a holder

A maximum of 30 samples can be loaded at a time, and the robotic arm enables autorunning. The experiments were conducted in a nitrogen environment and the operating temperature was 25°C. An automated knife-edge was fitted to reduce background scatter. The samples were scanned from 5 to 20° 2 θ with 0.02 step size without the spin of the sample holder for 23 minutes. As ettringite and other aluminoferrite phases are the focus of this research, a 5 to 20° slow scan was preferred over a typical 5 to 80° scan at relatively short time. From the collected XRD patterns, the background and K α 2 scatter was removed and then corrected for any displacement errors using EVA software. After these corrections were applied, peaks were qualitatively analysed to identify the hydrates or minerals. In addition, the cement hydrates database collected from various research articles and XRD OCD were used to identify the element

peaks. Ettringite (9.14°) and portlandite (19.09°) peak patterns were fitted using a Lorentzian system and the area under the curves was estimated for a semi-quantitative comparison. The curve fitting and area estimates were done in Origin pro-2019 software. Results are discussed in Chapters 6 to 9.

4.2.3.3 Thermogravimetric analysis (TGA)

TGA was used for the identification and quantification of the anhydrate cement composition, cement hydrates based on the measurement of mass loss during dehydration, dihydroxylation, decarbonation, decarboxylation, oxidation and phase transition reactions. In this research, TGA curves were used to analyse the aluminoferrite phases – especially ettringite – with respect to the changes in cementitious systems, curing regimes and age, in order to understand the occurrence of DEF.

**Table 4.9 Various mass loss peak positions of cement minerals and hydrates
Bizzozero (2014); Scrivener, Snellings & Lothenbach (2016)**

Cement mineral/hydrate	Reaction	Temperature range (°C)
Ettringite, C-S-H	Dehydration	60-150
Gypsum	Dehydration	140-160
Mono/hemicarboaluminate	Dehydration	150-180
Monosulfoaluminate	Dehydration	180-200
Mono/hemicarboaluminate, AH ₃	Dehydration	250-280
Calcium aluminate hydrate	Dehydration	290-310
Portlandite	dehydroxylation	400-530
Poorly crystallised CaCO ₃	decarbonation	400-530
well crystallised CaCO ₃	decarbonation	600-800
C-S-H (conversion to Wollastonite)	dehydroxylation	800-1000
Cement paste residue	Melting	above 1200

A summary of mass loss temperatures for various cement minerals and hydration products extracted from Bizzozero (2014); Scrivener, Snellings & Lothenbach (2016) is given in Table 4.9. From the table, it is evident that there are many temperature overlaps for

different hydrates, which presents a challenge when analysing TGA patterns. However, when used alongside other techniques such as XRD, TGA can provide valuable information.



Figure 4.11 TGA STA 449 Jupiter with auto-sampler

TGA patterns were collected using a Netzsch Jupiter F5 STA (Figure 4.11) instrument with helium flowing at 40 mL/min on 20 ± 0.3 mg cement powder placed in an open alumina crucible over a temperature range of 40 to 1000°C. For every series of experiments, one empty crucible curve was collected and used for background correction. DTG curves were normalised and presented in terms of mass change with respect to per unit change in temperature. Results are discussed in Chapters 6 to 9.

4.2.3.4 Fourier-transform infra-red spectroscopy (FTIR)

In cement and concrete research, hydrates and anhydrous phases can be identified from the FTIR absorption band (Ndiaye, Cyr & Ginestet 2017) resulting from the molecular bending and stretching vibrations. In this research, changes occurring in stretching vibrations associated with C-S-H (O-H, Si-O, Al-O), portlandite (O-H) and ettringite (S-O, Al-O), as well as bending vibrations of ettringite (O-H) were studied.

Table 4.10 FTIR wavenumbers of cement hydrates (Horgnies, Chen & Bouillon 2013; Trezza & Lavat 2001)

Wavenumber/cm ⁻¹	Assignment	Associated with	Assigned notation ^{##}
3676	O-H stretch	Mono/Hemicarboaluminates	O-H ^c
3660	O-H stretch	Hydrogarnet	O-H ^h
3654, 3645-3641	O-H stretch	Portlandite	O-H ^p
3555	H ₂ O stretch	Monocarboaluminates	H ₂ O ^c
3549, 3543	O-H stretch	Monosulphoaluminates	O-H ^s
3421	H ₂ O stretch	Ettringite	H ₂ O ^e
3352	O-H stretch	C-S-H & capillary water	O-H ^{csh}
1686-1680	H ₂ O bend	Ettringite	H ₂ O ^e
1647-1646	H ₂ O bend	Mono/Hemicarboaluminates	H ₂ O ^c
1450	C-O stretch	Ettringite	C-O ^e
1426-1419	C-O stretch	Monocarboaluminates	C-O ^c
1380	C-O stretch	Monosulphoaluminates	C-O ^s
1364-1363	C-O stretch	Mono/Hemicarboaluminates	C-O ^c
1190-1150	S-O stretch	Monosulphoaluminates	S-O ^s
1115-1110	S-O stretch	Ettringite	S-O ^e
1066	C-O stretch	Monocarboaluminates	C-O ^c
1000, 985, 965	Si-O stretch	C-S-H	Si-O ^{csh}
957	Al-O stretch	C-S-H	Al-O ^{csh}
950-940	Si-O stretch	C-S-H	Si-O ^{csh}
920-911	Si-O stretch	C-S-H	Si-O ^{csh}
877-873	C-O bend	Monocarboaluminates	C-O ^c
857-855	Al-O stretch	Ettringite	Al-O ^e
812-810	Al-O stretch	Hydrogarnet	C-O ^h
781,750	Si-O stretch	C-S-H	Si-O ^{csh}
670	S-O stretch	Ettringite	S-O ^e
667	S-O stretch	Monosulphoaluminates	S-O ^s
579	Al-O stretch	Monosulphoaluminates	A-O ^s
539	Al-O stretch	Monocarboaluminates	A-O ^c
537	Al-O stretch	Hydrogarnet	A-O ^h
535	Al-O stretch	Ettringite	A-O ^e
525	Al-O stretch	Monosulphoaluminates	A-O ^s

* Not all notations are mentioned in the results as many wavenumbers associated with different cement hydrates are too close.

[#]Superscripts: c-Carboaluminates, h – Hydrogarnet, p-Portlandite, s- Sulphoaluminates, e- Ettringite, csh- C-S-H.

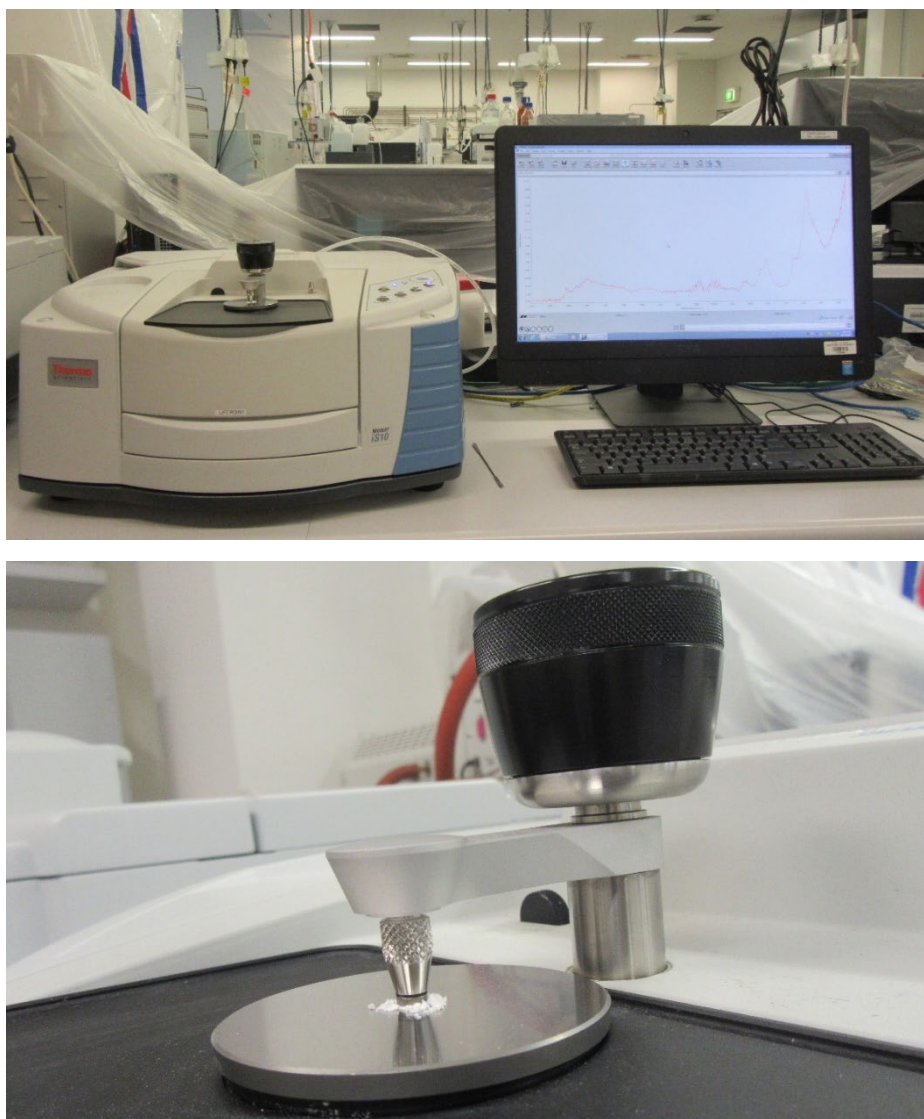


Figure 4.12 Thermo-Scientific Nicolet iS10 FTIR spectrometer b) Placing of hydrated cement powder in the sample stage.

The wavenumbers related to cement hydrates extracted from Horgnies, Chen & Bouillon (2013) and Trezza & Lavat (2001) are provided here in in Table 4.10 In this research, a Thermo Scientific Nicolet iS10 FTIR spectrometer (Figure 4.12.a) was used to collect spectra from powdered hydrated cement pastes, as shown in Figure 4.12.b. The optics of attenuated total reflection (ATR) spectroscopy was diamond crystal. Experimental settings and data logging were done through OMNIC software. The frequency used was $4000 - 400 \text{ cm}^{-1}$. Every time before collecting the spectrum of samples, background wavelength was obtained to remove water vapour and carbon dioxide from the spectrum.

64 scans were done per sample to reduce the noise. The running time was about a minute per sample. The collected spectrum bands were analysed using Table 4.10. Results are discussed in chapters 6 to 8.

4.2.4 Pore solution chemistry studies

Studying the ionic concentration of pore fluid extracted from cementitious systems can contribute to the understanding of hydration kinetics of cement (Vollpracht et al. 2016) and even deterioration mechanisms (Thomas, Hooton & Ramlochan 2010). In this research, pore solution chemistry was studied on cement paste samples to understand the aqueous phase composition differences raised due to the heat curing at different ages. The influence of adding sulphates, alkalis and fly ash in cement was also studied. This data was used to understand the chemistry of pore solutions when ettringite precipitates or is absent in the cement system, by comparing it with available XRD and TGA data. Preparation of samples, extraction and conditioning for analysis are as follows.

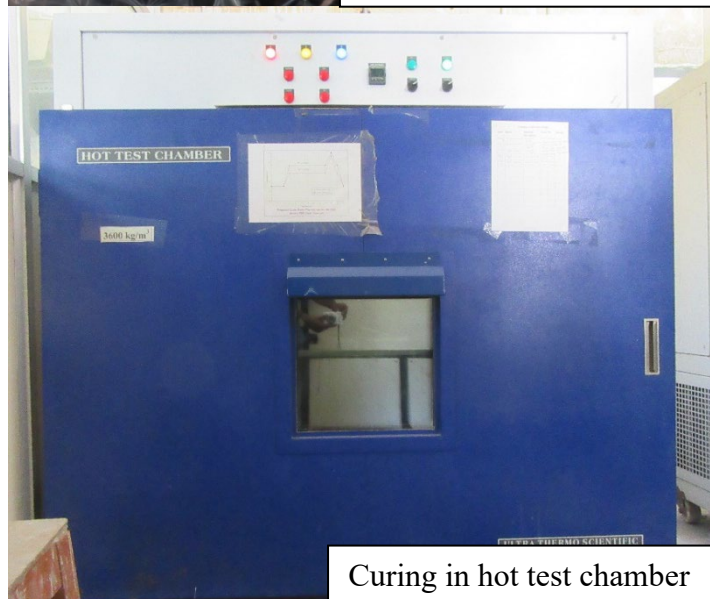
Cement paste preparation for pore solution studies is slightly different to preparation for other characterisation studies. Cement, gypsum, fly ash, sodium hydroxide and water were batched in airtight containers (Figure 4.13) and stored in a temperature-controlled room at 23°C for 24 hours before mixing. For the mixes involves alkali addition, sodium hydroxide was dissolved in water using a magnetic stirrer before storing. The water to cement ratio was 0.5 for pouring consistency, as samples were stored in narrow-neck containers. This was also to increase the chance of extracting the pore solution at later ages. Cement pastes were prepared with a high-performance mixer rotating at 1700 rpm for 2-3 minutes (Figure 4.13) and then poured into a sample container of dimension 50 mm × 150 mm with a lid and sealed with parafilm to avoid carbonation.



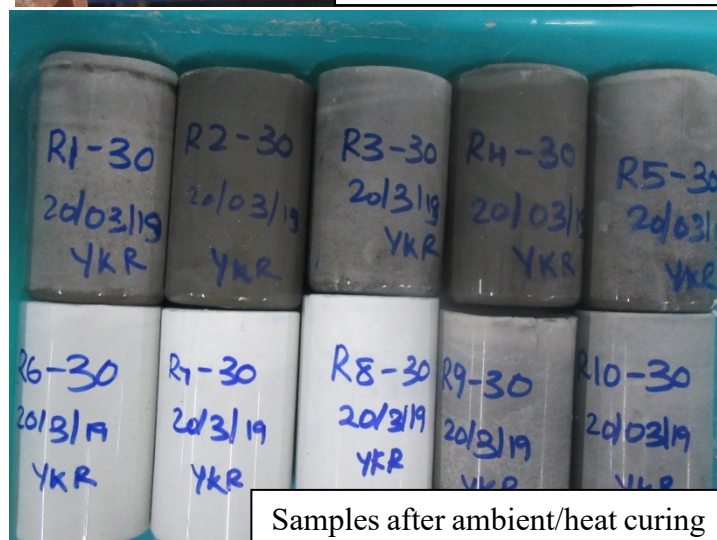
Figure 4.13 Cement paste preparation for pore solution extraction



Wrapping for heat curing



Curing in hot test chamber



Samples after ambient/heat curing

Figure 4.14 Heat curing steps for pore solution samples

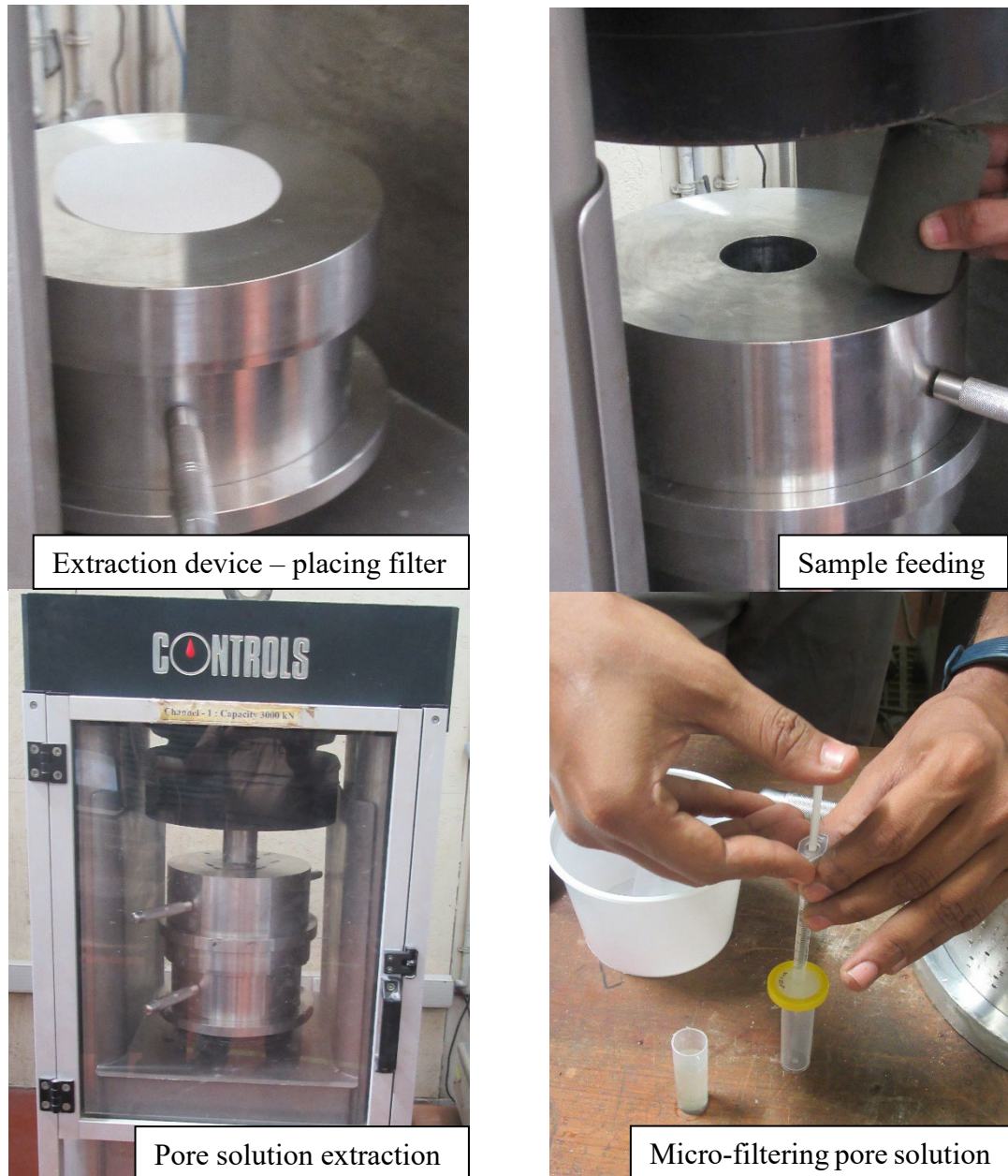


Figure 4.15 Pore solution extraction and micro-filtration

Ambient cured samples were kept in a temperature-controlled room at 23°C. In the case of heat-curing, samples were packed in an oven bag (Figure 4.14) with a steel tray water bath and cured in a cyclic hot test chamber at 90°C for 12 hours. After the initial curing, samples were demoulded (Figure 4.14) and stored in saturated lime water for further curing. A pore solution extractor (shown in Figure 4.15) fabricated in IIT Madras, India was used. Pore solutions were extracted from the samples at the ages of 4 hours, 30 hours,

7 days and 30 days using the extractor, by applying a load of 800 kN at a rate of 2000 N per second. The maximum load was then sustained for 5 minutes to extract the pore solution. In the case of 4-hour old samples, a maximum load of 50 kN was sufficient to obtain pore solution. 5-8 mL of pore solution was collected in a vial. This was then filtered using a 0.2 μm micro-filter (Figure 4.15). 1 mL of filtered pore solution was then transferred to a 15 mL centrifuge tube and diluted with 8.8 mL of ultra-pure water and 0.2 mL of 69% concentrated nitric acid as shown in Figure 4.16. Acidification was done to avoid precipitation of stable phases during storage. The total dilution ratio was 1:10. The centrifuge tube was tightly closed and sealed with parafilm to avoid carbonation and stored in the refrigerator below 5°C until testing. The remaining 4-7 mL of pore solution was used to measure pH with a EUTECH thermo-scientific electrode (as shown in Figure 4.16).

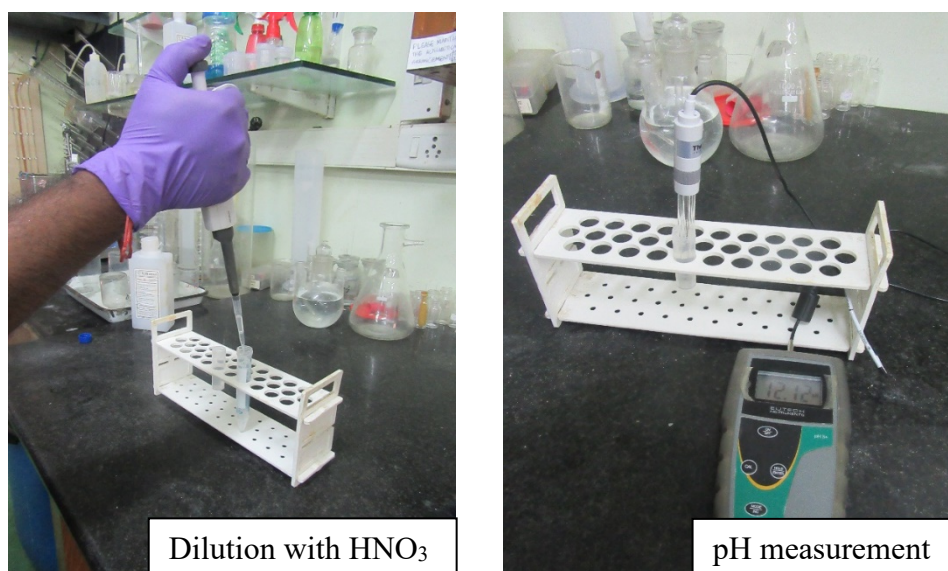


Figure 4.16 HNO₃ dilution and pH measurement of the un-diluted pore solution

After pH reading, the pore solution was poured into a plastic vial with a parafilm seal and stored in the refrigerator below 5°C as a backup. In case of any discrepancy in results, this backup pore solution could be diluted and acidified to re-test, rather than repeating

the entire process. The diluted pore solution was tested for ionic concentrations using Perkin Elmer Optima 5300 DV (Figure 4.17) inductively coupled plasma-optical emission spectroscopy (ICP-OES). The testing was outsourced to SAIF, IIT Madras, India. Calcium (Ca), aluminium (Al), silica (Si), sodium (Na), potassium (K) and sulphur (S) ion concentrations were recorded.

The detection limits and calibration range are given in Table 4.11. Hydroxyl ions (OH^-) were calculated using equation 4.3.

$$[\text{OH}^-] = 10^{(-\text{pH}/14)} \dots\dots\dots (4.3)$$



Figure 4.17 ICP-OES Perkin Elmer Optima 5300 DV

Table 4.11 Detection limits and calibration standard range of elements tested

Elements	Wavenumber (nm)	Detection limit (mmol/L)	Calibration standard range (ppm)
Al	308.215	0.017	0-100
Ca	317.933	0.002	0-100
K	766.490	0.000	0-1000
Na	589.592	0.030	0-100
S	181.975	0.007	0-100
Si	251.611	0.004	0-100

4.2.5 Scanning electron microscopy (SEM)

SEM was used to understand the later age ettringite deposit locations in the microstructure and the implications such as microstructural deterioration, expansion, etc. Representative specimens were prepared from selected mortar mix prisms, after the prisms reached saturation with respect to linear expansion (at age 500 days). Specimen preparation vital to this study and so the various steps involved in the sample preparation are given in Figure 4.18 and Figure 4.19 and explained in detail here. Prisms were thin-sectioned using a Struers labotom-15 to a thickness of around 5 mm. All representative samples were sectioned 20 mm from the edge of the prism, as higher localised accumulation of DEF is anticipated to occur in the edges of a specimen (Yang & Sharp 1996). Hydration was stopped by solvent exchange, by immersing the thin-sectioned sample in isopropanol for five days. The quantity of isopropanol was 50 to 100 times that of the sample mass. After five days, the sample was taken out and stored for 2-3 days in a desiccator for vacuum drying. The dried sample was then impregnated with Struers EpoFix low viscous epoxy resin and hardener (resin to hardener ratio of 3:1) under vacuum (1-3 mbar) by using Struers CitoVac impregnation unit. After 24 hours of curing, the resin-impregnated sample was removed. Before polishing both sides, the resin hardened specimens were checked for flatness. If the backside was not flat, this was corrected using a P400 or P600 paper level. Coarse polishing was done with a P1200 sheet until the resin on top of the specimen was cleared. Typically, this process took 5 to 10 minutes of polishing at 200 rpm. After that, the sample was rinsed in isopropanol under an ultrasonic bath to remove residues. The coarse P1200 was then removed, and a polishing disc was attached to the machine. The specimen was polished using Struers 9 μm diamond spray for about 60 minutes. A diamond dispersant was sprayed before the diamond spray to enhance the

uniform dispersion of diamond particles in the polishing disc. After 30 minutes, an ultrasonic bath with isopropanol was used to ensure no contamination remained.

After every round of polishing the specimen was checked using an optical microscope for the goodness of polishing. Before commencing the next polishing round, the disc was cleaned with dishwashing liquid and water to remove contaminants. These steps mentioned above was repeated at 3 μm and 1 μm . The polishing time with each size of diamond spray was not constant. Practice, personal adjustment and optical microscope checking are critical in achieving good polishing. Once the polishing was satisfactory, the specimen was coated with Au-Pd to a thickness of about 9-10 nm under vacuum. Until testing, specimens should be stored in a desiccator under light vacuum. With the prepared specimens, BSE imaging, EDS elemental mapping, line scan and point scans were done at the areas of interest. Since this research work is carried out in two different universities, two different SEMs were used for different purposes.

SEM-BSE imaging

SEM-BSE imaging was done using Quanta FEQ 200 microscope in IIT Madras, India as this microscope offers high-resolution images with proper grey contrast levels to differentiate various hydrates within the microstructure. The accelerating voltage was 20 to 30 keV under high vacuum mode, and the working distance was ~ 10 to 12 mm.

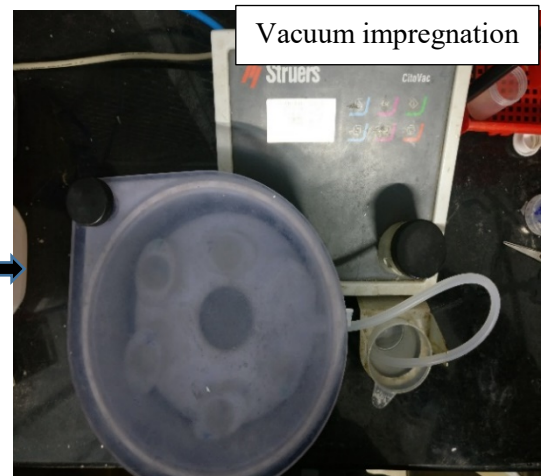
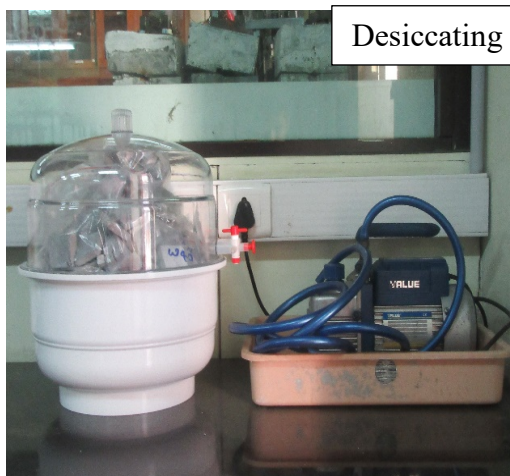
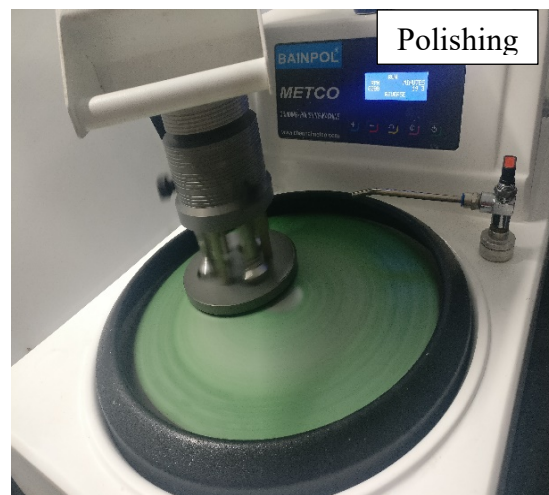


Figure 4.18 SEM sample preparation: Thin sectioning to resin mounting



Lubricant, diamond sprays



Polishing

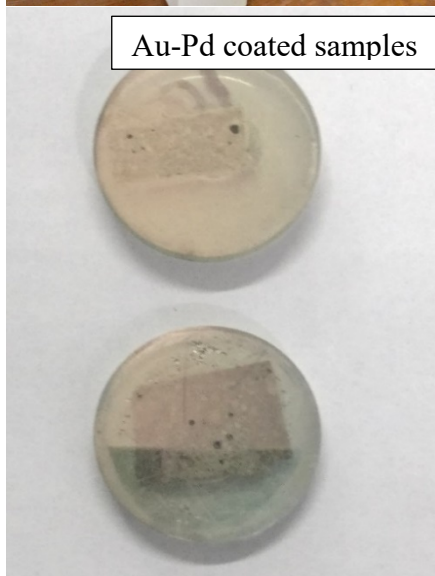


Optical microscope

To check polishing level



Spin coating



Au-Pd coated samples



Mounted samples in desiccators

Figure 4.19 SEM sample preparation: Polishing, Au-Pd coating and storage

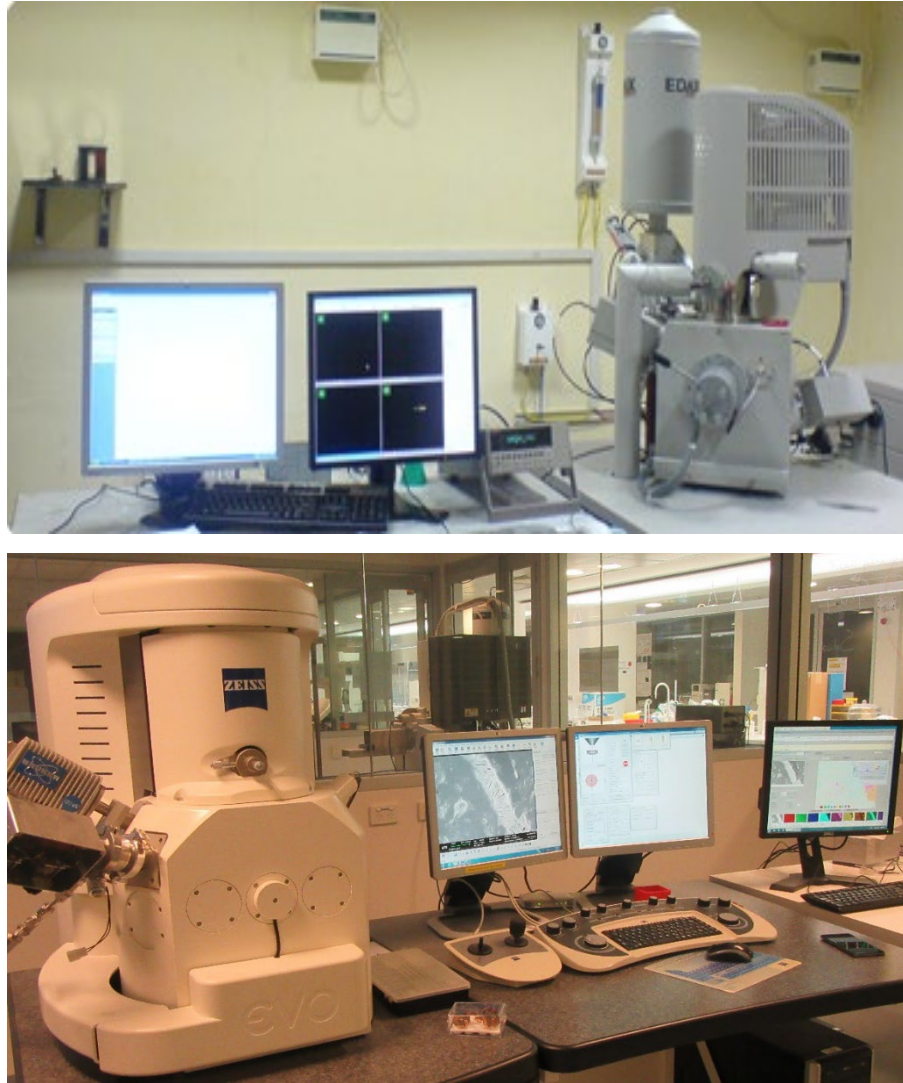


Figure 4.20 a) FEI Quanta FEG 200 High-resolution SEM with EDAX b) Carl ZEISS EVO SEM with EDS

Elemental mapping

Elemental mapping was done on areas of interest in a specimen with Zeiss EVO SEM fitted with Bruker Nano Quantax EDS detector in UTS Microstructural Analytical Unit. The accelerating voltage was 15 keV with a spot size I-probe 1nA under high vacuum mode. The working distance was ~10 to 12 mm. Elements such as Na, K, Ca, C, Si, S and Al were identified and allocated a fixed colour. Overlapping of the elements was checked to determine the cement hydrates such as ettringite.

EDS point scanning

Point scanning was done at multiple locations (~50 to 75) of interest in a sample. The Zeiss EVO SEM fitted with Bruker Nano Quantax EDS detector was used. The accelerating voltage was 15 keV with a spot size I-probe 1 nA and the minimum working distance was 10 mm. Elements such as Na, Mg, K, Ca, C, O, Si, S, Fe and Al were quantified. In this report, an elemental intensity graph of each point is not presented, considering the ~50 to 75 points taken per sample. Instead, the EDS data is presented as atomic ratio plots (using S/Ca and Si/Ca).

4.2.6 Electrochemical impedance spectroscopy analysis

A cementitious system (cement paste/mortar/concrete) is electrically conductive when a potential difference is applied as it has pores and cracks filled with pore solution (Christensen et al. 1994). The electrical impedance shall be attributed to cement hydrates.

The degree of electrical conductivity mainly (up to 90%) depends on the amount Na^+ , K^+ and OH^- ions present in the pore solution (Snyder et al. 2003). However, the connectivity of pores and cracks decides the path of movement of ions in pore solution, thereby presenting a physical component that impacts conductivity (Guangling 2000). Henceforth, by principle the electrical impedance gives vital information about the degree of hydration (Christensen et al. 1994; Kim, Kim & Yoon 1995), quality of microstructure (Xu et al. 1993) and physical properties (Taylor & Arulanandan 1974; Wei, Tian & Xiao 2010). Recently the deterioration of mortars due to ASR was studied by Shi, Zheng & Xu (2017) denoting the potential of this technique to study other similar deterioration mechanisms such as sulphate attack and DEF.

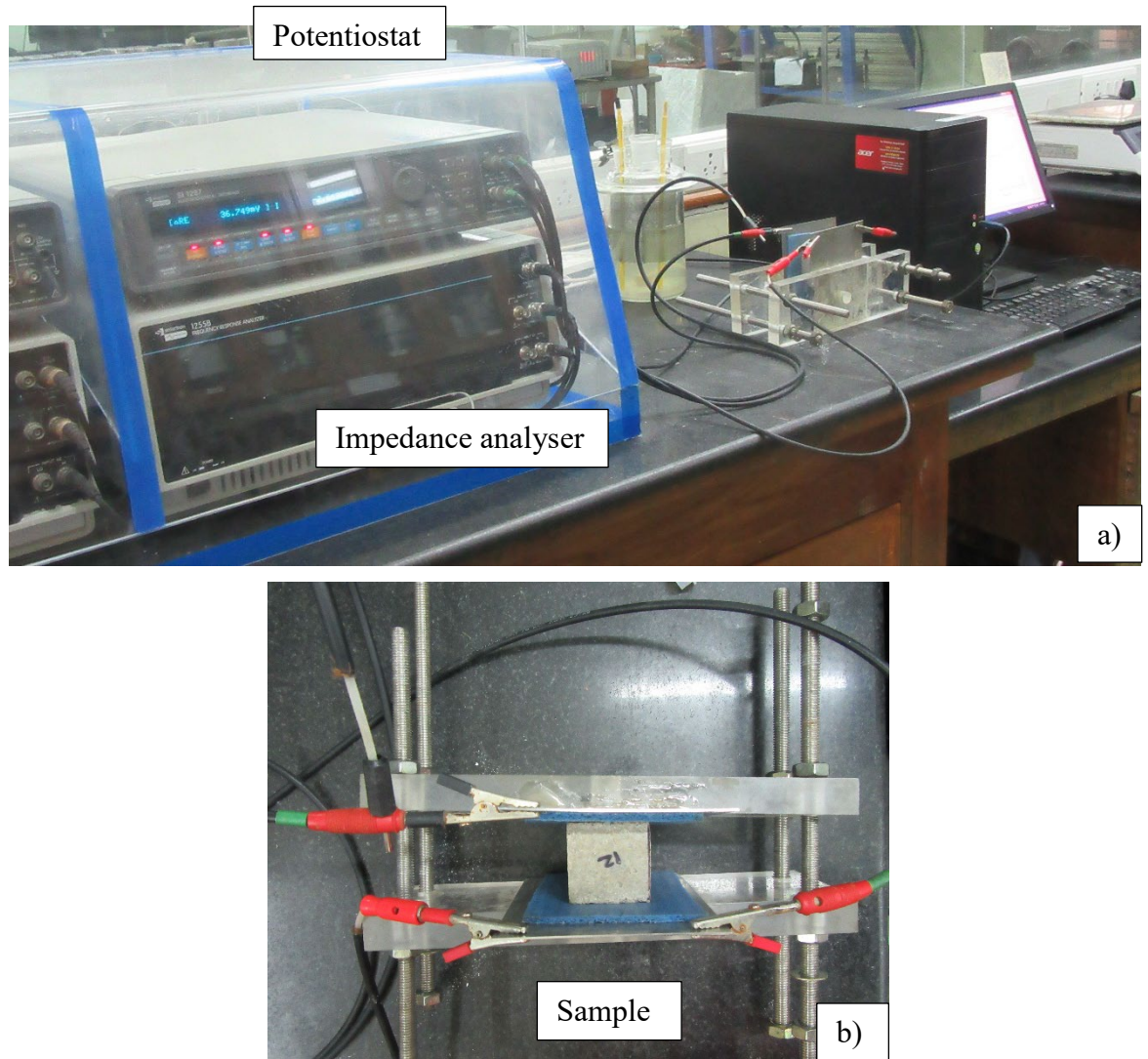


Figure 4.21 a) EIS setup with a potentiostat and impedance analyser b) a mortar sample clamped in the cell set up

In this research, electrical impedance spectroscopy (EIS) is used to understand the impact of heat-curing in various cementitious systems on microstructure and its relevance on DEF. A computer-controlled Solartron 1260 EIS instrument, comprising a potentiostat and impedance analyser, was used to record impedance over a frequency range 0.1 Hz to 1 MHz with an AC voltage of 250 mV. The experimental setup is shown in Figure 4.21.a. The equivalent circuit for cement mortar and electrode used in testing equipment is given in Figure 4.22, along with the corresponding theoretical Nyquist plot from EIS. The

equivalent circuit was modelled in ZView® software. The technical details about modelling equivalent circuits for cementitious systems can be found elsewhere (Guangling 2000; Sun et al. 2017); only information essential to follow this thesis is provided here. The arc starting (Figure 4.22) from R0 to R1 corresponds to the impedance response for the applied AC voltage offered by a specimen under test. The arc starting from R1 corresponds to the impedance response offered by the electrodes in the testing equipment. The greater the offset distance from the axis origin to the abscissa R0, lesser the porosity in the specimen (Shi, Zheng & Xu 2017). A larger arc between R0 to R1 indicates a less conductive pore solution, less connected pores and a higher degree of hydration. However, the R0 can be influenced by the conductive nature of the coaxial cables and sample holder, especially in the higher-order frequency range, so the data must be interpreted with caution. R1, the intersection point between the mortar and electrode is the lowest impedance offered by the specimen, and is more reliable than R0 (Christensen et al. 1994).

Mortar cubes of 40 × 40 × 40 mm dimensions were used for this study and kept in saturated lime water prior to testing. The specimens were about 500 days old, similar to the SEM studies. As shown in Figure 4.21.b, the mortar cubes were clamped to the sample holder along with a wet sponge and positive/negative terminals were clipped to the electrodes. The measurements were recorded at a constant temperature of 20°C. A sample result obtained for a mortar specimen has been given here in Figure 4.23, which is called as Nyquist plot. Unlike the theoretical spectrum in Figure 4.22, the impedance spectrum of mortar is not a perfect semi-circle. For analysis, the mortar impedance arc (marked) alone is considered, eliminating the electrode impedance.

The intersection point between the mortar and electrode is taken for the bulk resistivity calculations as described by Christenssen et al. (1994) and McCarter, Garvin & Bouzid (1988) with geometry factor correction of the specimen.

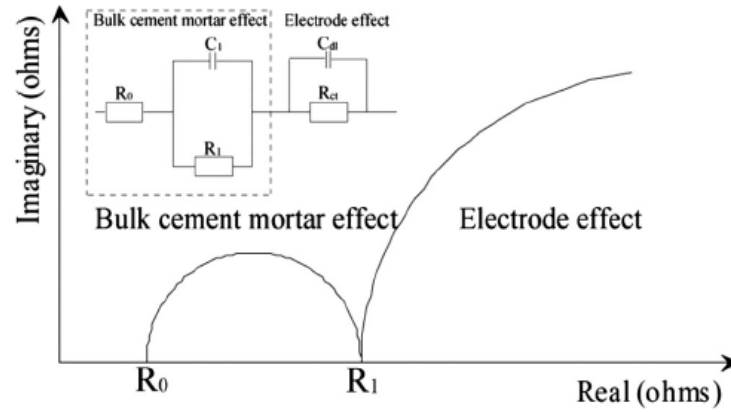


Figure 4.22 Electrical equivalent circuit for cement mortar with an electrode and resultant theoretical impedance spectrum (Sun et al. 2017)

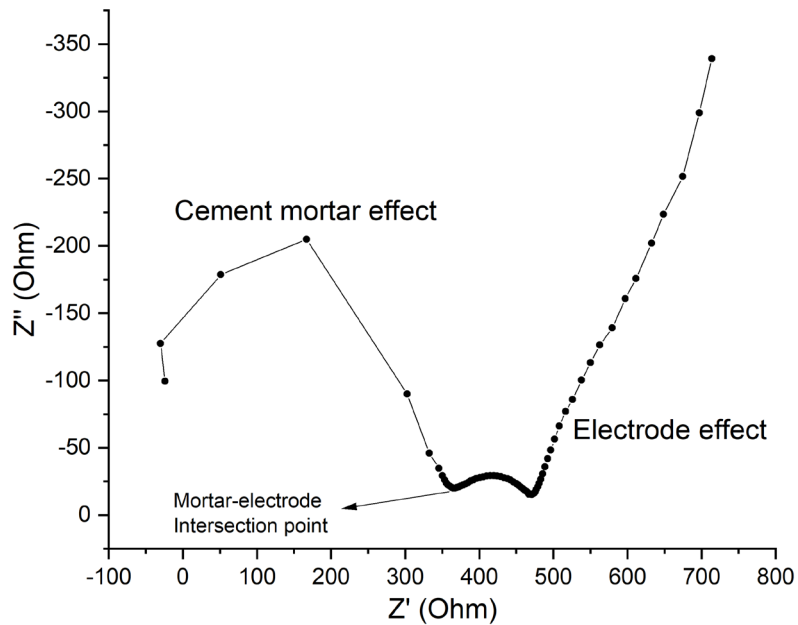


Figure 4.23 Typical EIS Nyquist plot for a cement mortar along with electrode

The relation between resistivity and impedance (Spragg et al. 2014) is as follows,

$$\rho = I \cdot K \quad (4)$$

Where,

ρ – bulk resistivity

I – Lowest impedance value of mortar

$K = A/L$ – Geometry correction factor; A – area of the specimen, L – length of the specimen

The impedance arcs and bulk resistivity of various cement mortars are discussed in chapters 6 to 9.

Chapter 5 Early age hydration characteristics of various cementitious systems

This chapter presents a detailed study of the early age hydration characteristics of cementitious systems of interest. The literature review suggests that curing temperature and cement sulphate, alkali and aluminate contents are vital factors in contributing to DEF. Hence, studying the impact of identified DEF factors in early age hydration is a prerequisite in understanding the later age implications. In this study, the effect of increasing cement sulphate, alkali content and incorporating fly ash are studied, in terms of hydration kinetics, changes in alite (C_3S), aluminate (mostly C_3A) hydration, ettringite precipitation and total energy evolved under two different temperatures: 23°C and 55°C. Refer Table 4.1 for the mixes used in this study. Cement in as-received condition, i.e., with no additional sulphate, alkali or fly ash addition, is taken as the reference hydration curve. First, 24 hours of hydration behaviour is collected and presented here, after normalising with respect to per gram of binder. XRD data was collected at the age of 15 hours (time elapsed since adding water to cement) to understand the ettringite precipitation to support the hydration curves.

5.1 Early age hydration of sulphate and alkali modified cements at 25°C

Figure 5.1.a and b show the hydration evolution and cumulative heat energy of Cement 1 (C1) mixes with variable sulphate and alkali. Typical cement hydration stages are marked on the reference mix C1-25°C. The rapid dissolution of potassium, sodium, calcium, aluminium and silicate ions in the higher degree undersaturated solution leads to the “heat of wetting” that is apparently visible during the first few minutes of hydration. This rapid dissolution of the ions in the higher degree of undersaturated pore solution forms etch pits over C_3S (Juilland et al. 2010) that are partly responsible for the released heat, with an

enthalpy of -138 kJ/mol (Thoenen et al. 2014). In this stage, some calcium silicate hydrate (C-S-H) and ettringite (Et) are formed.

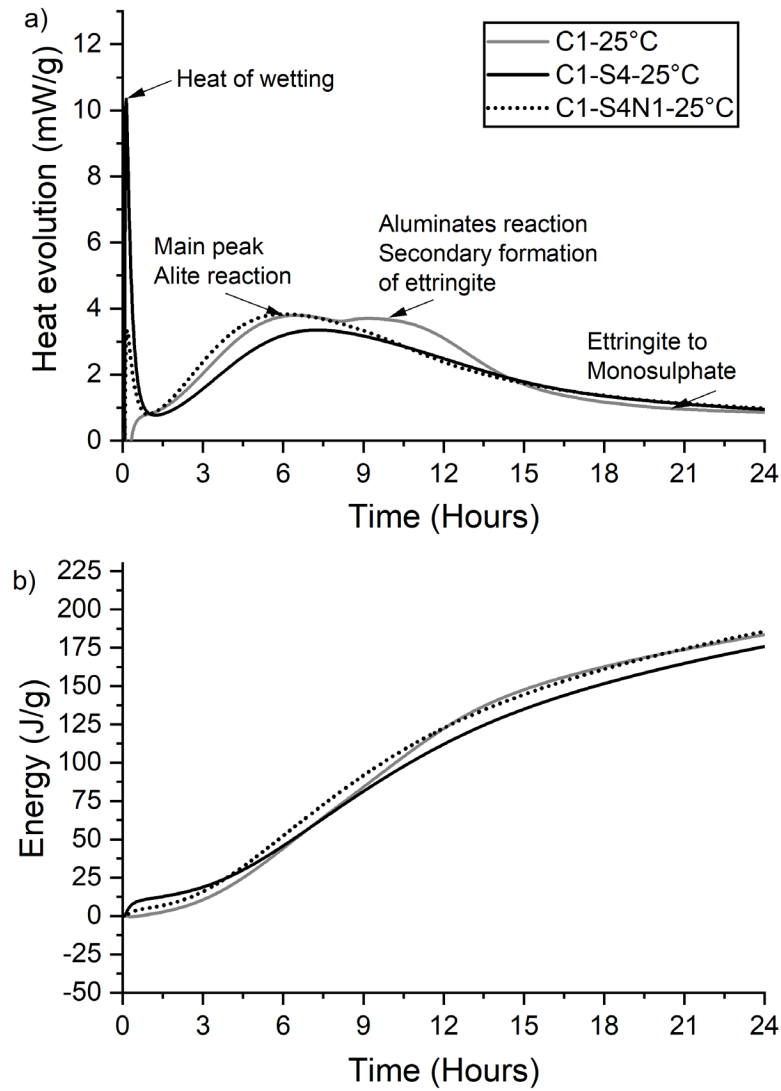


Figure 5.1 a) Hydration and b) cumulative heat evolution of Cement 1 (C1) mixes at 25°C with variable sulphate and alkali

After the initial burst, the rate of hydration slows down and enters the dormant stage. The slow rate of hydration and lower heat evolution are attributed to the less under saturated pore solution, which drastically reduces the rate of dissolution (Scrivener, Juilland & Monteiro 2015). Sulphates in the pore solution also retard the dissolution of C_3A during the dormant phase. After the latent period, hydration reactions are accelerated to form

C-S-H and CH from C_3S , which is marked as the main hydration peak in Figure 5.1.a. After the alite reactions, hydration of C_3A dominates and gives a second peak in the hydration curve. In this stage, Et precipitates, often termed as ‘secondary formation of Et or renewed Et (Bullard et al. 2011). After renewed Et precipitation, the rate of hydration slows down. Around 20-24 hours, a mild shoulder in the rate of hydration denotes the reaction of Et (part of) with C_3A to give monosulphate (Ms).

When the cement sulphate content was increased to 4% (C1-S4-25°C), the dormant period was sustained for longer. The increase in retardation stems from the availability of more sulphates ions adsorbing to C_3A , thus decreasing dissolution (Zhang 1990). The duration of the induction period depends on the amount of sulphates (Chen & Juenger 2011; Lerch 1946). Because of this, the main hydration peak was delayed by about an hour for C1-S4-25°C when compared to C1-25°C. Also, the alite peak was reduced by a magnitude of 0.45 mW/g for C1-S4-25°C compared to C1-25°C. The same trend was reflected in the cumulative heat energy (Figure 5.1.b). In 4% sulphate and 1% alkali cement mix (C1-S4N1-25°C), the impact on retardation of C_3A hydration recovered. Furthermore, hydration was accelerated, resulting in a mixture of alite and aluminate reactions that reached a peak at 6 hours, which is 0.5 hours faster than C1-25°C. The faster reaction could be due to the additional alkali ions increasing the dissolution of C_3A . In terms of peak height, C1-S4N1-25°C was higher than the other two mixes, as was the cumulative heat. In both mixes with added sulphates (C1-S4-25°C and C1-S4N1-25°C), the aluminates reaction peak to form Et was not separately visible, suggesting it may have occurred alongside the alite reactions. The peak corresponding to partial conversion of Et to Ms was also not visible.

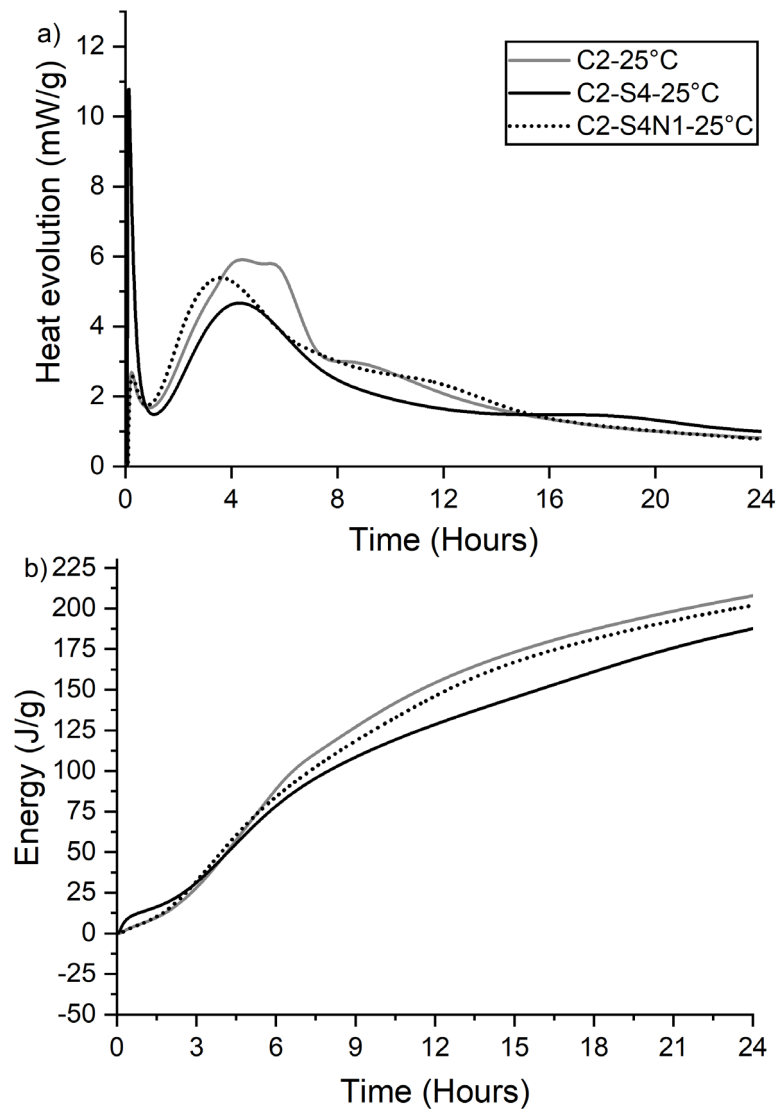


Figure 5.2 a) Hydration and b) cumulative heat evolution of Cement 2 (C2) mixes at 25°C with variable sulphate and alkali

In Cement 2 (C2) mixes, similar trends of C_3S hydration were observed (Figure 5.2.a) for sulphate and alkali increase. However, the differences lie in the rate of hydration reactions and in the heat energy evolved. Comparing C1 and C2 reference mixes (C1-25° & C2-25°), C2 reached the main peak height 2.1 hours sooner and the heat evolved was 2.12 mW/g higher. The accelerated reaction and higher heat evolution could be attributed to the higher specific surface area (Hu, Ge & Wang 2014) and C_3S content of Cement 2 (420 m^2/kg , 56.3%) compared to Cement 1 (395 m^2/kg , 49.9%). Further, the aluminate reaction

peak of C2-25°C is much higher than the C1-25°C, possibly due to the higher C₃A content (7.4 % for C1 and 11.2 for C2). Another notable difference in C2 mixes is in the partial conversion of Et to Ms. While in C1 mixes the conversion of Et to Ms shoulder peak is not visible, C2 mixes exhibit it clearly. The time of Et to Ms occurrence varies according to the chemical modifications to C2 (with respect to sulphate and alkali).

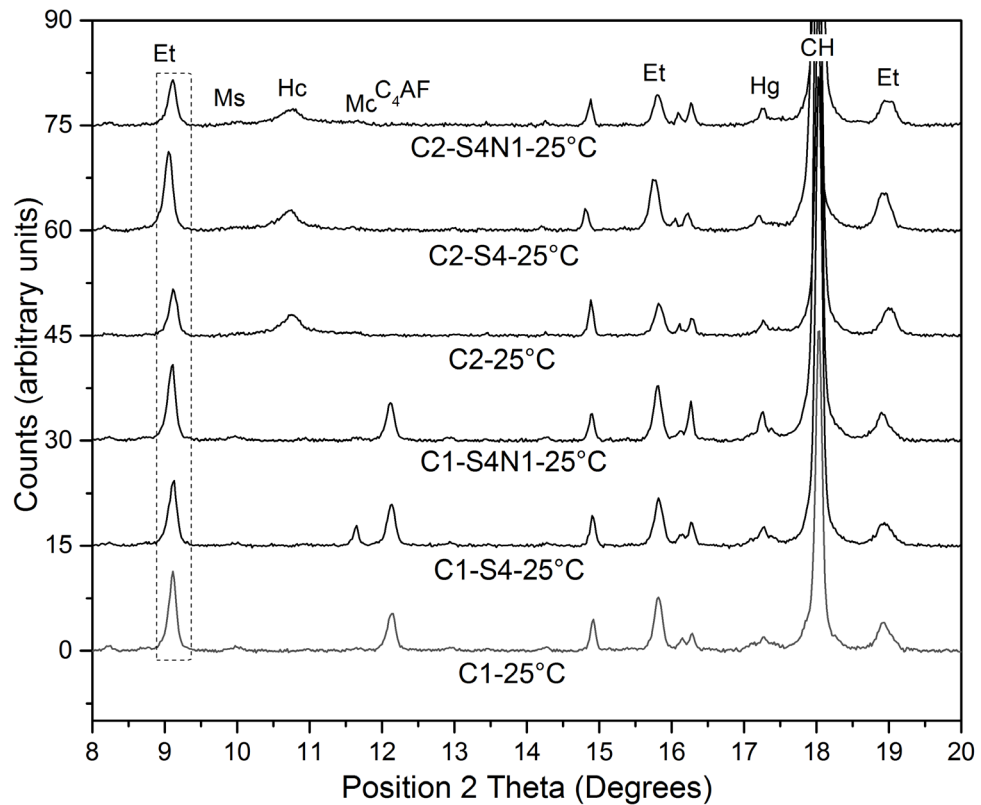


Figure 5.3 XRD patterns of Cement 1 (C1) and Cement 2 (C2) mixes at 25°C-15 hours with variable sulphate and alkali

In the reference mix C2-25°C, the Et to Ms occurred at 9-11 hours (Figure 5.2.a). In 4% sulphate cement (C2-S4-25°C), it pushed to around 17-22 hours. In 1% alkali cement (C2-S4N1-25°C), the Et to Ms conversion occurred much earlier at about 10-13 hours. XRD patterns of all the mixes discussed above are presented in Figure 5.3. It is evident that when the isothermal condition is 25°C the Et peaks are steady in all mixes, irrespective of different cements and chemical modifications.

5.2 Early age hydration of sulphate and alkali modified cements at 55°C

The cement systems discussed in Section 5.1 Early age hydration of sulphate and alkali modified cements at 25°C then subjected to isothermal conditions of 55°C. The impact of the elevated-temperature environment on hydration reactions and crystalline phase evolutions is discussed here. Since cement hydration is an exothermic reaction (de Rojas et al. 1993), the additional thermal energy supplied accelerated the process (Tydlitát et al. 2012), and more heat was evolved compared to the 25°C conditions (Escalante-García & Sharp 1998) (Figure 5.4). The initial 15-hour rate of heat evolution data has been presented here as a 24 hours scale was insufficient to distinguish the different peaks, given the accelerated timeline of the reactions.

By comparing Figure 5.1.a and Figure 5.4.a, the C1 reference mix reached the main hydration peak around 2.13 hours at 55°C curing compared to 6.5 hours at 25°C. Additionally, the heat evolution increased from 3.8 to 27.7 mW/g. The other two cement systems C1-S4 and C1-S4N1 also followed the same trend, with relatively less heat evolved from the hydration reactions. In C1-55°C, the aluminate reactions started to dominate the alite, resulting in a shoulder peak for C_3S at around 1.5 hours. However, in the C1-S4-55°C and C1-S4N1-55°C mixes a clear differentiation of alite and aluminates hydration peaks can be seen, indicating the accelerated formation of C-S-H before Et and other aluminoferrite phases from aluminates.

Although it is normal for alite to react earlier than aluminates when cements are properly sulphated, the elevated temperature changes the dynamics here. At the higher temperature, the sulphate content (2.37%) in the reference cement C1 (relatively less sulphate content than C1-S4 and C1-S4N1 mixes), was not sufficient to retard the

aluminates for a longer time, resulting in an aluminate-dominated reaction before alite sufficiently hydrates (Figure 5.4).

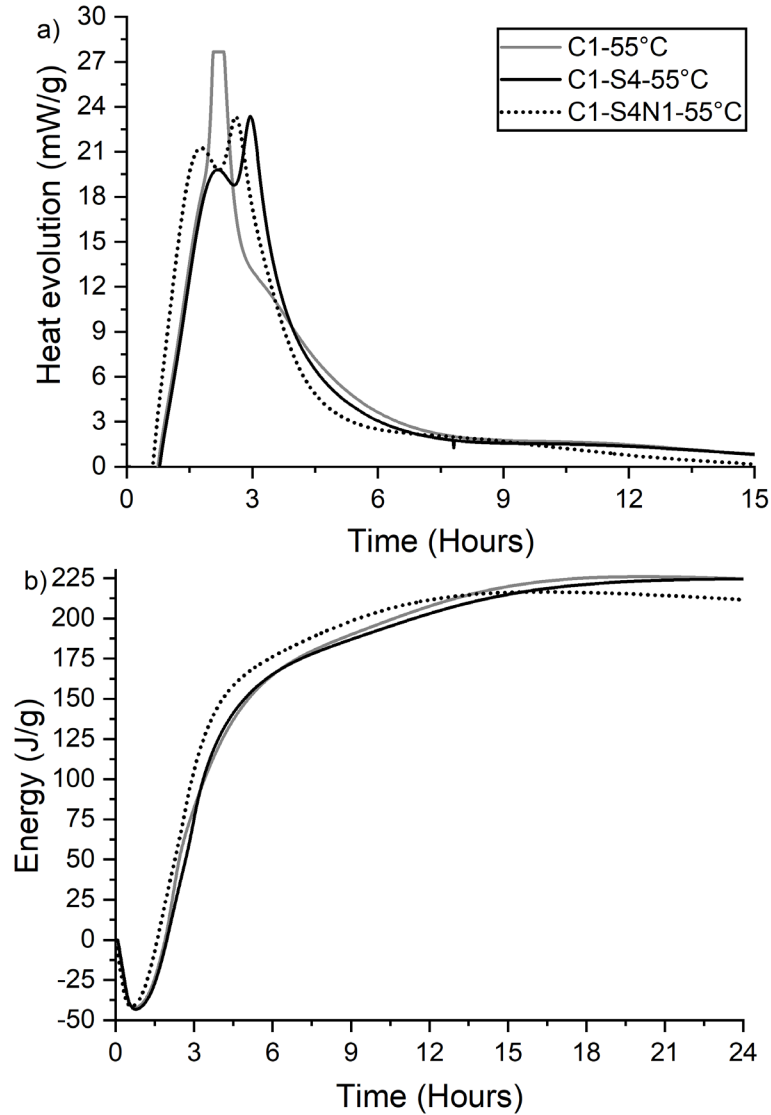


Figure 5.4 a) Hydration and b) cumulative heat evolution of Cement 1 (C1) mixes at 55°C with variable sulphate and alkali

As the sulphates increased to 4%, the C1-S4 and C1-S4N1 mixes showed improved retardation of aluminates even at 55°C temperature curing. The increase in curing temperature also resulted in increased total heat energy evolved (J/g) when compared to 25°C (Figure 5.1.b & Figure 5.4.b). In C2 mixes (Figure 5.5.a & b), the rate of heat evolution accelerated, and cumulative heat energy increased similar to the C1 mixes at

higher curing temperature. The maximum heat flow limit of the apparatus appears to be around 27.5 mW/g. All the C2 mixes reached 27.5 mW/g and so the graphs do appear truncated; thus, making it difficult to differentiate different cement systems with respect to maximum heat-rate. Further, in common among C2 mixes, there is no differentiation between C_3S and C_3A reactions. This result suggests that both reactions may overlap in the high-temperature conditions. For both cement mixes, at elevated temperature the conversion of Et to Ms was not visible.

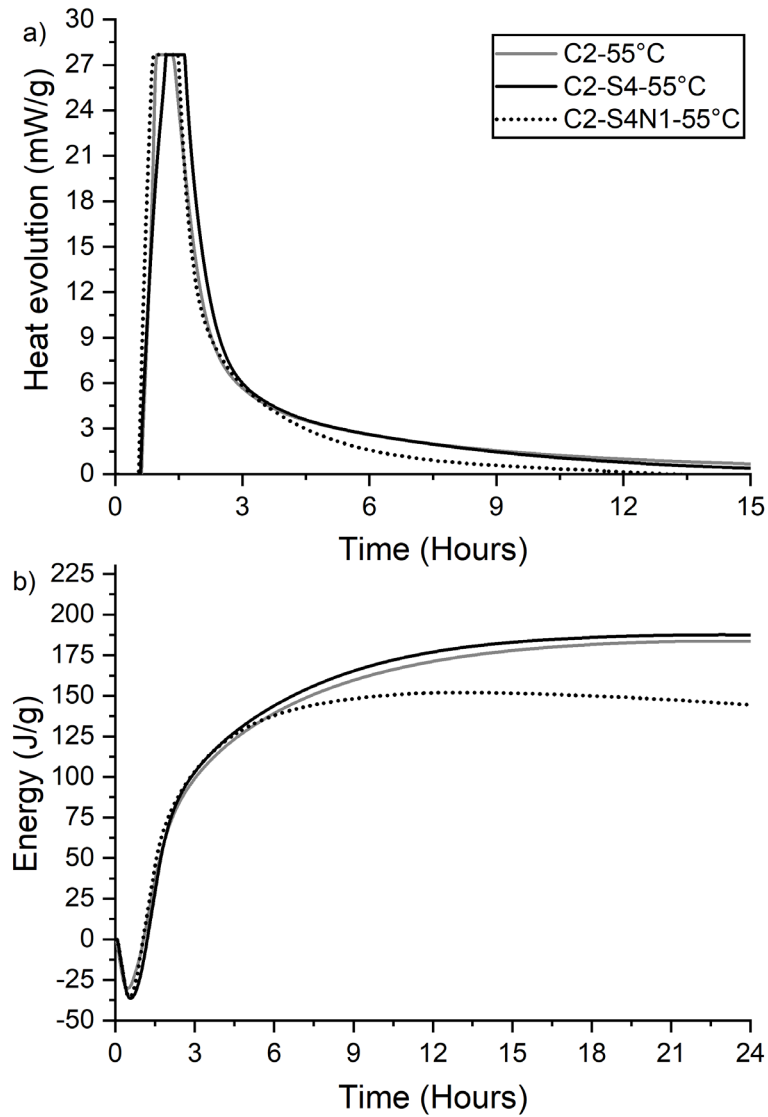


Figure 5.5 a) Hydration and b) cumulative heat evolution of Cement 2 (C2) mixes at 55°C with variable sulphate and alkali

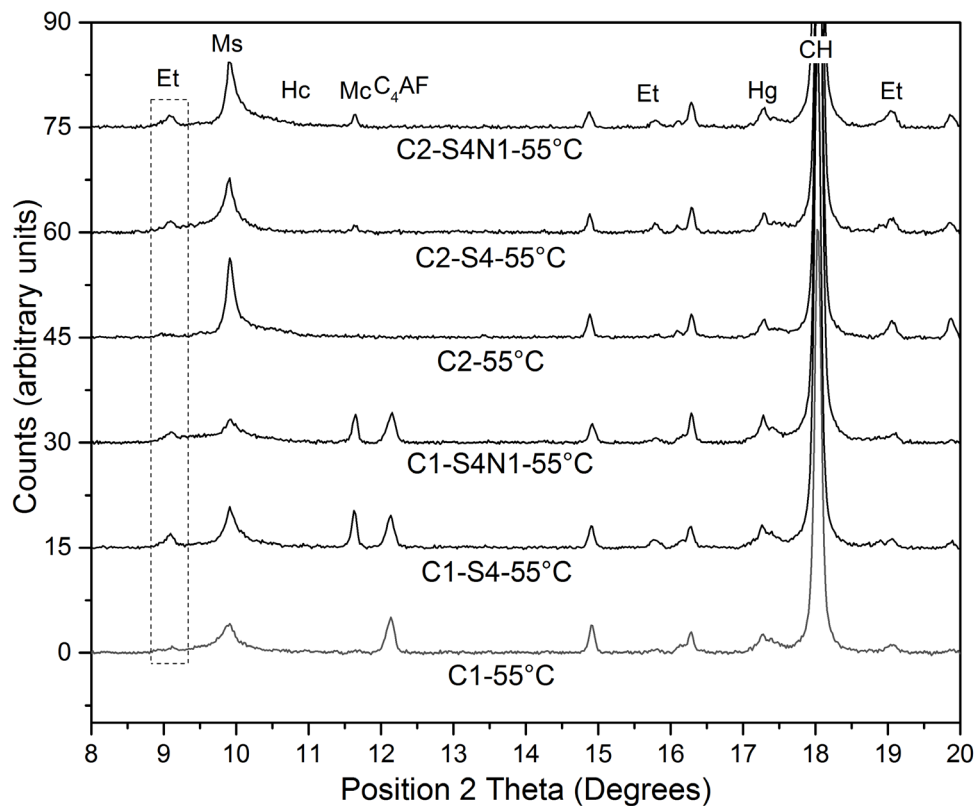


Figure 5.6 XRD patterns of Cement 1 (C1) and Cement 2 (C2) mixes at 55°C-15 hours with variable sulphate and alkali

The XRD results (Figure 5.6) show Ms phases dominate at the end of 15 hours of hydration, leaving little ettringite. This suggests the absence of the Et to Ms peak in calorimetry curves is due to either suppression of Et at elevated temperatures or that Et might have precipitated during the aluminates reactions and deformed into Ms before the deceleration peak. Either way, the absence of ettringite forms the basis for DEF at a later stage.

5.3 Early age hydration of cements with fly ash at 25°C

Fly ash (FA) was included in the binder by replacing 25% of the cement weight. In one set, FA was added to the chemically unmodified cements (C1, C2) and in another set was added to sulphate (4%), and alkali (1%) modified cements (C1-S4N1, C2-S4N1).

Hydration curves of FA-free mixes are included as references. From Figure 5.7.a in C1-F-25°C, an increased dormant period and a significant reduction in the rate of heat evolution were noted when compared to the FA-free mix C1-25°C. The increase in the dormant period can be attributed to the dilution effect of FA in the mix, reducing the calcium ion concentration and thereby delaying the C-S-H nucleation (Deschner et al. 2012). Further, from the aluminate reaction peak, it is evident that renewed Et formation is significantly higher for the C1-F-25°C mix. In the 4% sulphate and 1%, alkali mix (C1-S4N1-F-25°C), FA substitution resulted in an increase in dormant period and reduction in overall heat evolution compared to the FA free mix C1-S4N1-25°C. The separate aluminate peaks were not visible in C1-S4N1 mixes where the presence or absence of FA has no effect. An overall reduction in total heat evolution was observed in FA mixes (C1-F-25°C, C1-S4N1-F-25°C). In the case of C2 mixes, the rate of heat evolution was higher in C2-F-25°C (Figure 5.8.a) than the reference mix C2-25°C. The increase in heat evolution could be due to the higher alumina content in C2 (11.2%) compared to C1 (7.4%) and the additional alumina contribution from FA. The higher alumina contribution can be inferred from the dominant aluminate reaction that results in a shoulder peak alite reaction.

In mixes C2-S4N1 and C2-S4N1-F-25°C there is clear separation of alite and aluminate reaction peaks, indicating that 4% sulphate is the ideal sulphation for C2 cement under ambient curing temperatures, in contrast to C1 mixes; this could be due to the difference in alumina content of C1 and C2. In all the FA added mixes, the Et to Ms conversion shoulder peak was not visible. Further, the cumulative heat energy evolution of FA mixes was always lower in comparison to reference mixes (Figure 5.7.a & Figure 5.8.b). From the XRD patterns in Figure 5.9, it is evident that primary ettringite is stable at 25°C curing. In C2 FA mixes, the presence of early age hemihydrate (Hc) is attributed to higher

alumina content. The absence of an Ms peak in C1 and C2 FA samples correlates with the absence of the Et to Ms conversion peak in the respective hydration curves.

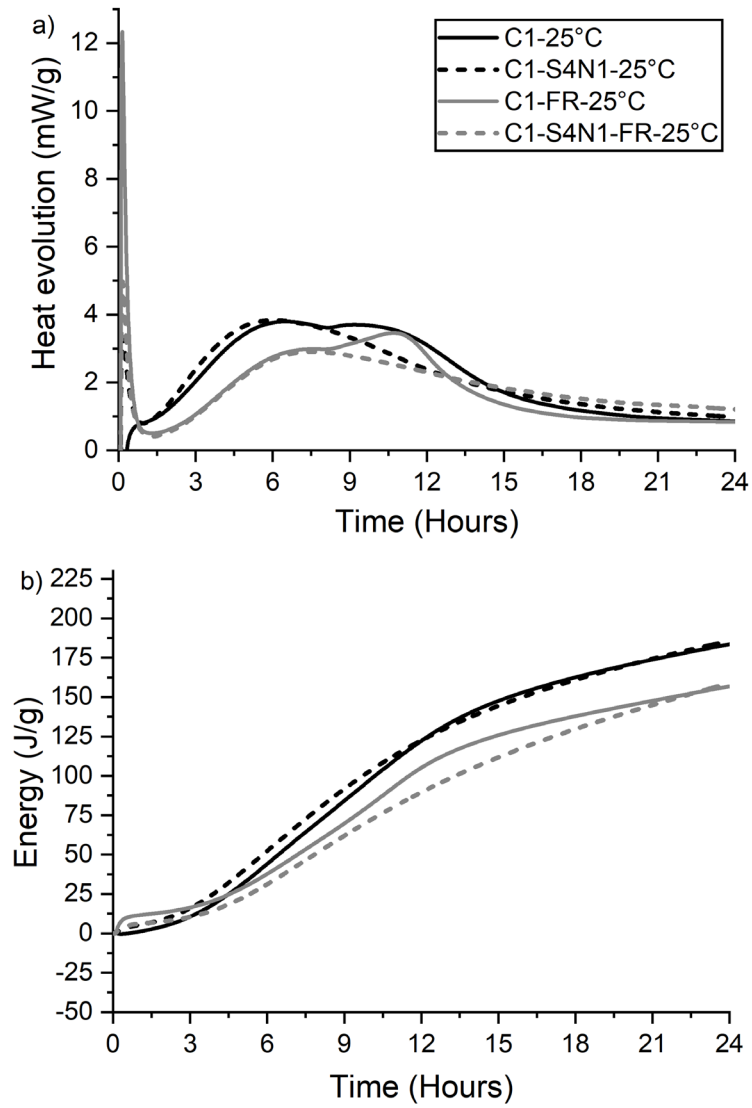


Figure 5.7 a) Hydration and b) cumulative heat evolution of fly ash incorporated Cement 1 (C1) mixes at 25°C

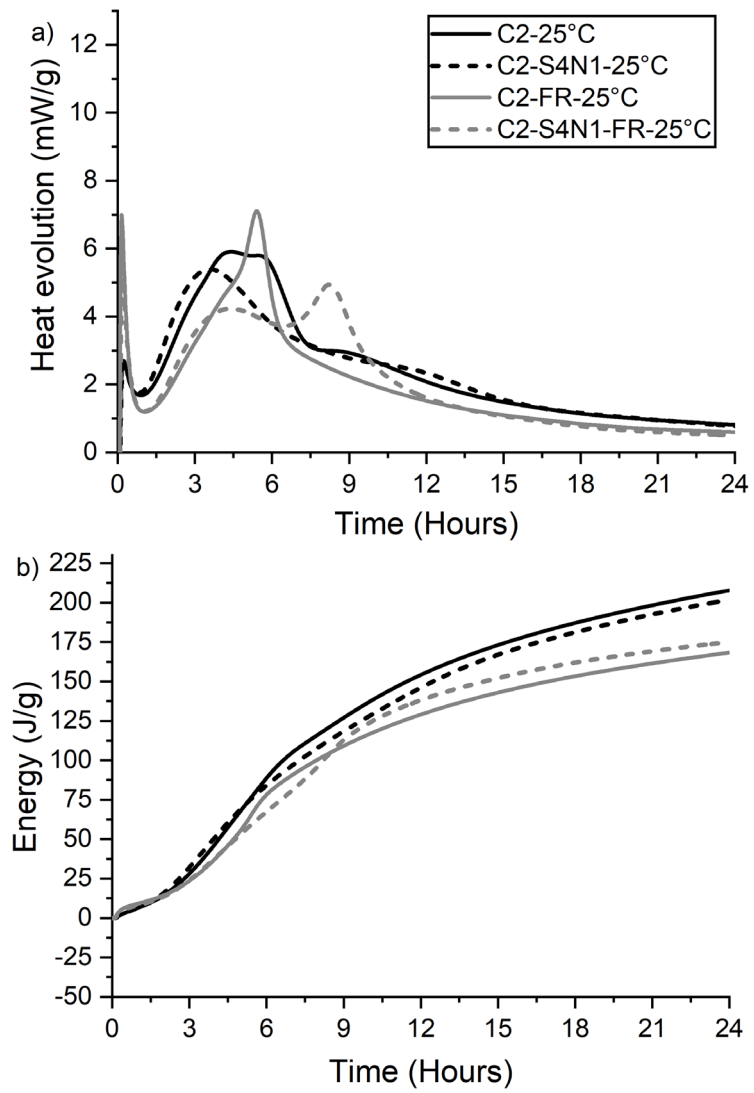


Figure 5.8 a) Hydration and b) cumulative heat evolution of fly ash incorporated Cement 2 (C2) mixes at 25°C

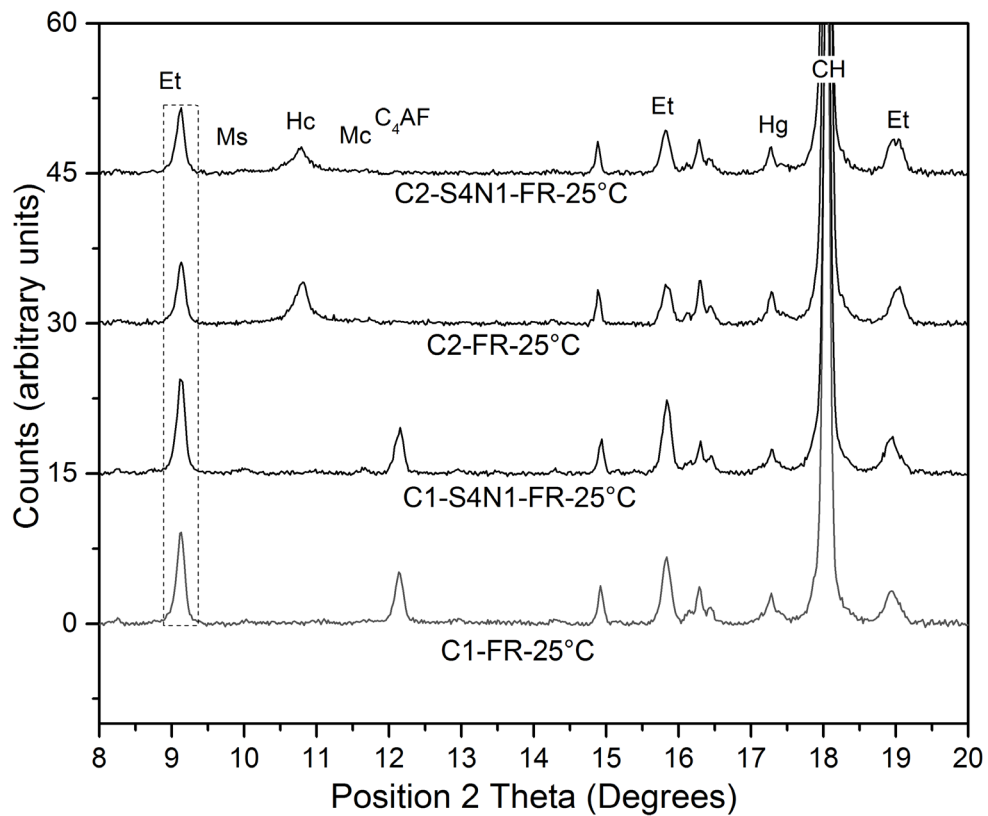


Figure 5.9 XRD patterns of fly ash incorporated Cement 1 (C1), and Cement 2 (C2) mixes at 25°C-15 hours

5.4 Early age hydration of cements with fly ash at 55°C

The same set of mixes discussed in Section 5.3 Early age hydration of cements with fly ash at 25°C were studied with isothermal conditions at 55°C. As expected, the elevated temperature accelerated the hydration reactions. Due to the presence of FA in C1-F-55°C and C1-S4N1-F-55°C mixes, the heat evolution trend was significantly reduced (Figure 5.10.a) compared to FA free mixes (C1-55°C, C1-SF-55°C). Further, the impact of FA reflected well as it reduced the cumulative heat energy significantly, as shown in Figure 5.10.b. Among the FA added mixes, C1-S4N1-F-55°C, showed a faster reaction rate and with a higher rate of heat evolution; this is certainly not because of increased sulphate (4%), but possibly due to the alkali (1%) content. These heat evolution peak differences are not visible in the C2 mixes (Figure 5.11.a), suggesting the presence or absence of FA

makes no significant difference to the rate of hydration. Despite that, the cumulative heat energy showed the impact of FA addition (Figure 5.11.b). In terms of alite and aluminate peak differences, the C1 mixes show a clear indication of accelerated aluminate reaction, as discussed in other sections of this chapter. The partial conversion of Et to Ms occurs in all the C1 mixes; the addition of FA only shifts the occurrence to a later period of hydration.

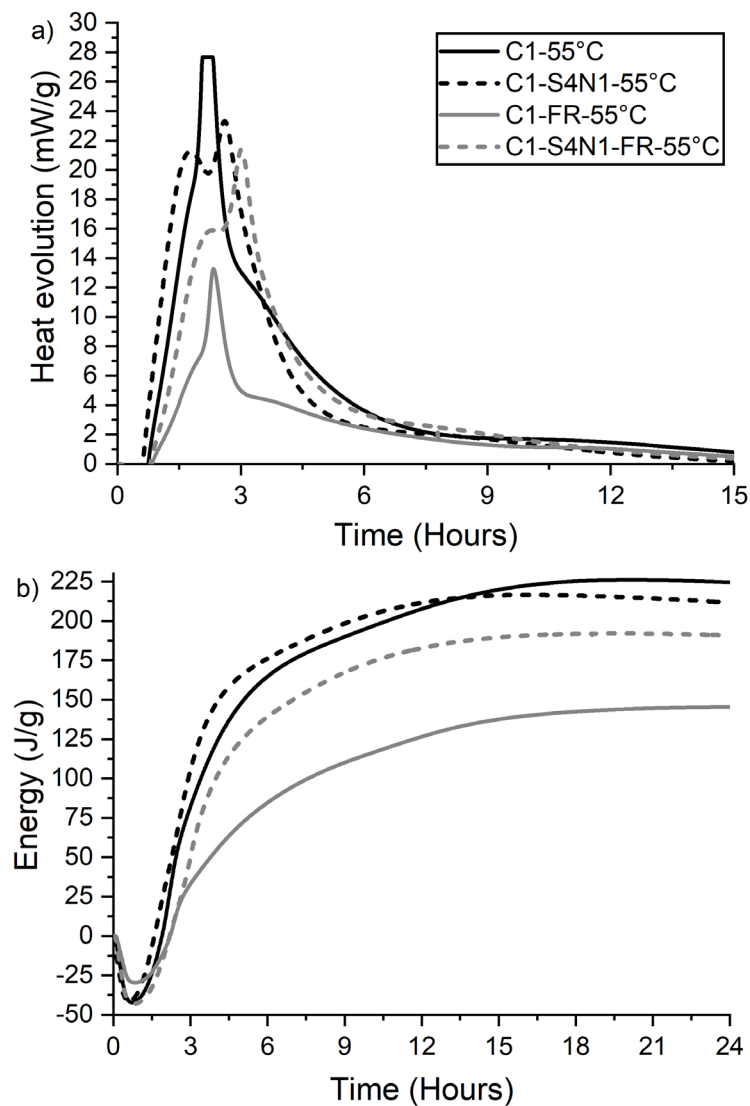


Figure 5.10 a) Hydration and b) cumulative heat evolution of fly ash incorporated Cement 1 (C1) mixes at 55°C

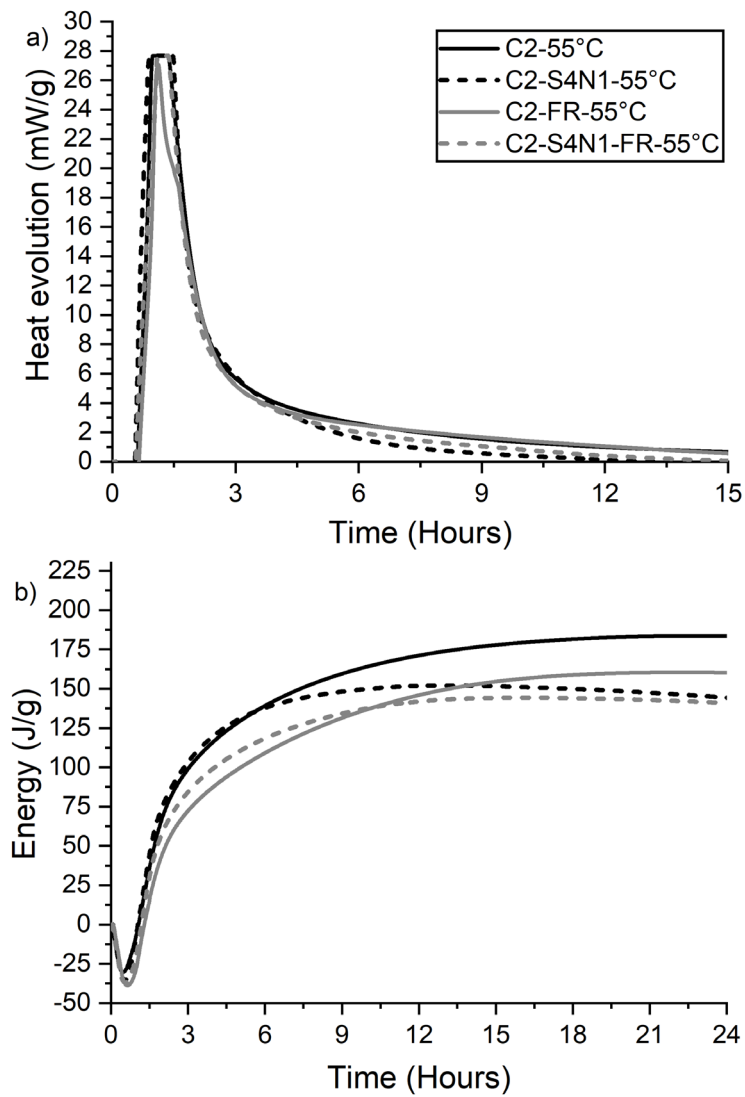


Figure 5.11 a) Hydration and b) cumulative heat evolution of fly ash incorporated Cement 2 (C2) mixes at 55°C

However, the differences in alite and aluminate reaction peaks and the Et to Ms conversion shoulder peak are not apparent in C2 mixes, suggesting an overlap of all significant hydration reactions. Similar to the other 55°C cured mixes, Et was absent at the end of 15 hours, suggesting the Et to Ms conversion was highly influenced by the temperature (Figure 5.12).

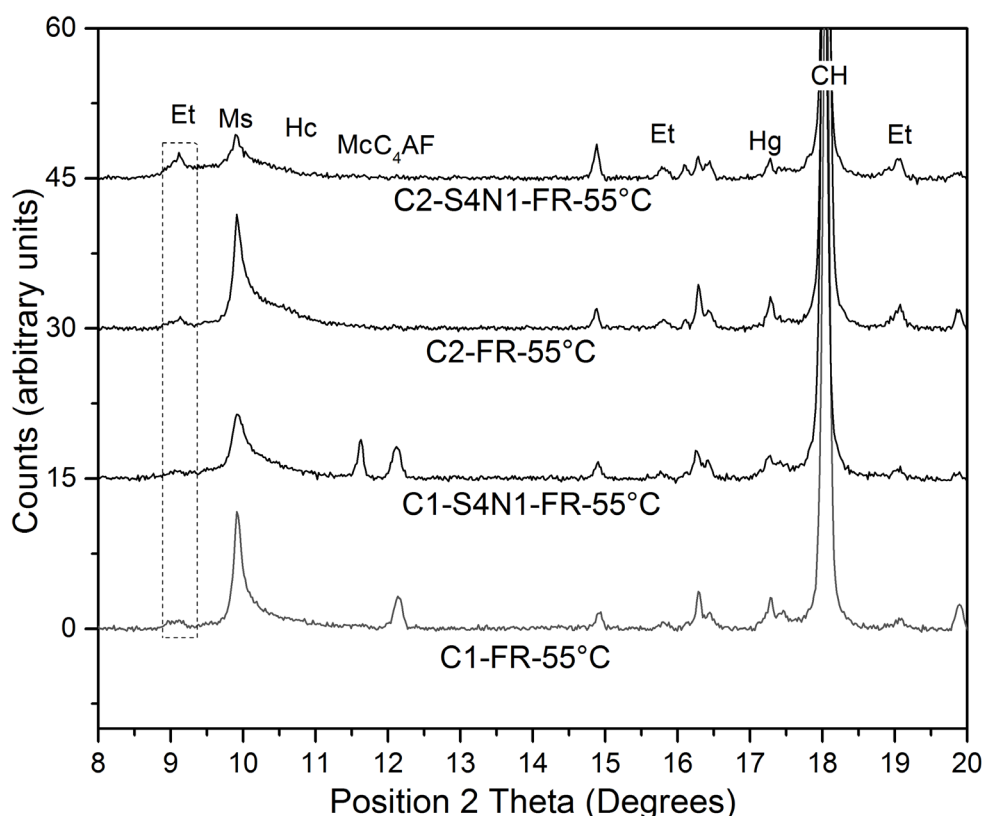


Figure 5.12 XRD patterns of fly ash incorporated Cement 1 (C1), and Cement 2 (C2) mixes at 55°C-15 hours

5.5 Summary

In general, it was challenging to deconvolute the hydration behaviour of various cementitious systems with calorimetric studies alone. XRD studies at 15 hours of age helped to explain somewhat. Despite the difficulties, the hydration of C1 and C2 are significantly different where rate and amount of heat evolved in total are concerned. The higher alumina content in C2 was found to be causing most of these differences. Additional sulphate increased the dormant period by delaying the aluminate reaction for both cements (C1, C2) at 25°C and 55°C, with visible differences noticed only in C1. With additional alkali, the effect of sulphate on the rate of reaction was nullified. Although the rate of reaction and total heat evolution varied significantly for different cementitious systems, ettringite was stable in all mixes cured at 25°C. At elevated

temperature accelerated rates of reaction and increased total heat evolution were noted in all cementitious systems compared to the corresponding mixes cured at 25°C. Further, at 55°C the aluminate reaction dominated before the alite was properly hydrated, especially in C2 mixes. However, it was not consistent for all mixes and varied with respect to sulphate and aluminate content. The addition of FA reduced the overall heat evolved in most cases due to the dilution effect (with few exceptions in C2 mixes). More importantly, in all 55°C cured samples including FA mixes, early age ettringite is essentially absent, forming the basis for DEF. However, the occurrence of DEF or its susceptibility cannot be explained with calorimetry studies. Despite the shortcomings of the technique, C1-S4N1 and C2-S4N1 may pose a higher DEF risk at an elevated curing temperature due to the combination of accelerated hydration, associated increase in total heat evolution and absence of early ettringite. Further tests are needed to validate the DEF risk, and these are covered in upcoming Chapters 6 to 9.

Chapter 6 Effect of heat curing in standard GP cement systems

This chapter presents a detailed study on the impact of different heat curing regimes on DEF in standard GP cement systems (without any chemical additions). Refer Table 4.2 for the detailed description of mixes used in this chapter. Linear expansions were recorded to up to 600 days to differentiate expansive and non-expansive DEF occurrence in heat-cured mortars. Mass changes in mortar prisms were noted up to 600 days. Changes in the dissolution of different ions due to varying curing temperature was studied by analysing pore solutions extracted from cement pastes. Further, the development of crystalline phases in heat-cured systems was studied using FTIR, TGA and XRD. XRD semi-quantitative analysis was used to study changes in ettringite precipitation due to heat curing. Microstructural changes, in particular ettringite deposition within cementitious systems, were investigated using BSE-SEM imaging and EDS mapping. The electrical resistivity of selected mortars was studied using EIS to understand the changes in porosity properties of mortars due to heat curing. This chapter serves as a reference for the upcoming result Chapters 7, 8 and 9.

6.1 Linear expansion and mass changes

Figure 6.1 and Figure 6.2 illustrate the linear expansion of Cement 1 and 2 mortar prisms subjected to different heat curing regimes. The non-expansive nature of ambient-cured mortars is very well understood from prior research (Collepardi 2003; Fukuda et al. 2010; Silva et al. 2010a; H. F W Taylor, Famy & Scrivener 2001). However, the heat-cured mortars did not show significant expansion, irrespective of curing temperatures (23°C to 90°C), prolonged duration of heat-curing (8-12 hours) and reduced pre-cure time (4-0 hours). DEF literature suggests that microstructural damage does not occur for specimens below 0.4% expansion (Silva et al. 2010, Tosun 2006).

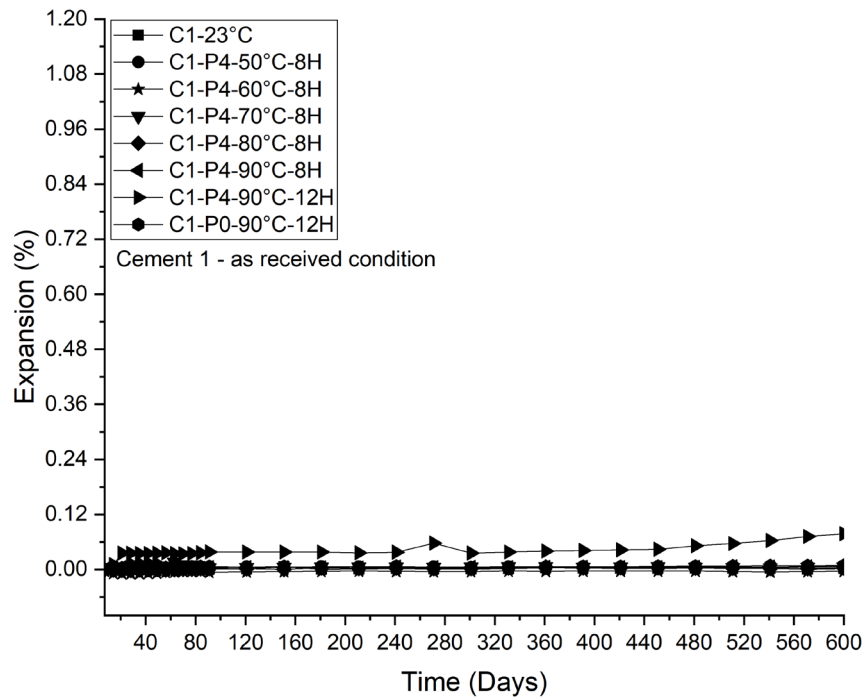


Figure 6.1 Linear expansive behaviour of Cement 1 mortars cured at 23°C-90°C

However, the mass change presented in Figure 6.3 and Figure 6.4 shows that heat-cured specimens gain mass over time. The rate of mass gain is higher for specimens cured at 90°C for 12 hours with 4 hours pre-cure time for both cements. However, the ultimate degree of mass gain is almost the same for specimens cured at 90°C for 12 hours with 0 hours pre-cure time. The mass increase during storage in saturated lime water can be linked to water absorption (Santhanam 2001; Shao et al. 1997). However, if mass gain happens because of sulphate attack, then it may be an indicator of deterioration in the specimen and reduction in compressive strength is expected (Santhanam 2001). The sudden loss of mass at a certain age and its recovery, as seen in Figure 6.3 and Figure 6.4 can be attributed to the occurrence of later age ettringite formation (Shao et al. 1997).

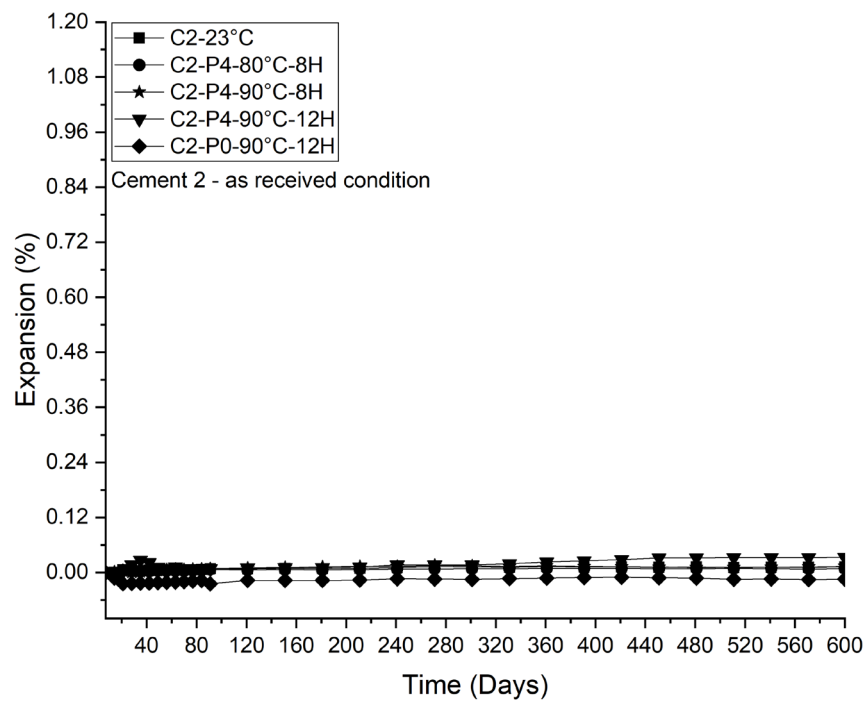


Figure 6.2 Linear expansive behaviour of Cement 2 mortars cured at 23°C-90°C

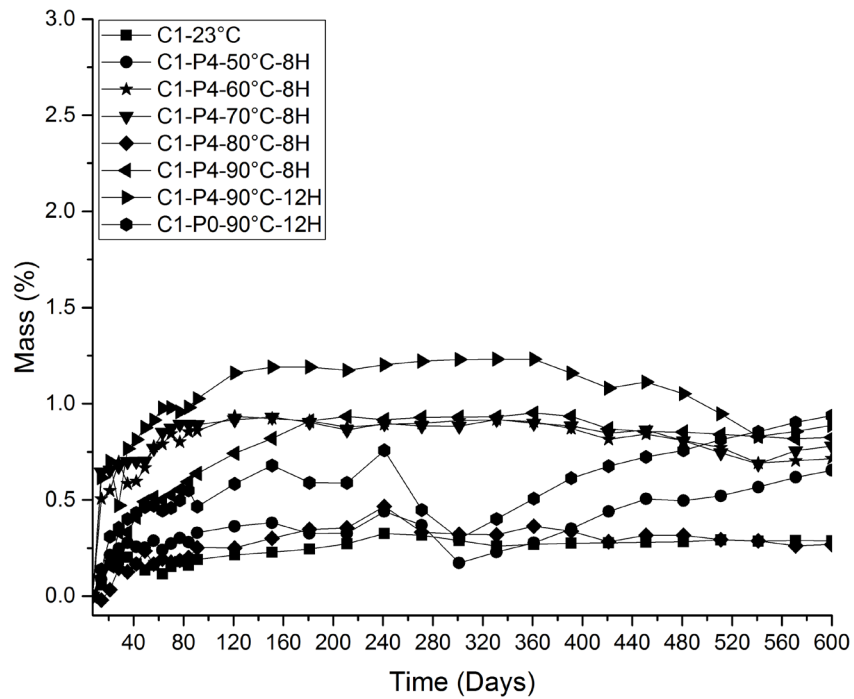


Figure 6.3 Mass changes of Cement 1 mortars cured at 23°C-90°C

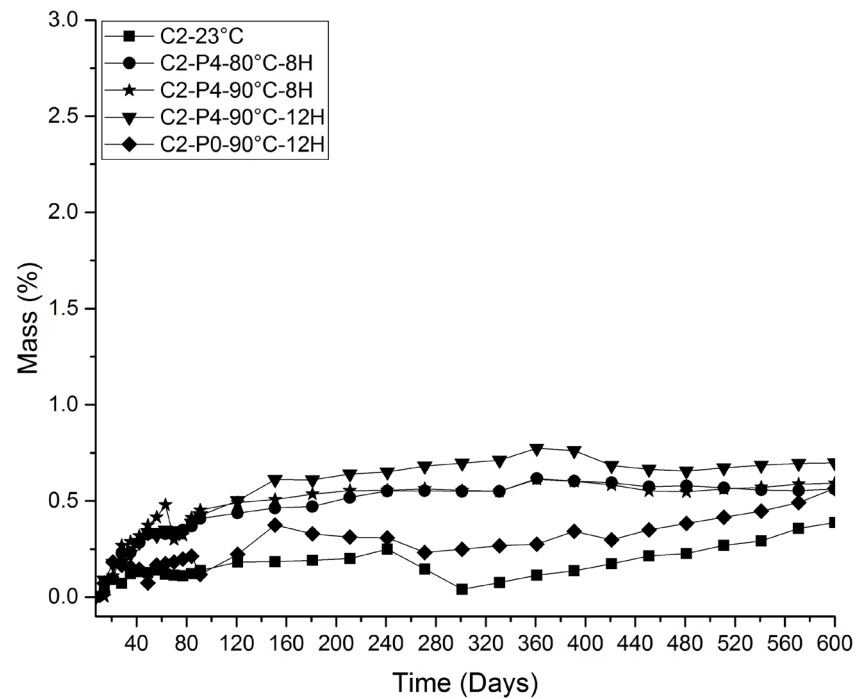


Figure 6.4 Mass changes of Cement 2 mortars cured at 23°C-90°C

6.2 Evolution of ionic pore solution characteristics and crystalline phases

6.2.1 GP cement systems cured at 23°C

Ionic concentrations of pore solutions from Cement 1 (C1) and Cement 2 (C2) pastes cured at 23°C over a period of 4 hours to 30 days are given in Figure 6.5 and Figure 6.6. For both cements, concentrations of Al and Si were always in the range 0.0-0.1 mmol/L and 0.1-0.5 mmol/L respectively, without any appreciable difference. Significant changes with respect to hydration occurred for four ions: Ca, K, Na and S. Calcium ion concentration gradually decreased from 19.3 to 0.9 mmol/L for C1 and 7.2 to 0.5 mmol/L for C2 over a month. This decrease is due to the consumption of Ca ions to form various hydration products such as C-S-H, CH and ettringite (Et), monosulphate (Ms) and hydrogarnet (Hg). At the age of 4 hours, Na and K ions in the pore solution were higher for C2 (4.3, 54.2 mmol/L) than C1 (1.9, 35.9 mmol/L), indicating that the faster dissolution rate of alkali ions contributed to accelerated hydration of C2 over C1. The alkali ion concentrations drop gradually from day 1 to 30 (Figure 6.5 Figure 6.6). A

reduction in pH and alkalinity (OH^-) from day 1 to 30 is also noted as given in Table 6.1; this can be partly attributed to the leaching of alkalis (Lindgård, Thomas, et al. 2013). The reduction of free S ion concentration in the pore solution correlates well with the precipitation of ettringite from XRD and TGA results (Figure 6.7 and Figure 6.8). The precipitation of ettringite could be attributed to the leaching of alkalis (Aubert, Escadeillas & Leklou 2009). In Figure 6.7, mass loss around 90-100°C corresponds to the dehydration of ettringite and C-S-H. Though there is temperature overlap, C-S-H can be identified by a broad decomposition DTG peak in contrast with a narrow ettringite decomposition DTG peak (Scrivener, Snellings & Lothenbach 2016). Various mass loss peak positions can be referred to from Table 4.9.

Table 6.1 Measured pH and calculated OH^- ions concentrations of C1 & C2 pastes cured at 90°C for 12 hours

Mix ID	pH		OH^- (mmol/L)	
	1 day	30 day	1 day	30 day
C1-23°C	13.2	12.7	154.9	44.7
C2-23°C	13.3	12.7	195.0	49.0
C1-90°C	13.2	12.6	151.4	37.2
C2-90°C	13.2	12.4	158.5	25.7

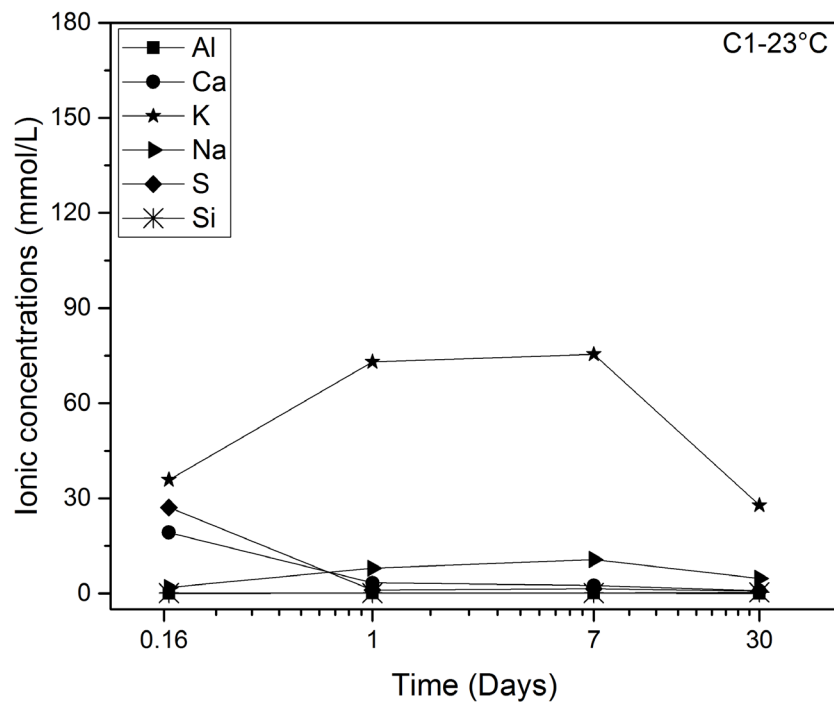


Figure 6.5 Ionic concentrations of pore solution from Cement 1 paste cured at 23°C

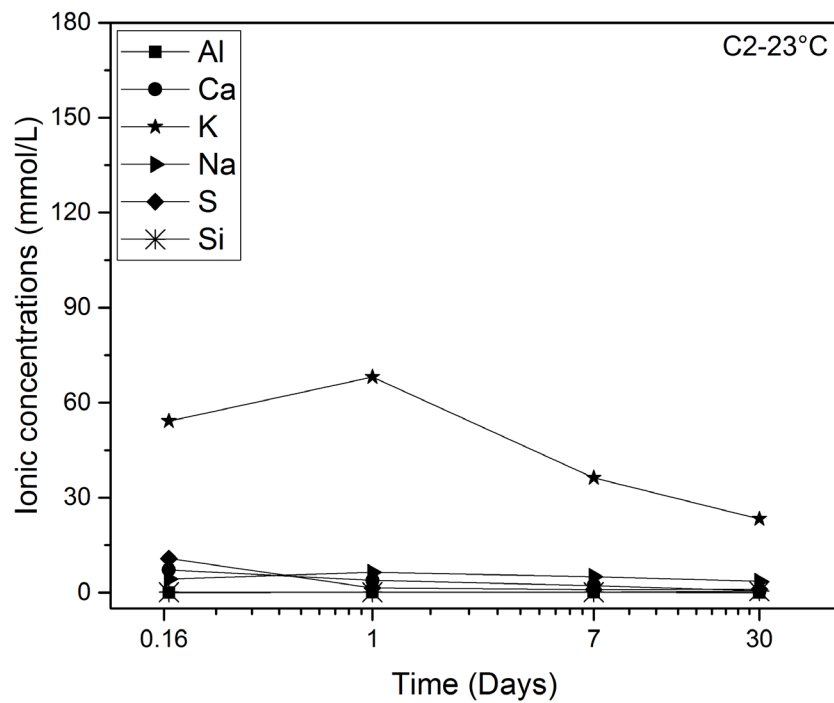


Figure 6.6 Ionic concentrations of pore solution from Cement 2 paste cured at 23°C

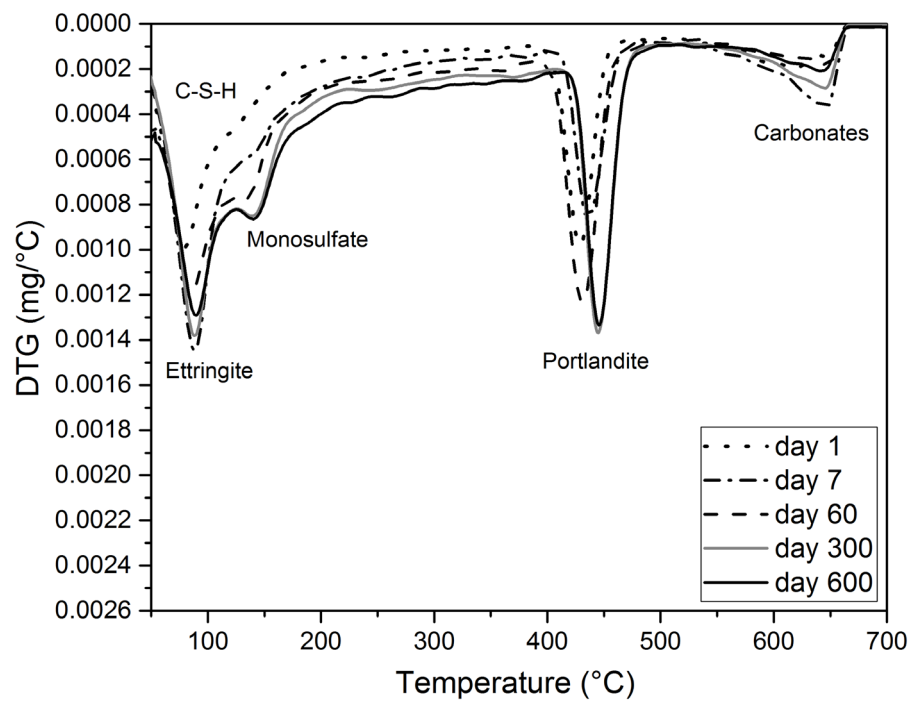


Figure 6.7 TGA mass loss curves of Cement 1 paste cured at 23°C – day 1 to 600

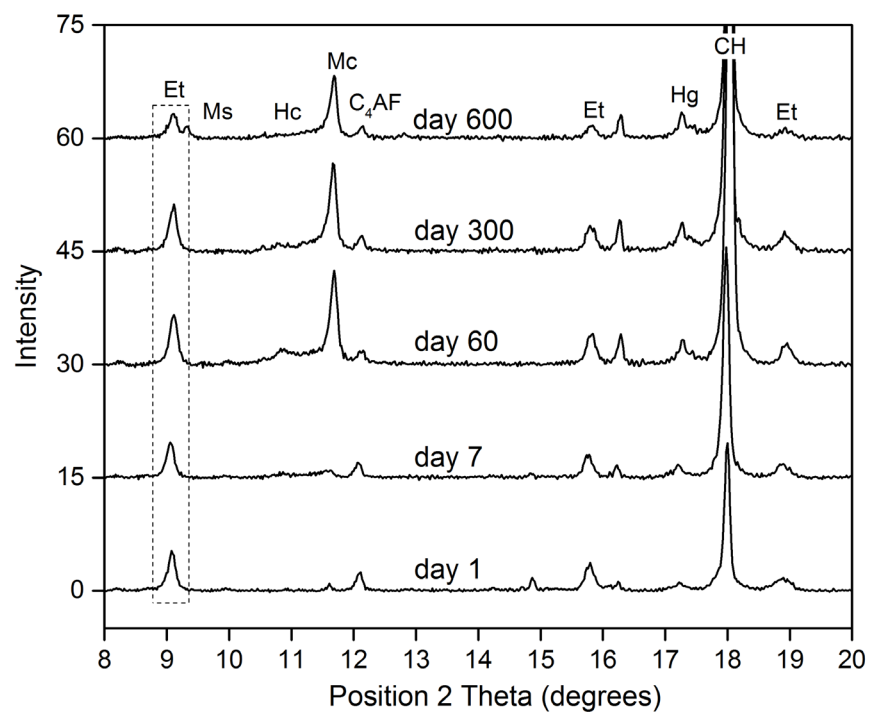


Figure 6.8 XRD patterns of Cement 1 paste cured at 23°C – day 1 to 600

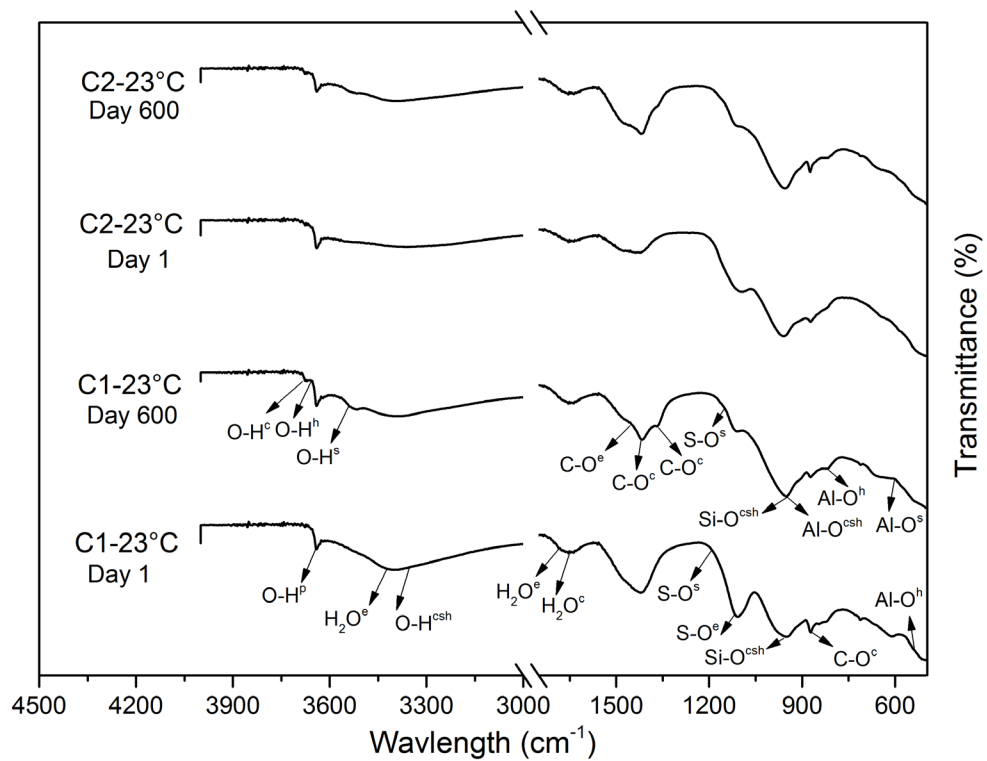


Figure 6.9 FTIR spectrum of Cement 1 & 2 paste cured at 23°C – day 1 and 600

The FTIR spectrum for C1 day 1 shows a strong sulphate S-O stretch at 1100 cm^{-1} (Barnett, Macphée & Crammond 2003; Ma et al. 2006) and Al-O at 535 cm^{-1} (Trezza & Lavat 2001) confirming the presence of ettringite (Refer to Table 4.10 for various FTIR wavenumbers assigned for a particular stretch or bend and check superscripts for associated cement hydrates). The total consumption of sulphate to form ettringite might happen anywhere between 60 to 300 days, as beyond day 300 a reduction in ettringite was noticed from TGA and XRD results. The decrease in ettringite is due to ettringite reacting with aluminates (Taylor 1997a; Yang & Sharp 2001a) to precipitate other mono-aluminoferite (AFm) phases, clearly visible in the day 600 TGA pattern (Figure 6.7). However, among AFm phases, differentiating monosulphate (Ms) and monocarbonate (Mc) by TGA appears difficult as both have a dehydration temperature overlap between $130\text{-}200^\circ\text{C}$. XRD and FTIR have different characteristics peaks for Ms and Mc. From

Figure 6.8, peaks at 9.8 and 11.7 degrees correspond to Ms and Mc, respectively. In Figure 6.9, the 600 day C1 spectrum shows two different OH peaks, those being O-H^c associated with Mc at 3676 cm⁻¹ and O-H^s associated with Ms at 3549 cm⁻¹ (Table 4.10). In addition, the day 1 C1 spectrum only has the C-O^c band at 1419 cm⁻¹ associated with Mc, but at 600 days hemicarbonate (Hc) at 1363 cm⁻¹ is also present, showing the growth of aluminoferrite phases other than ettringite. From Figure 6.8 among AFm phases, it is evident that Mc predominates over Ms which is usual for cements containing limestone (Lothenbach et al. 2008).

Unlike C1, the TGA results in Figure 6.10 suggest that the consumption of sulphate to form ettringite continues until 600 days in C2. However, the ettringite peak intensity is slightly less at day 600 compared to day 300 (Figure 6.11). Since C2 does not contain added limestone, Ms peaks are higher than Mc at later hydration ages (Lothenbach et al. 2008). Hc formation is also visible from day 1 to day 60. From Figure 6.9, the C2 day 600 spectrum, the presence of Mc and Ms can be noted from the vibration of O-H bands at 3676 and 3549 cm⁻¹ respectively, however the peaks are not as pronounced as in the case of C1. The reason behind the non-expansive nature of mortars cured at 23°C is due to the stability of ettringite during the early ages of hydration (Scrivener & Taylor 1993) and the formation of AFm phases such as Ms and Mc. Mono-aluminoferrite phases have less volume-occupying or space-filling characteristics due to their shorter interlayer spacing; 8.9 Å for Ms (Allmann 1977) and 7.8 Å for Mc (François, Renaudin & Evrard 1998) compared to 11.23 Å for ettringite (Cody et al. 2004).

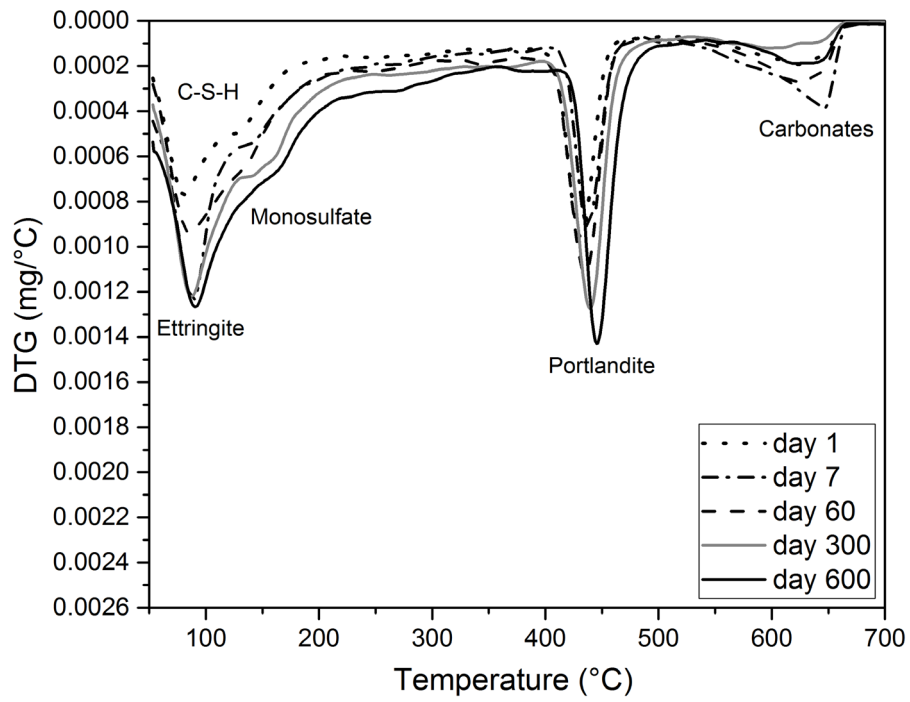


Figure 6.10 TGA mass loss curves of Cement 2 paste cured at 23°C – day 1 to 600

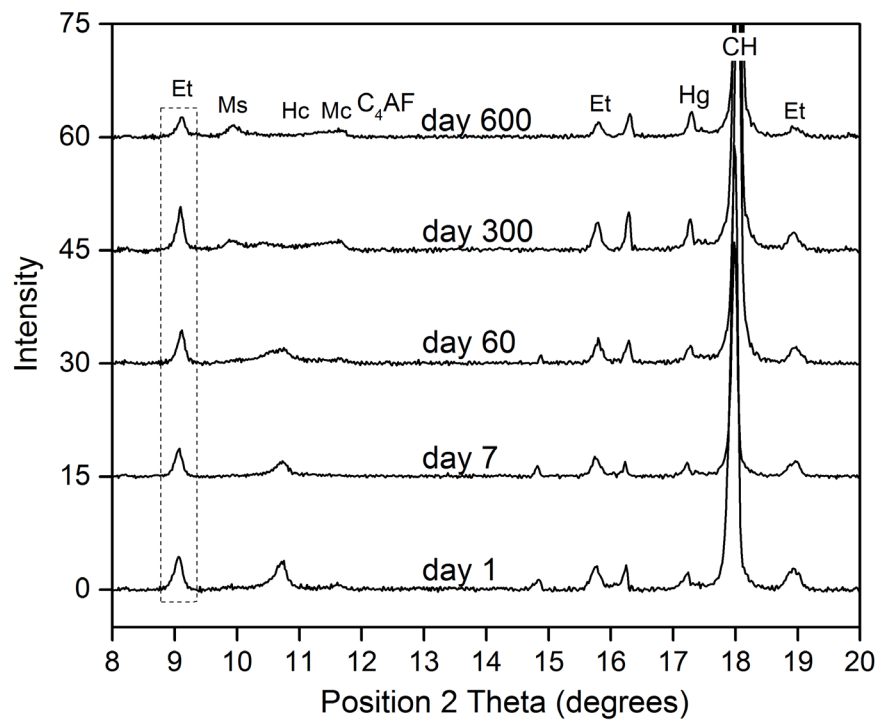


Figure 6.11 XRD patterns of Cement 2 paste cured at 23°C – day 1 to 600

6.2.2 GP cement systems cured at 90°C for 12 hours

The impacts of heat curing on pore solution ionic concentrations of C1 and C2 pastes are shown in Figure 6.12 and Figure 6.13, respectively. The day 1 data represents the ionic concentrations of pore solution immediately after the end of the heat-curing cycle. Raising the curing temperature from 23°C to 90°C increased the dissolution of K, Na and S ions. At the end of day 1, compared with 23°C cured C1 pastes, K ions rose from 73.1 to 91.9 mmol/L. Similarly, Na ions rose from 8.0 to 12.8 mmol/L. The increased alkalinity and temperature prompts dissolution of early ettringite (or suppress its formation), resulting in an increase in free S ions (from 1.1 to 63.7 mmol/L) in the pore solution (Lothenbach et al. 2007; Scrivener & Skalny 2005; Thomas, Hooton & Ramlochan 2010). In contrast, in C2 pastes only a marginal increase in K and no increase in Na ions is noted, which is in agreement with the results obtained by Thomas et al. (2003). The faster reactivity of C2 cements could be the reason, as discussed in section 6.2.1 GP cement systems cured at 23°C. The S ion concentration exhibited a rise from 1.47 to 29.3 mmol/L, which – without alkali addition – suggests that higher curing temperature alone can dissolve early ettringite. However, dissolution of S ions into pore solution due to the temperature rise (23° to 90°C) of C2 paste is (1.5 to 29.3 mmol/L) only 20 times higher compared to a 56 times increase in C1 (1.1 to 63.7 mmol/L). The observed increase in S ions in the pore solution due to the ettringite decomposition is reflected in the TGA and XRD results (Figure 6.14 to Figure 6.15). A complete absence of ettringite is noted in the day 1 TGA mass loss curves and XRD patterns in both C1 and C2 pastes. A similar trend of the disappearance of ettringite in heat-cured samples was observed by Scrivener & Taylor (1993) and Taylor, Famy & Scrivener (2001). Instead of a strong S-O^e band as in the 23°C cured pastes, FTIR results show a shoulder S-O^e peak at 1100 cm⁻¹ (Figure 6.16)

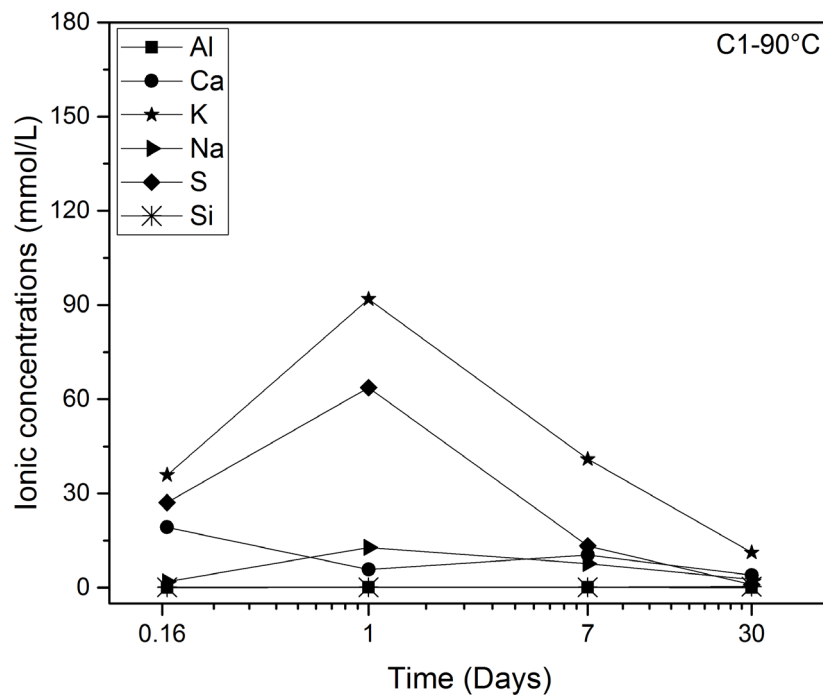


Figure 6.12 Ionic concentrations of pore solution from Cement 1 paste cured at 90°C

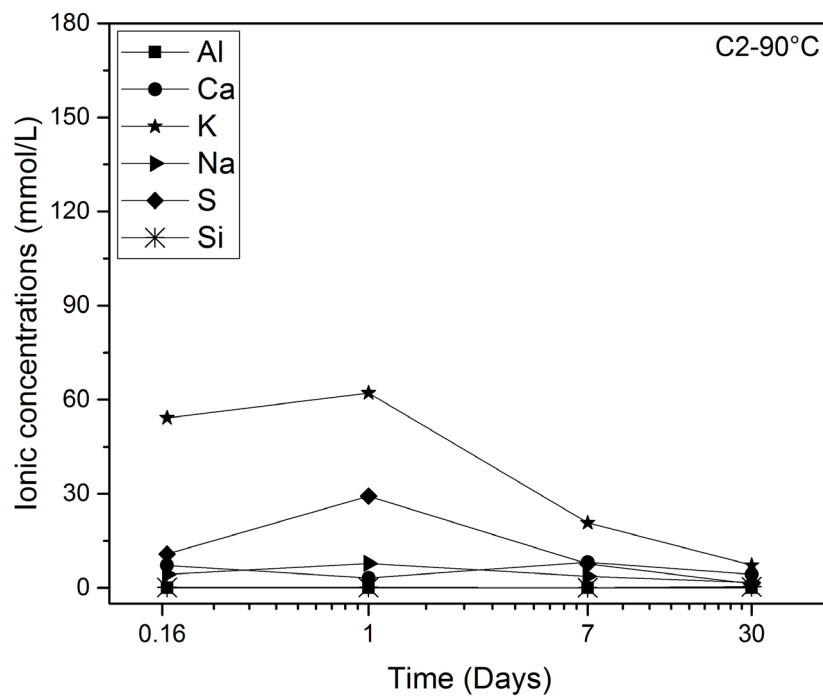


Figure 6.13 Ionic concentrations of pore solution from Cement 2 paste cured at 90°C

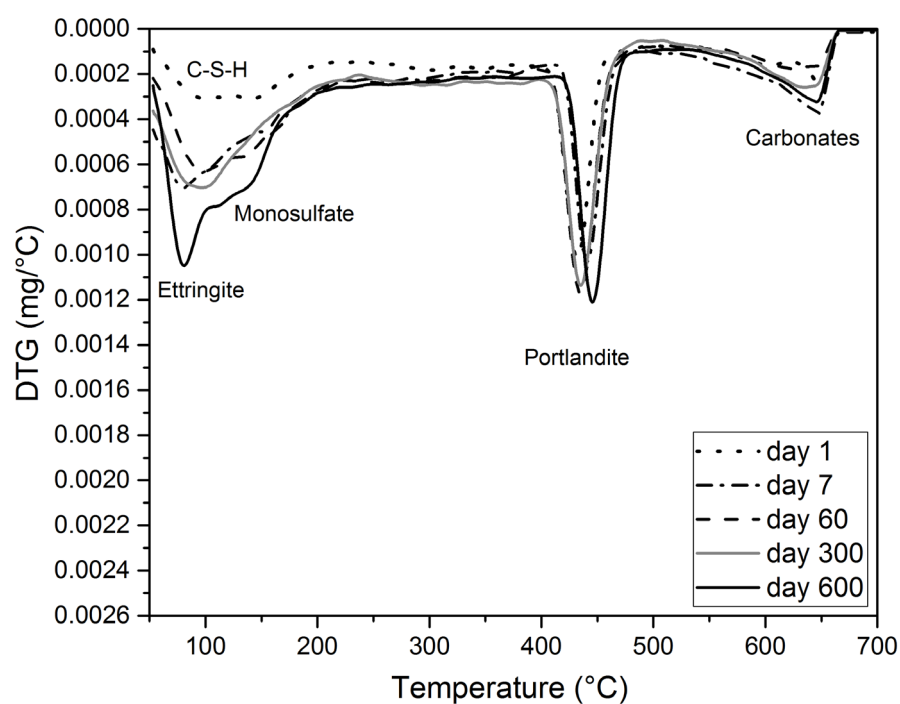


Figure 6.14 TGA mass loss curves of Cement 1 paste cured at 90°C for 12 hours – day 1 to 600

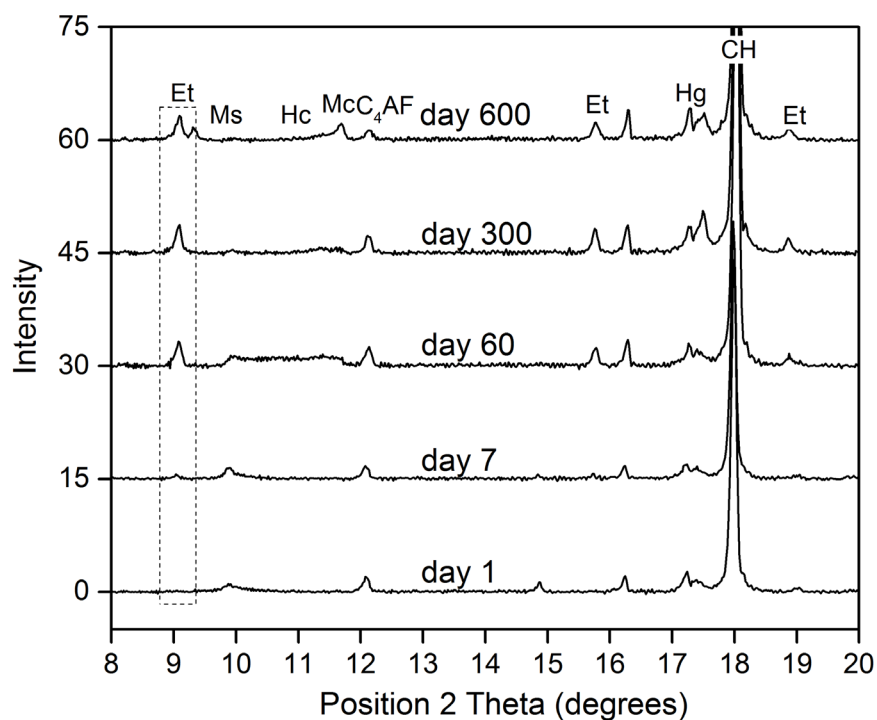


Figure 6.15 XRD patterns of Cement 1 paste cured at 90°C for 12 hours – day 1 to 600

In addition to the ettringite decomposition, loss of water from C-S-H and capillary pores due to heat-curing is noticeable in Figure 6.16, with the absence of an O-H^{csh} peak at 3352 cm^{-1} (Horgnies, Chen & Bouillon 2013) for both C1 and C2 day 1 FTIR spectra. Upon further curing in saturated lime water, ettringite precipitates from day 7 to 600; this is evident from the increase in mass loss around 100°C (Figure 6.14 & Figure 6.17) and the visible ettringite peak in XRD (Figure 6.15 & Figure 6.18) denoting the occurrence of DEF. From Figure 6.16, the 1100 cm^{-1} S-O^e stretch is visible, indicating the regrowth of ettringite. Similar to the 23°C cured pastes, C1 shows the formation of Mc over Ms, but in C2 the presence of Ms can be seen from day 1 to 600. Between C1 and C2, the ettringite peak intensity differences from TGA and XRD are not clear enough to make any distinction. Hence, XRD ettringite area under the peak at 9.14° was calculated as described in Section 4.2.3.2 for a semi-quantitative comparison.

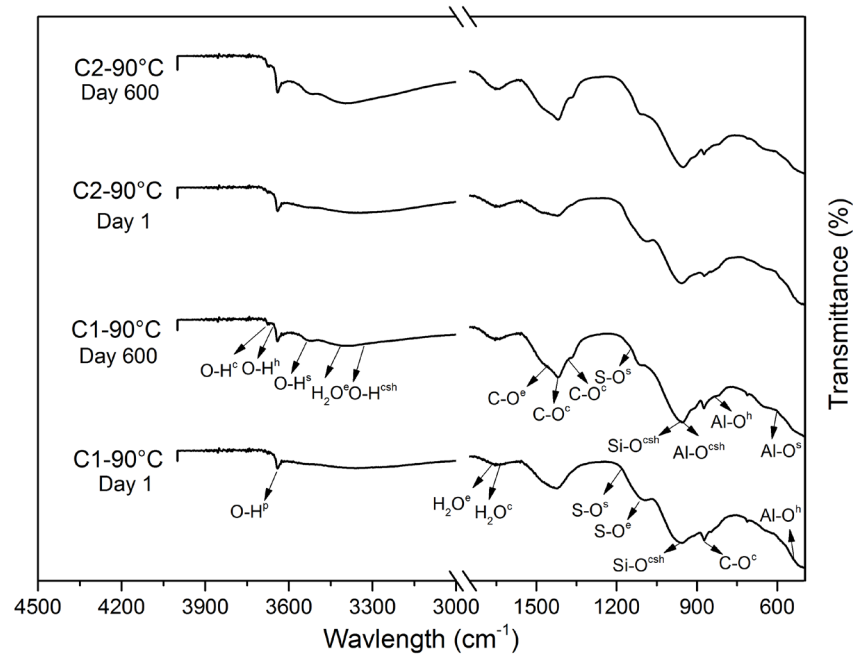


Figure 6.16 FTIR spectrum of Cement 1 & 2 paste cured at 90°C – day 1 and 600

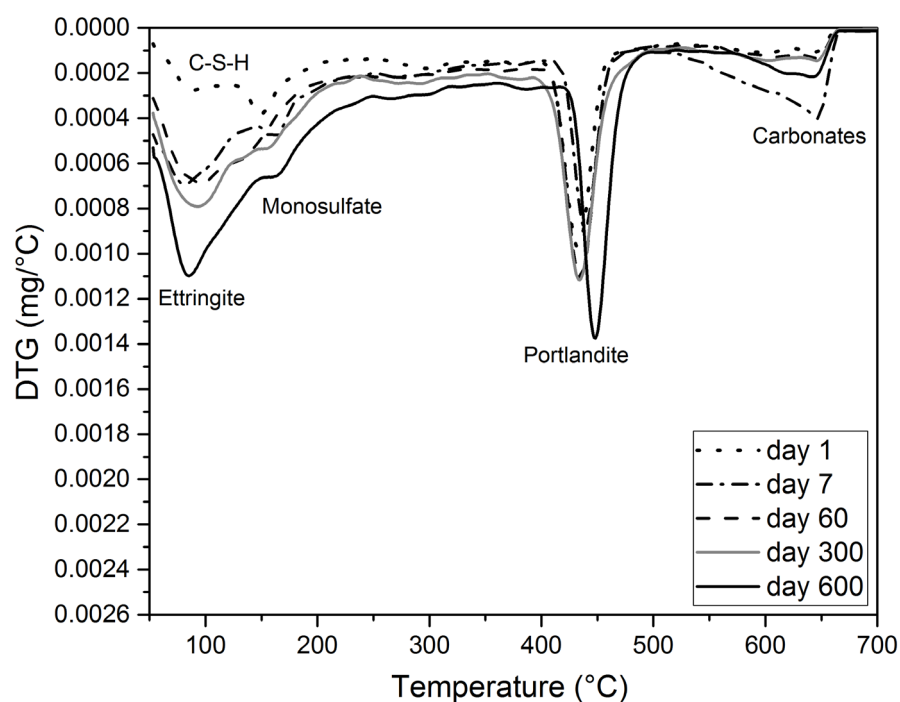


Figure 6.17 TGA mass loss curves of Cement 2 paste cured at 90°C for 12 hours – day 1 to 600

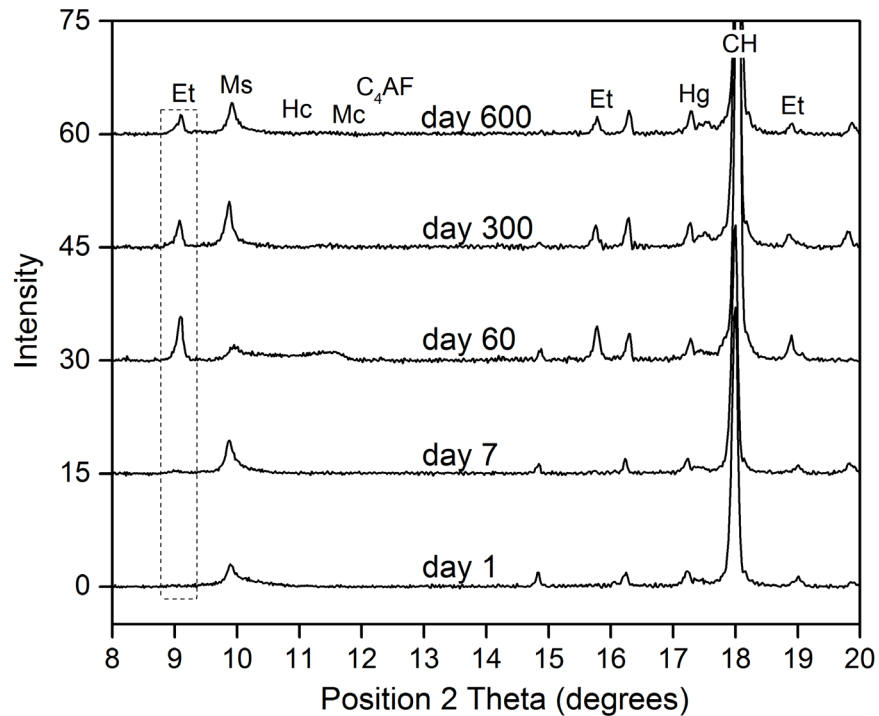


Figure 6.18 XRD patterns of Cement 2 paste cured at 90°C for 12 hours – day 1 to 600

Figure 6.19 shows the results of the ettringite area comparison for both 23° and 90°C cured samples. The reformed ettringite in heat-cured systems is always less abundant than in ambient cured systems. A maximum formation of ettringite at day 60 is common for all systems. The trend of reduction in ettringite quantity at later ages is due to conversion into other aluminoferrite phases.

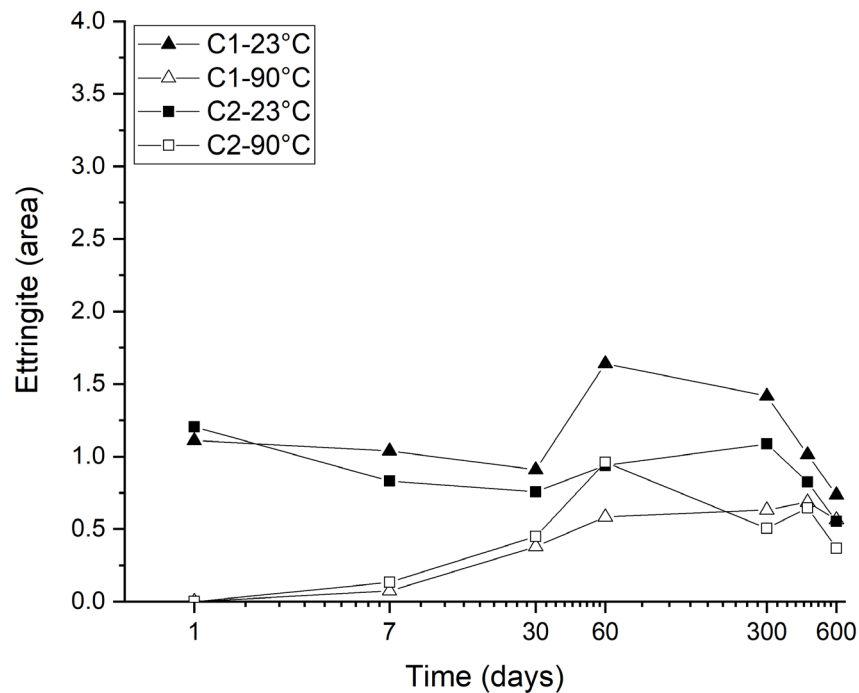


Figure 6.19 Cement pastes ettringite content (semi-quantitative) evolution over time

Despite the occurrence of ettringite reformation (DEF) in the heat-cured cement systems, significant expansion did not occur for either of the cement mortars (Figure 6.1 Figure 6.2). Similar non-expansive, innocuous DEF has been observed by many researchers (Famy 1999; Scrivener & Lewis 1997; Scrivener & Taylor 1993).

6.3 Microstructural investigation

6.3.1 GP cement systems cured at 23°C

The microstructures of C1 and C2 reference mortars cured at 23°C and stored in saturated lime water for approximately 500 days are given in Figure 6.20 and Figure 6.21. From

Section 6.1 Linear expansion and mass changes it was observed that ambient mortars were non-expansive and showed little difference in mass change. Further, the ettringite formed was stable in the cementitious system; no DEF is expected in these mortars. As the age of mortar at the time of testing was about 500 days, unhydrated cement grain was observed at one location only. However, in the C2 mortar a few more unhydrated or partially hydrated bright cement grains are visible, suggesting faster hydration kinetics (Figure 3.3) do not always mean better hydration of clinker phases. Cracks appearing (Figure 6.20 and Figure 6.21) at the interfacial transition zone (ITZ) are empty, suggesting they might be formed during the sample preparation process. EDS point scans were taken to understand the intermixed hydrates. Three different micrographs per sample and a total of 70-75 points were taken for EDS analysis. Points within the cement paste and at the ITZ were collected.

Atomic weight percentages were used to calculate S/Ca and Al/Ca ratios and plotted against each other. In the C1 mortar (Figure 6.22), apart from C-S-H gel, the atomic ratios suggest the presence of Hc and Mc hydrates, which is in agreement with the C1 XRD patterns (Figure 6.8) beyond an age 300 days. In the case of C2 mortar (Figure 6.23), a mixture of Ms, Hc and Mc hydrates present, not correlating well with the C2 XRD patterns as it had strong ettringite presence (Figure 6.11). EDS elemental mapping was used to understand the distribution of crucial cement and cement hydrate elements such as calcium (Ca), silica (Si), aluminium (Al), carbon (C), sulphur (S), potassium (K), and sodium (Na).

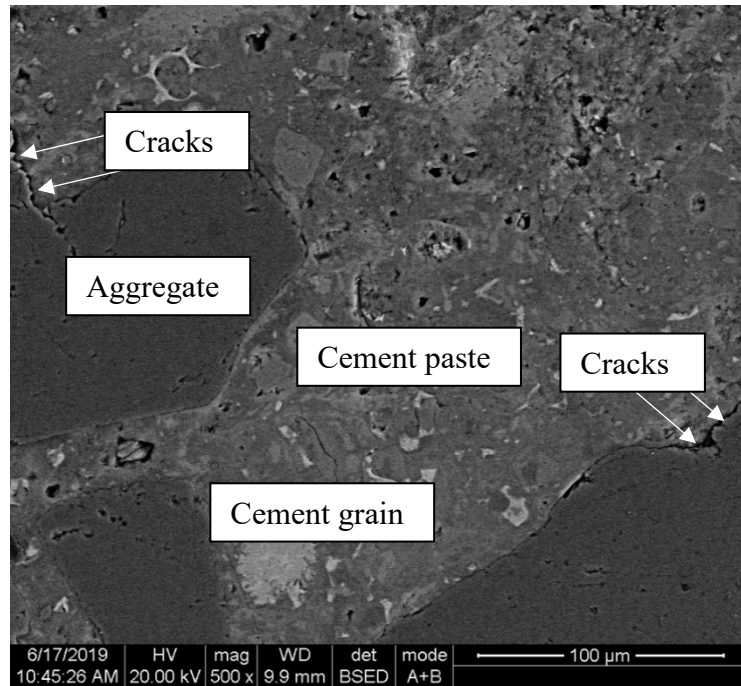


Figure 6.20 Microstructure of ambient cured (23°C) C1 mortar stored in saturated lime water for 500 days

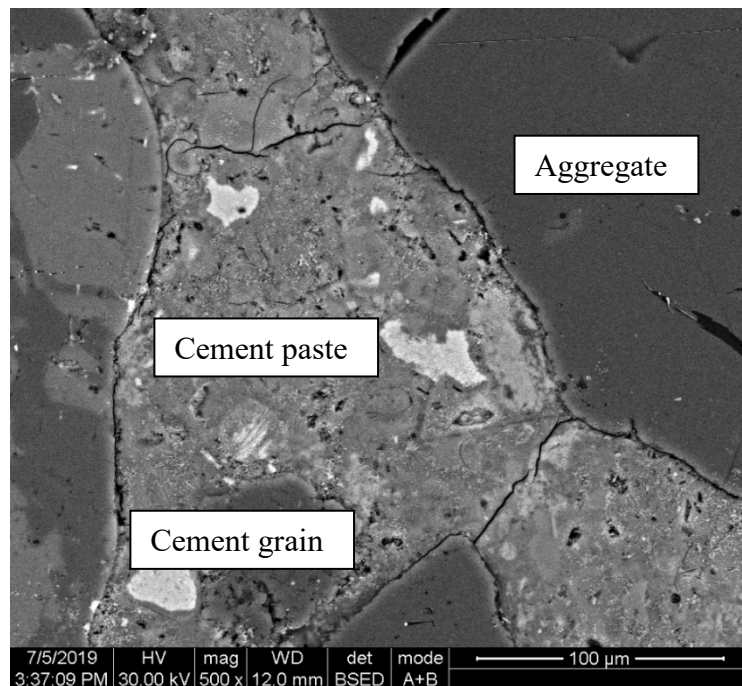


Figure 6.21 Microstructure of ambient cured (23°C) C2 mortar stored in saturated lime water for 500 days

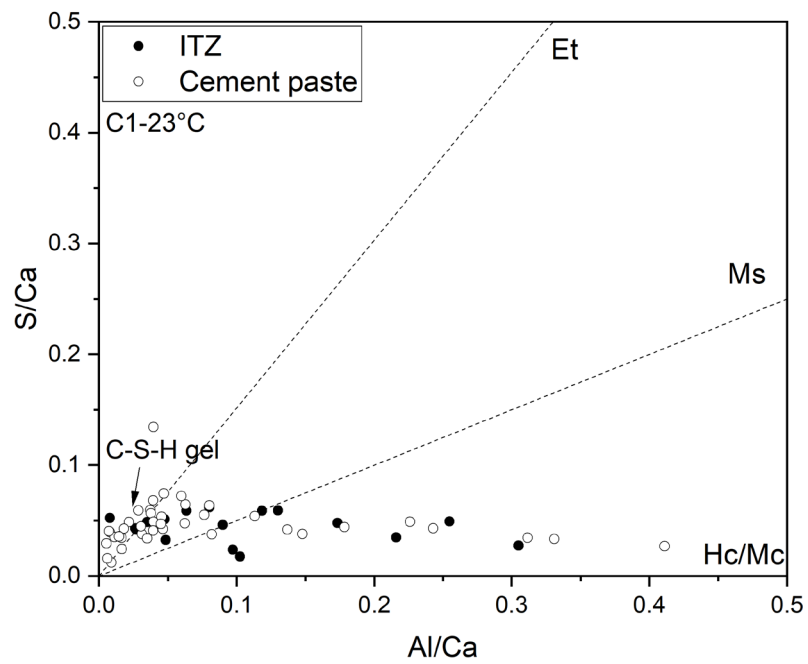


Figure 6.22 Atomic ratio plots of S/Ca vs Al/Ca of ambient cured (23°C) C1 mortar stored in saturated lime water for 500 days

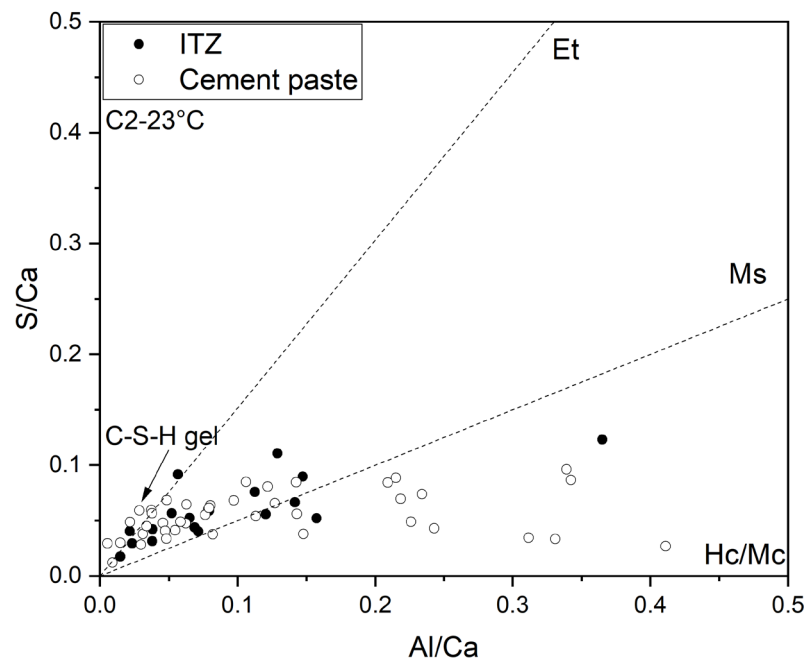


Figure 6.23 Atomic ratio plots of S/Ca vs Al/Ca of ambient cured (23°C) C2 mortar stored in saturated lime water for 500 days

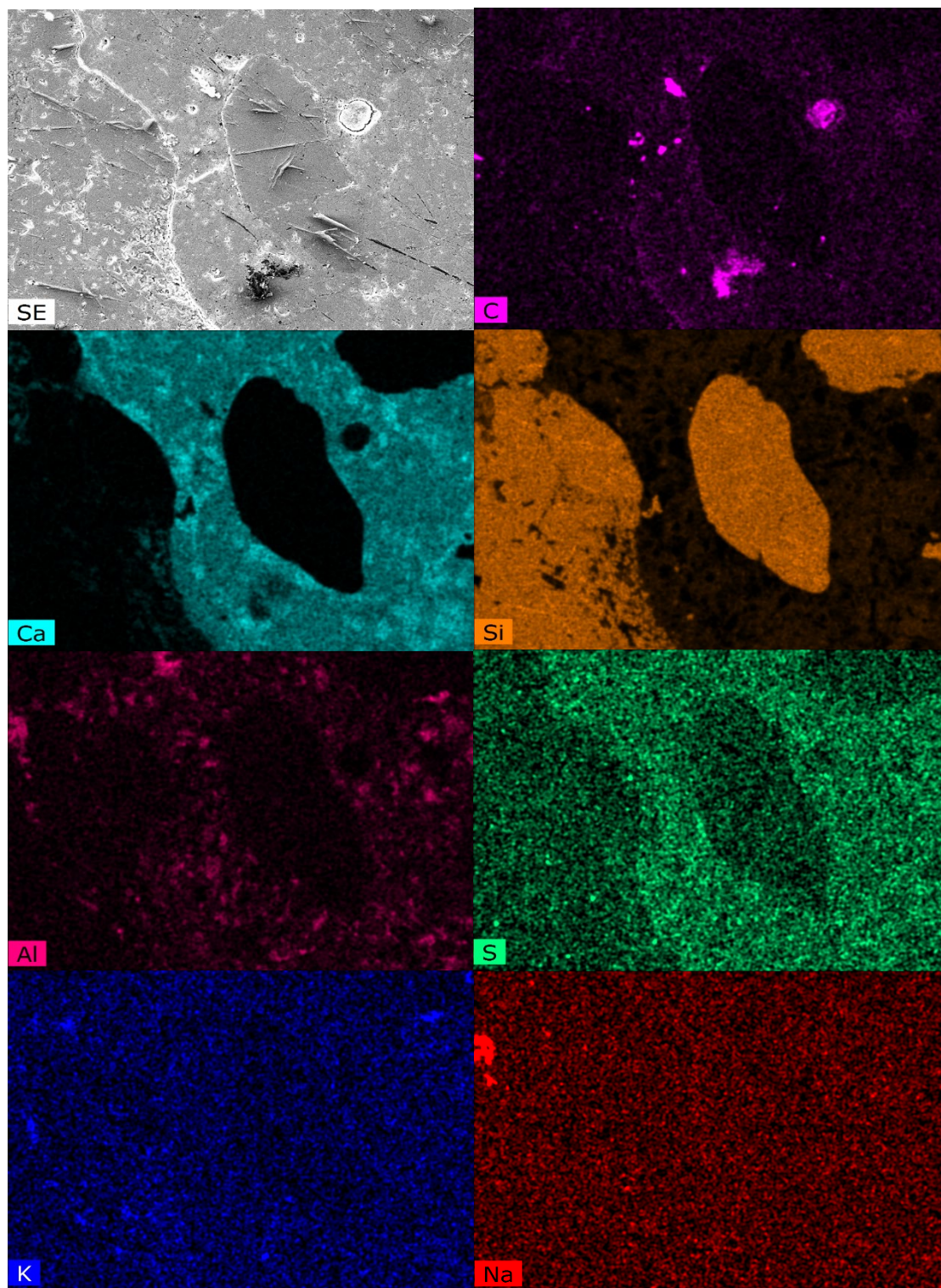


Figure 6.24 Elemental mapping of Ca, Si, Al, S of ambient cured (23°C) C1 mortar stored in saturated lime water for 500 days

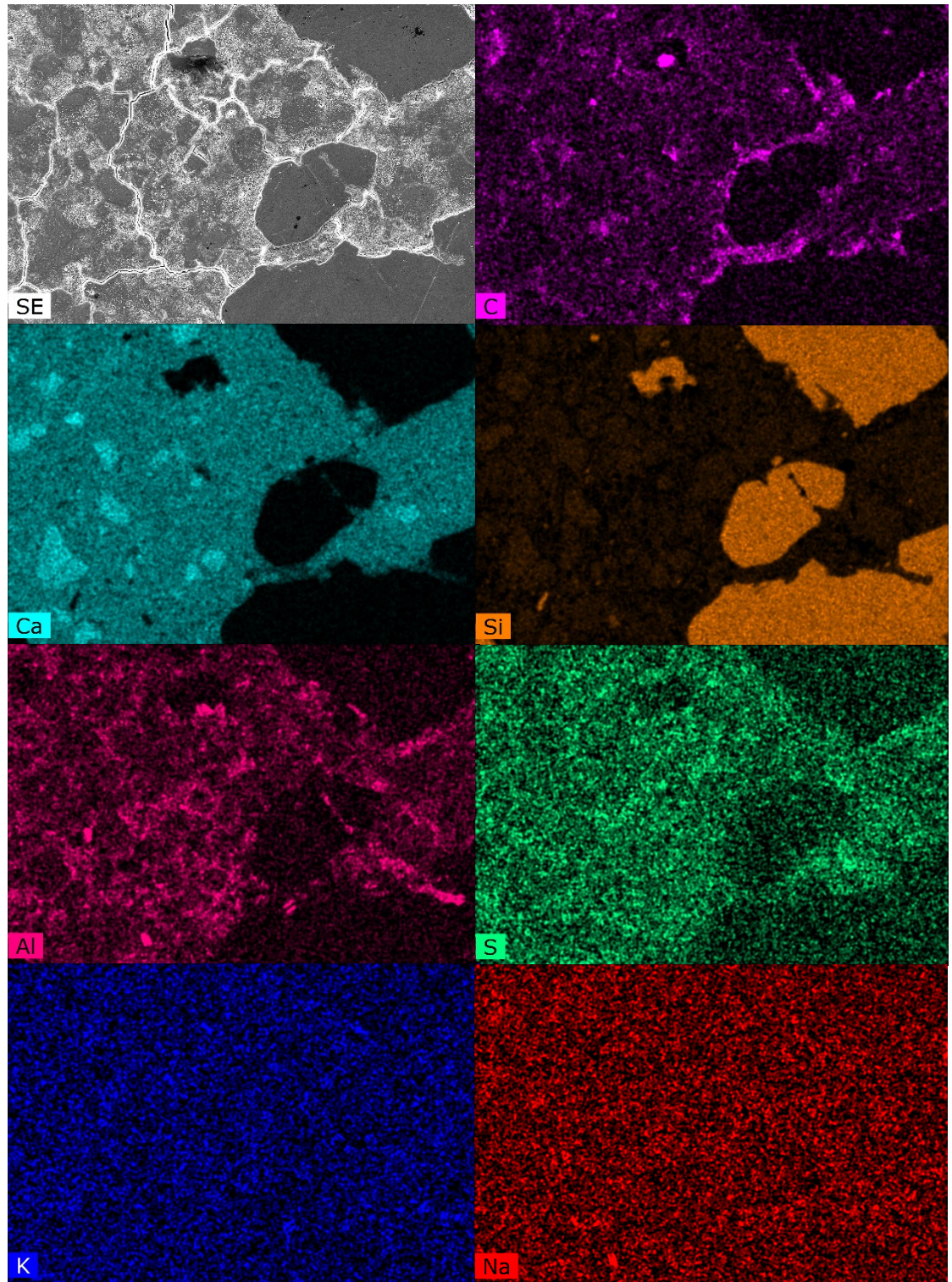


Figure 6.25 Elemental mapping of Ca, Si, Al, S of ambient cured (23°C) C2 mortar stored in saturated lime water for 500 days

The results demonstrate that sulphur is present in the C1 mortar system only sparsely (Figure 6.24), suggesting low levels of intermixed ettringite in the system. Results for the C2 mortar (Figure 6.25) are identical to C1, with no apparent difference.

6.3.2 GP cement systems cured at 90°C for 12 hours

The results and discussion of sections 6.1 and 6.2 Evolution of ionic pore solution characteristics and crystalline phases confirm the occurrence of non-expansive DEF in heat-cured systems. The impact of non-expansive DEF in the microstructure is studied here. Compared to the ambient-cured C1 mortar (Figure 6.20), the microstructure of the 90°C cured mortar (Figure 6.26) shows a higher degree of hydration with far fewer unhydrated clinker grains.

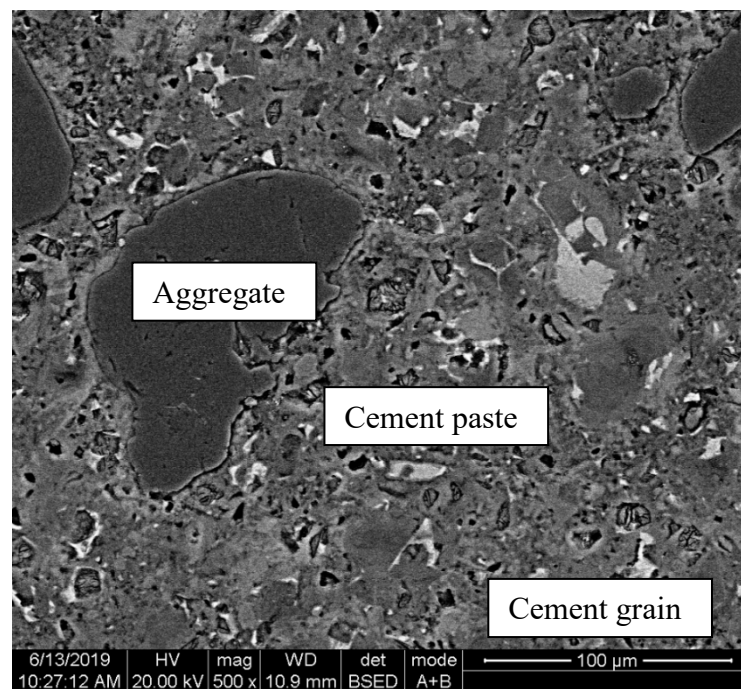


Figure 6.26 Microstructure of heat-cured C1 mortar at 90°C for 12 hours and subsequently stored in saturated lime water for 500 days

Cavities in the microstructure are due to the accelerated hydration induced by heat-curing at 90°C (Scrivener & Taylor 1993); this can lead to coarse porosity (Kjellsen & Detwiler 1992). Some of the cavities contain ettringite. A concentrated ettringite band at the ITZ

or within the cement paste is not visible from the micrograph, yet the atomic ratio plot S/Ca vs Al/Ca (Figure 6.27) confirms the presence of some ettringite within the cement paste. Further, limited Hc and Mc is detected, which is less than the C1 mortar cured at 23°C (Figure 6.22); this is in accordance with the XRD patterns (Figure 6.15). The elemental mapping (Figure 6.28) shows an overlap of Ca, S and Al within the cement paste (marked), indicating DEF.

In the case of the heat-cured C2 mortar, Figure 6.29 shows clear two-tone inner C-S-H products; outer, lighter C-S-H was formed during the heat curing, whereas inner, darker C-S-H was formed during the storage period (Scrivener & Taylor 1993; Yang et al. 1999). Much like the C1 mortar, cavities appear at many locations in the C2 heat-cured mortar.

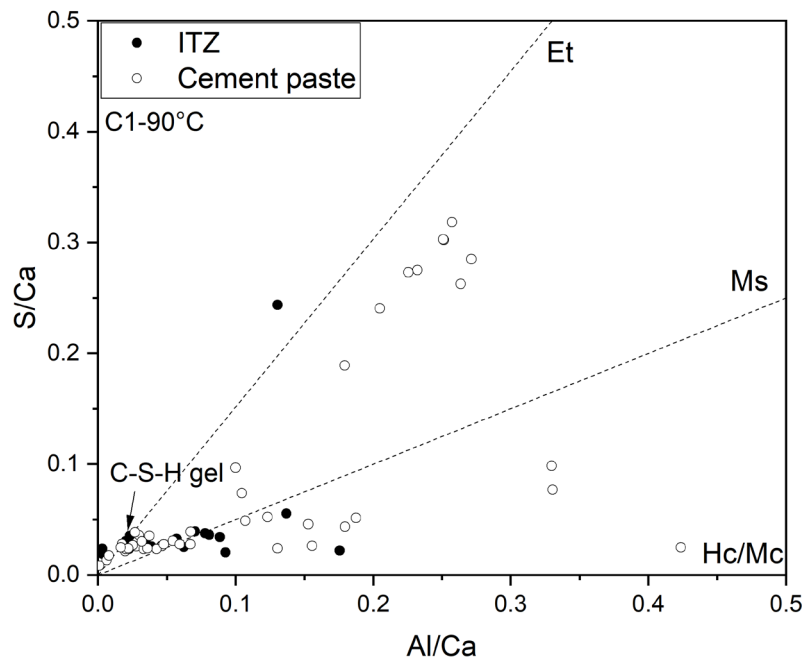


Figure 6.27 Atomic ratio plots of S/Ca vs Al/Ca of heat-cured C1 mortar at 90°C for 12 hours and subsequently stored in saturated lime water for 500 days

The absence of an ettringite band in the ITZ and cracks in the micrograph correlate well with the non-expansive nature of C2 heat-cured mortar. However, the presence of ettringite near the ITZ is noted from the atomic ratio plots (Figure 6.30). The elemental

mapping in Figure 6.31 shows a random distribution of Ca, Al and S throughout the microstructure, suggesting the presence of intermixed ettringite within the cement paste.

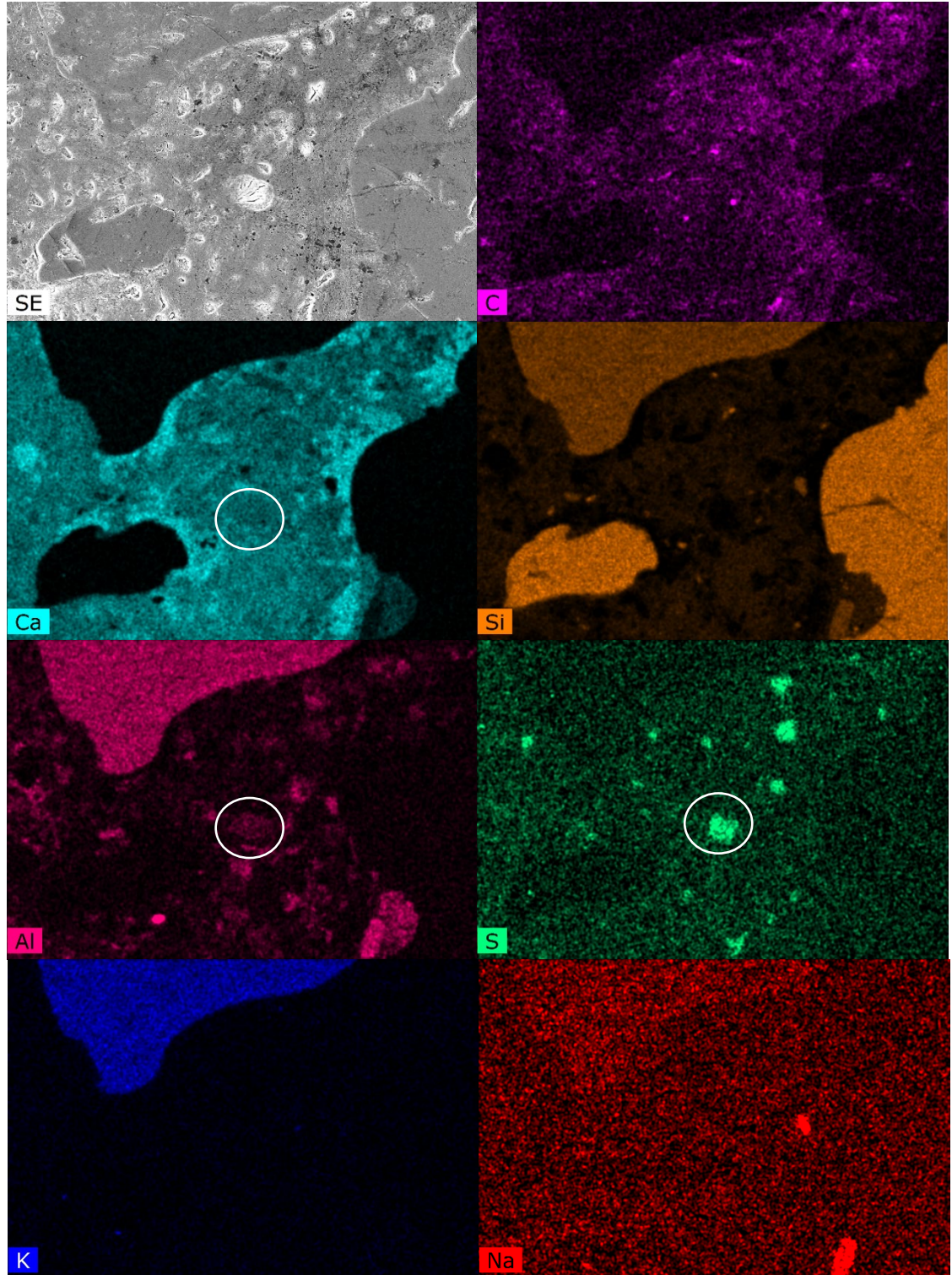


Figure 6.28 Elemental mapping of Ca, Si, Al, S in heat-cured C1 mortar at 90°C for 12 hours and subsequently stored in saturated lime water for 500 days

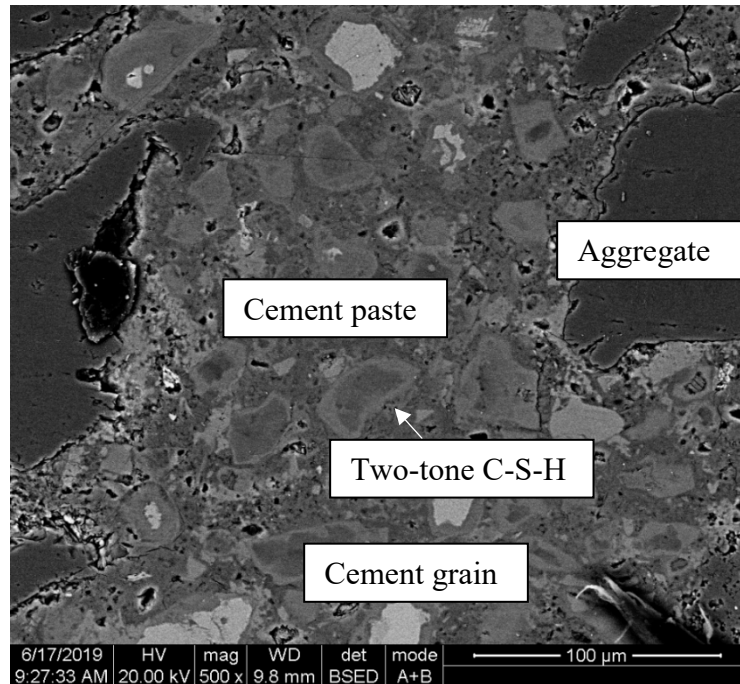


Figure 6.29 Microstructure of heat-cured C2 mortar at 90°C for 12 hours and subsequently stored in saturated lime water for 500 days

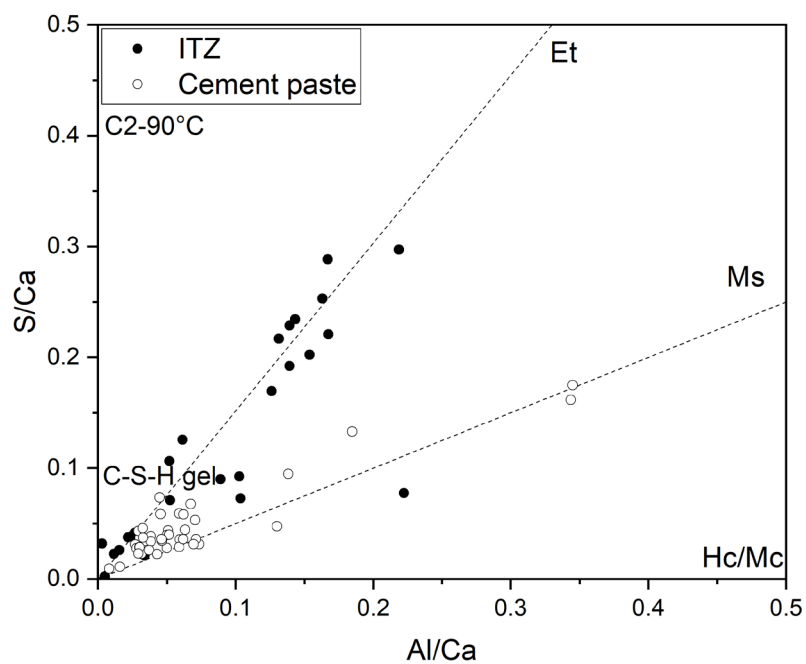


Figure 6.30 Atomic ratio plots of S/Ca vs Al/Ca of heat-cured C2 mortar at 90°C for 12 hours and subsequently stored in saturated lime water for 500 days

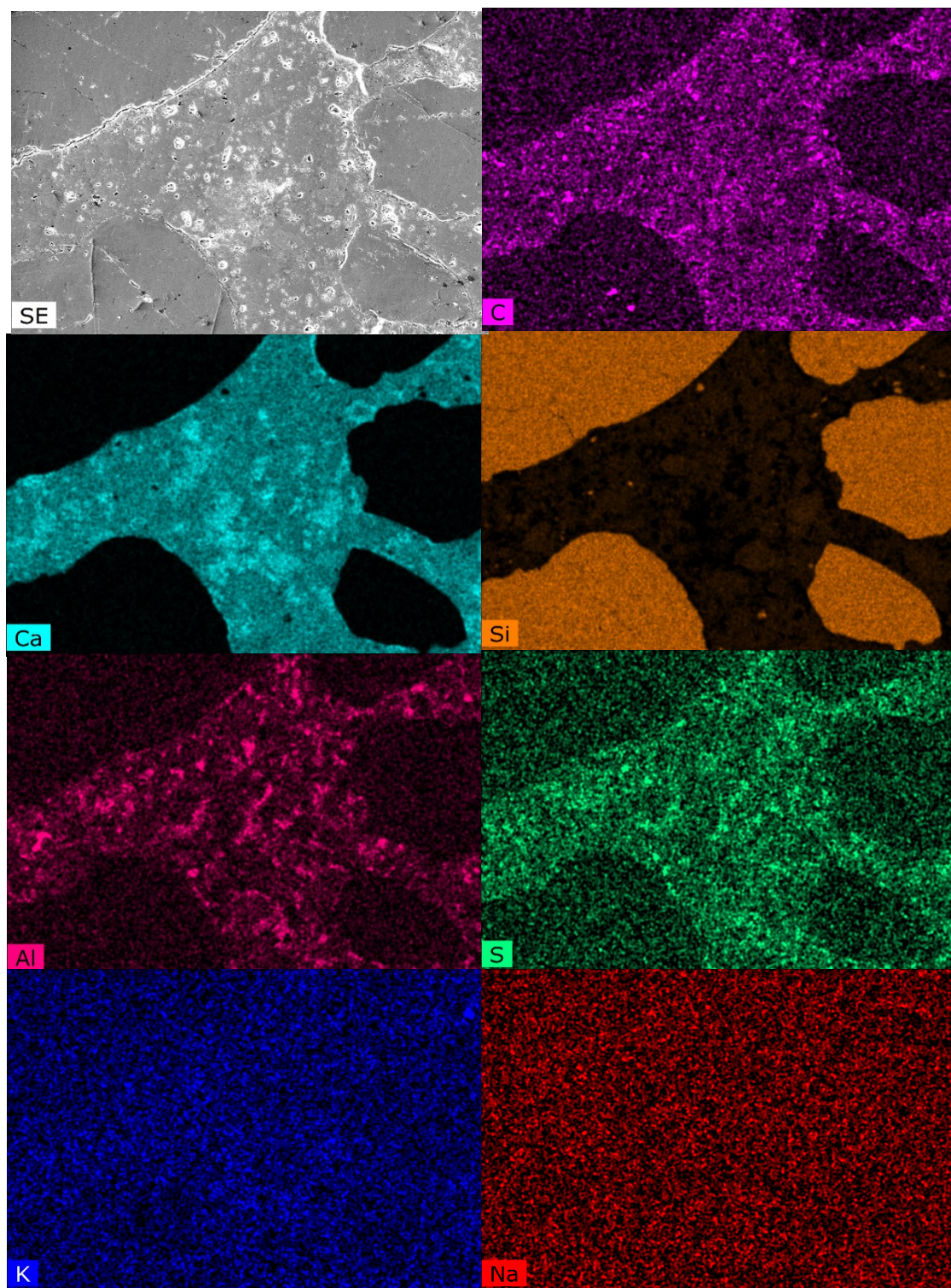


Figure 6.31 Elemental mapping of Ca, Si, Al, S in heat-cured C2 mortar at 90°C for 12 hours and subsequently stored in saturated lime water for 500 days

6.4 Electrical resistivity

The Nyquist plots obtained for C1 and C2 mortars by electrochemical impedance spectroscopy (EIS) are provided in Figure 6.32 and Figure 6.33. The electrode effect is removed and analysed based on the relative size of the arcs obtained for different mortars, as described in Section 4.2.6. From Figure 6.32Figure 6.33, it is clear that the ambient-cured C1 and C2 mortars have larger impedance arcs than the heat-cured mortars. Among heat-cured mortars, reducing the pre-cure time to zero did not result in any significant reduction to the impedance arc as it almost overlaid with the 4-hour pre-cured mortars. The results suggest that heat curing certainly affects the permeability of the mortar, which can be attributed to the cracks and coarse porosity formed due to accelerated hydration.

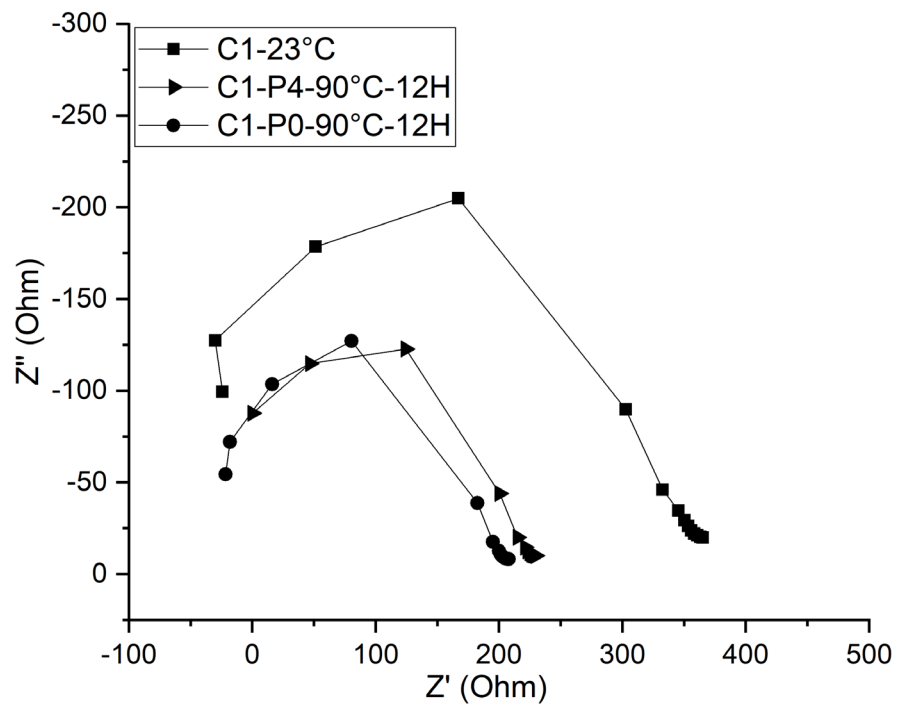


Figure 6.32 Nyquist plots of C1 mortars showing the effect of heat-curing – 500 days

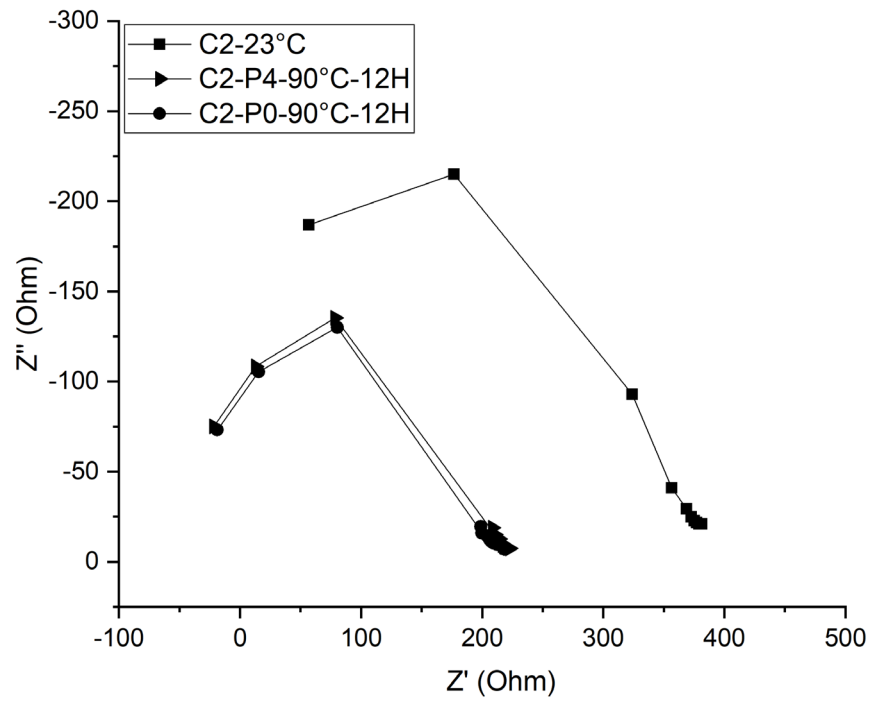


Figure 6.33 Nyquist plots of C2 mortars showing the effect of heat-curing – 500 days

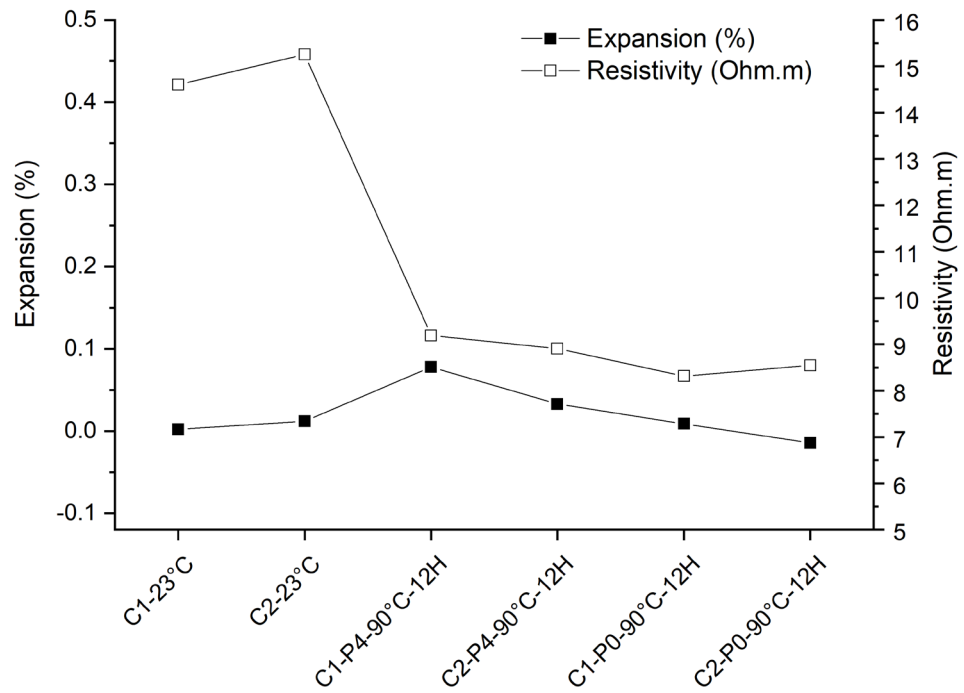


Figure 6.34 Impact of heat-curing in C1, C2 mortars at 500 days - electrical resistivity and expansion comparison

The mortar-electrode intersection impedance value from the Nyquist plot was taken and electrical resistivity was calculated using equation (4) given in Section 4.2.6. The

resistivity of mortars cured at 23°C is in the range of 14.5-15.3 Ohm.m and drops to 9.1-8.9 Ohm.m with a small increase in expansion due to heat-curing at 90°C. In the case of a zero-hour pre-cure, despite no observed expansion, electrical resistivity values drop further to 8.5-8.3 Ohm.m; this may be attributed to porosity caused by heat-curing.

DEF formed in standard cement systems (C1, C2) due to heat-curing might not have a significant role in lowering the electrical resistivity. A recent study by Gu et al. (2019), postulated that a reduction in pore volume might result if DEF fills the cracks. If that is true, then DEF occurring within the cement paste and cracks should increase the electrical resistance. However, in the present case DEF did not fill any cracks (Figure 6.26Figure 6.29), and in fact correlated with a reduction in electrical resistivity. The impact on electrical resistivity due to DEF filling the cracks and pores within cement pastes are discussed in Section 8.4.

6.5 Summary

The ambient-cured mortars did not expand significantly, primarily due to the stable primary ettringite phase in the cementitious systems. Heat-cured standard GP cement systems showed relatively higher sulphate ion concentrations in the pore solution at day 1, indicating that ettringite precipitation was suppressed; this was confirmed by TGA and XRD. Precipitation of ettringite at later ages, i.e., DEF, occurred during subsequent curing in saturated lime water. However, heat-cured mortars made with standard GP cements did not expand significantly. In the microstructural analysis there was no evidence of an ettringite band in ITZ. However, finely intermixed ettringite in ITZ and within the cement paste was indicated by EDS atomic ratio plots and elemental mapping. The electrical resistance dropped significantly for heat-cured mortars, primarily due to an increase in permeability and not to DEF.

Chapter 7 Effect of heat-curing in chemically modified cement systems

In Chapter 6 it was observed that two commercial GP cement systems did not experience expansive DEF when subjected to heat-curing. To understand the susceptibility of DEF expansion in cements having higher sulphate and alkali content, in this chapter the chemistry of the cements were altered to have different SO_3 (~2.35 to 6%) and $\text{Na}_2\text{O}_{\text{eq}}$ (~0.35 to 1.5%) contents and subjected to heat-curing at 90°C for 8 hours. Detailed description of mixes used in this chapter is provided in Table 4.3 to Table 4.5. One set of mortars was cured at 23°C as a reference. Further, a combined increase of SO_3 - 4% + $\text{Na}_2\text{O}_{\text{eq}}$ -1% in cements was tested for DEF potential by subjecting it to heat-curing at temperatures ranging from 50°C with an increment factor of 10°C until 90°C for 8 hours (including a reference mortar at 23°C). Linear expansion and mass changes were studied for all mortars as in Chapter 6. The presence of ettringite in ambient (23°C) systems and its complete absence and reformation in heat-cured (90°C) cement systems were well established in Chapter 6, and so will not be discussed in Chapter 7. However, the impact of increased sulphate and alkali on ettringite quantity will be discussed in Chapter 8 for 12-hour heat-cured samples. This chapter mainly focuses on expansion, mass changes and porosity by the electrical resistivity of 8 hour heat-cured mortars.

7.1 Linear expansion and mass changes

7.1.2 Impact of increasing sulphate content

Figure 7.1 and Figure 7.2 illustrate the linear expansion behaviour of C1 & C2 mortar prisms with increasing sulphate content after being subjected to 8-hour curing at 23°C and 90°C, respectively. None of the mortar prisms show any significant expansion. Heat-cured cement systems (C1, C2) containing 6% sulphate show slightly higher expansion at 600 days; about 0.04% while the other prisms show expansion in the range of 0.01-0.02%. This expansion shall be treated as innocuous as discussed in Section 6.1.

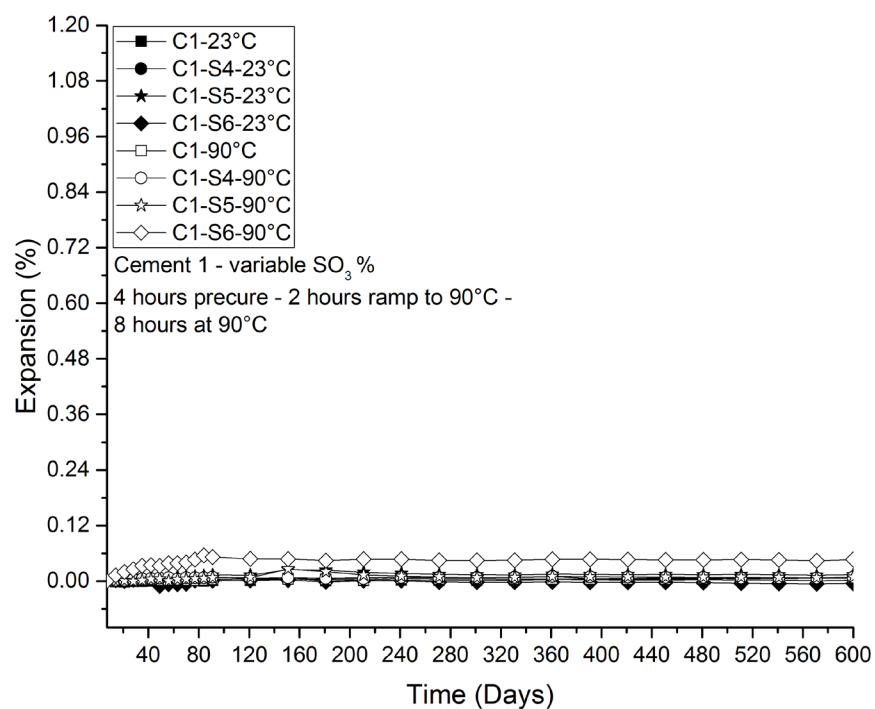


Figure 7.1 Linear expansive behaviour of Cement 1 mortars with increasing sulphate content cured at 23°C and 90°C

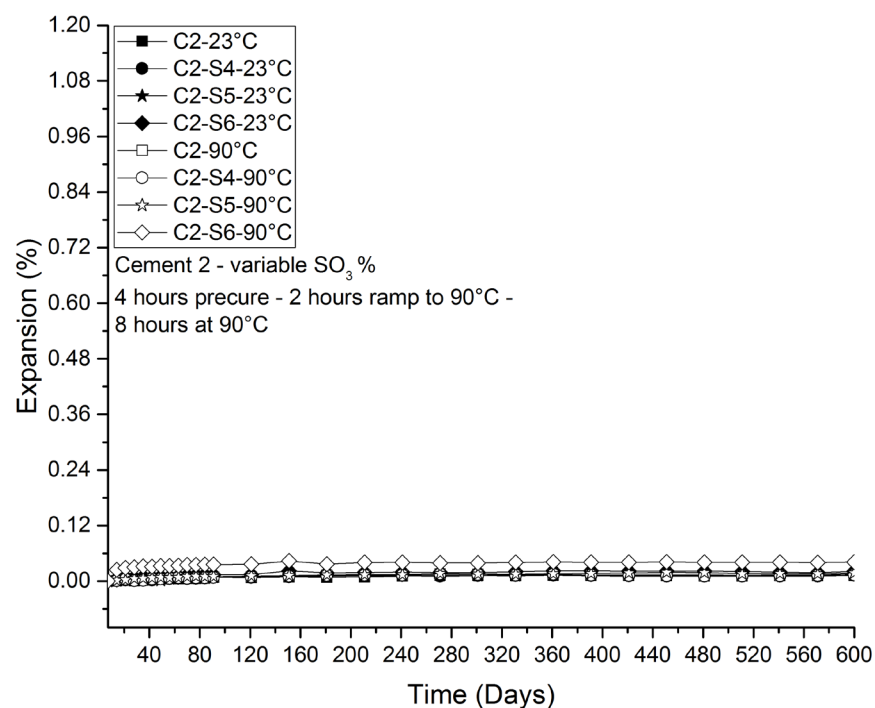


Figure 7.2 Linear expansive behaviour of Cement 2 mortars with increasing sulphate content cured at 23°C and 90°C

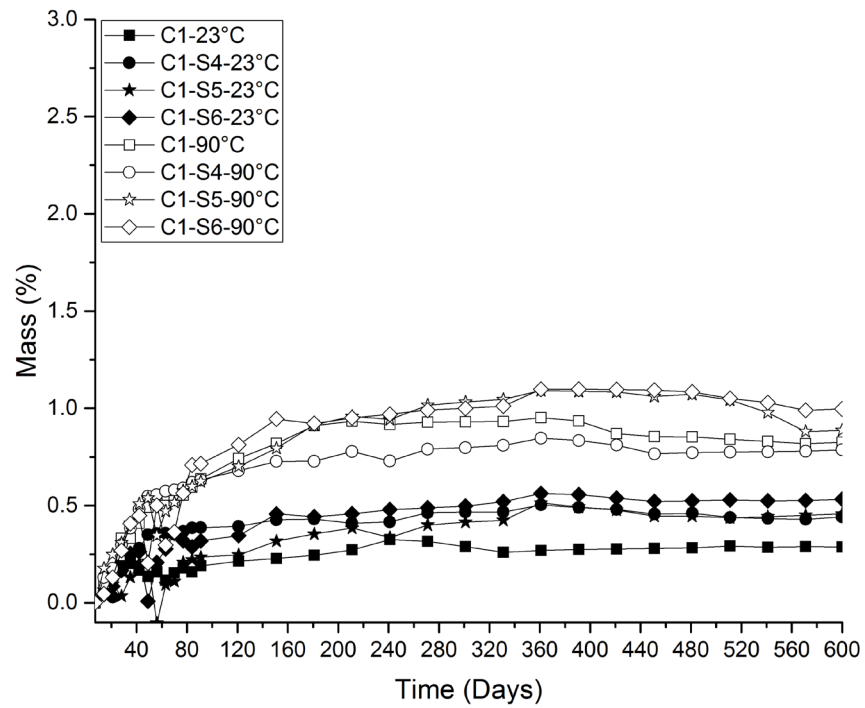


Figure 7.3 Mass changes of Cement 1 mortars with increasing sulphate content cured at 23°C and 90°C

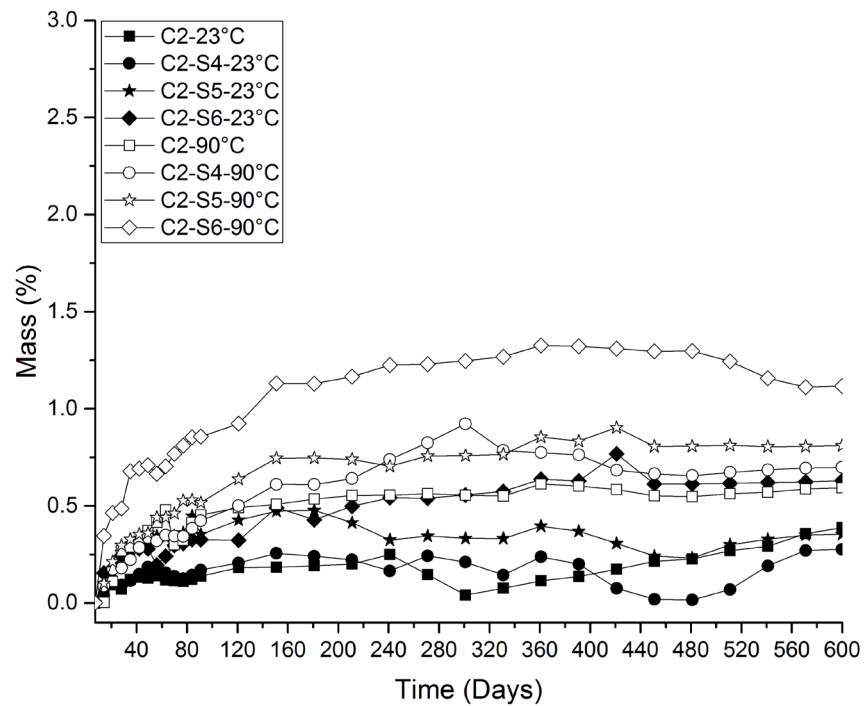


Figure 7.4 Mass changes of Cement 2 mortars with increasing sulphate content cured at 23°C and 90°C

Table 7.1 Shift in sulphate to alumina molar ratio due to additional sulphates

Cement	Molar ratio of (SO₃/Al₂O₃)			
	SO₃ wt. : C1-2.37% & C2- 3.07%	SO₃- 4%	SO₃- 5%	SO₃- 6%
C1	0.63	1.08	1.38	1.66
C2	0.89	1.17	1.48	1.79

The insignificant expansion observed when the sulphate content was raised is related to the shift in the molar ratio of (SO₃/Al₂O₃). Research works by Escadeillas et al. (2007); Famy (1999); Fu, Ding & Beaudoin (1997); and Zhang, Olek & Diamond (2002) showed a clear indication that cement systems with a molar ratio of (SO₃/Al₂O₃) less than 0.8 and above 1.2 would not give any significant expansion despite being heat-cured. So, the expansion of mortars between 0.8 to 1.2 molar ratios of (SO₃/Al₂O₃) is due to the availability of sufficient sulphates (in terms of molar %) to alumina, which is vital to react and precipitate ettringite in the system. The change in the molar ratios of (SO₃/Al₂O₃) for C1 and C2 cements are provided in Table 3.1. C1 and C2 containing 5-6% SO₃ and C1 with 2.37% sulphate are out of the critical range in terms of the SO₃/Al₂O₃ molar ratio. However, this does not explain the reason behind the non-expansive nature of C1 and C2 containing 4% SO₃ and C2 with 3.07% SO₃ as they are within the potential expansive (SO₃/Al₂O₃) molar ratio range. This may be due to the differences in the form of alumina available for the reactions. For instance, the Al₂O₃ content of C1 (4.78%) and C2 (4.38%) is almost the same (Table 3.1), but in C1 from the alumina comes from C₃A and C₄AF, whereas in C2 all the alumina is from C₃A, since C₄AF is nearly absent (Table 3.2). This implies that the alumina from C2 is more readily available to react with sulphates to form ettringite, as the reactivity of C₃A is faster than C₄AF. This still does not fully explain why C2 cement systems are not expansive, despite being a heat-cured system. It could be

due to the low alkali content of C2 (0.35%) (Kelham 1996), which is not sufficient to dissolve the available sulphates into the pore solution while heat curing (Thomas, Hooton & Ramlochan 2010). From the perspective of DEF, the total weight percentage of sulphate in cement becomes immaterial when C_3A and alkali levels are insufficient. It is also possible that the 8-hour heat curing duration might not be sufficient to cause expansive DEF as research by Fu, Ding & Beaudoin (1997) showed that similar sulphate content cements (3.46 to 4.08%) with comparable alkali and C_3A content expanded significantly (1.2 to 1.5%) when heat-cured for 12 hours.

The mass changes are illustrated in Figure 7.3 and Figure 7.4, which show an apparent higher mass gain in heat-cured mortars compared to the reference mortars cured at 23°C. Among the heat-cured specimens, cements with 6% SO_3 showed a higher degree and rate of mass gain than other specimens. Among cements, the C2-S6 mix specimens exhibited more mass gain. As discussed in Chapter 6 Section 6.1, the mass gain in the heat-cured mortars is linked with water absorption during curing storage, and can lead to a reduction in vital mechanical properties such as compressive strength.

7.1.2 Impact of increasing alkali content

Figure 7.5 and Figure 7.6 illustrate the expansive behaviour of C1 and C2 mortar prisms with increasing alkali content subjected to curing 8-hour curing at 23°C and 90°. It is evident from the graphs that no expansion was observed for the whole 600 days of testing. The additional alkali content from added sodium hydroxide and heat curing did not impact the expansion as it can be seen to overlap with reference mortars. The maximum expansion observed was 0.017%, which in fact for an ambient (23°C) cured C2 mortar with 1.5 % alkali suggests that specimens with added alkalis shrink when heat cured. Further, with the increase of alkalis, (Figure 7.7 and Figure 7.8) a reduction in mass gain was observed in heat-cured mortars that correlates with the shrinking behaviour. The non-

expansive response despite increasing alkalis is due to low sulphate content in the C1 (2.37%) and C2 (3.07%) specimens (H. F W Taylor, Famy & Scrivener 2001). If the alkali increase were to create DEF expansion in heat-cured mortars then sulphate-containing alkalis would need to be introduced, e.g., as sodium sulphate (NaSO_4) or potassium sulphate (K_2SO_4). Alternatively, if hydroxides such as sodium hydroxide (NaOH) or potassium hydroxide (KOH) were used, additional sulphates such as calcium sulphate would be needed (Famy 1999; Kelham 2002).

7.1.3 Impact of range of curing temperature in sulphate and alkali modified cement

From the above sections 7.1.2 Impact of increasing sulphate content and 7.1.2 Impact of increasing alkali content, an increase in sulphate or alkali alone might not make a cement vulnerable to expansive DEF when heat-cured. Optimum sulphate and alkali content along with sufficient alumina (more likely from C_3A) are required for the cement to become susceptible to expansive DEF. It may also help to identify the critical heat-curing temperature to create expansive DEF under laboratory conditions.

Furthermore, many research works including those by Barbarulo et al. (2005); Ekelu, Thomas & Hooton (2007); Famy (1999); Grabowski et al. (1992); Lawrence (1995); Mulongo & Ekelu (2013b), (2013a); Ramlochan, Thomas & Hooton (2003); Yang et al. (1997); Yang & Sharp (1996); and Zhang, Olek & Diamond (2002b, 2002a) show that DEF expansion occurred in heat-cured mortars when cement had about 4% sulphate and 1% alkali content. Hence the cements C1 and C2 were modified to contain $\text{SO}_3 - 4\% + \text{Na}_2\text{O}_{\text{eq}} - 1$ and then tested for DEF potential under different heat-curing temperatures (50 to 90°C). Results of expansive behaviour are illustrated in Figure 7.9 and Figure 7.10. These show that, in the case of C1, no expansion was observed until 90°C . Heat curing at 90°C resulted in significant DEF expansion.

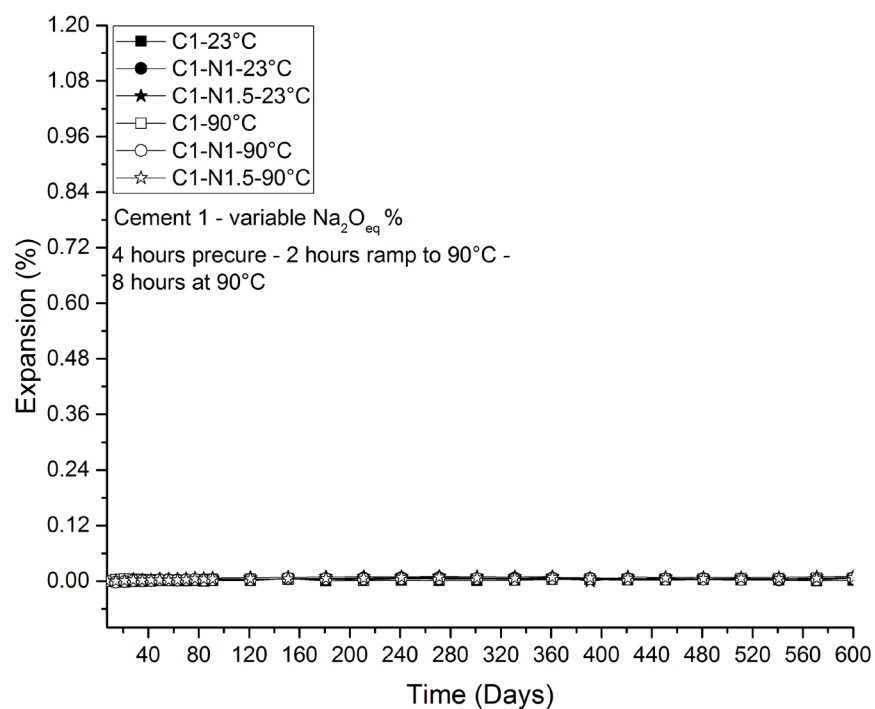


Figure 7.5 Linear expansive behaviour of Cement 1 mortars with increasing alkali content cured at 23°C and 90°C

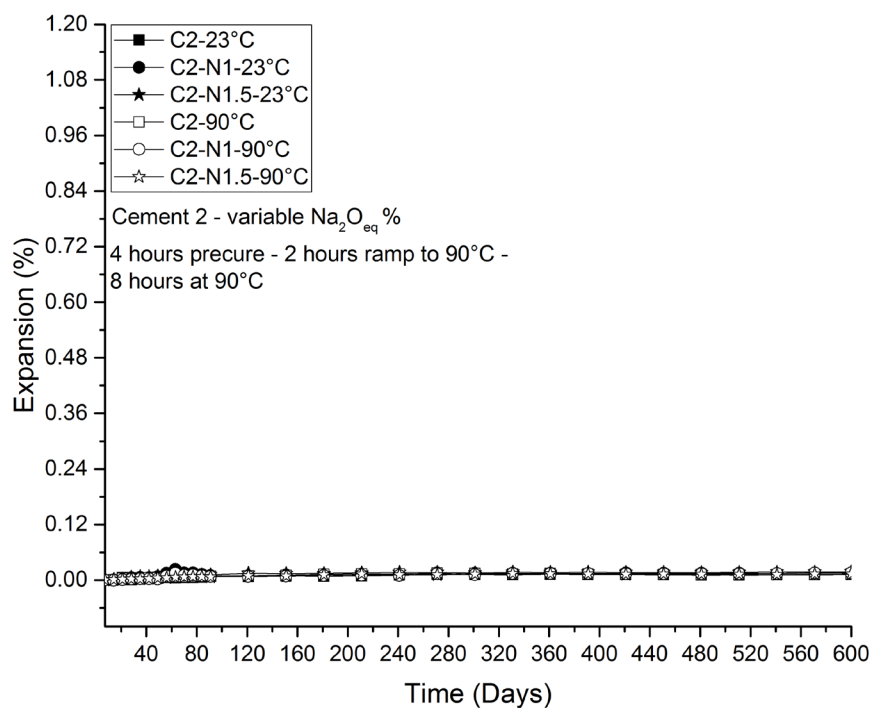


Figure 7.6 Linear expansive behaviour of Cement 2 mortars with increasing alkali content cured at 23°C and 90°C

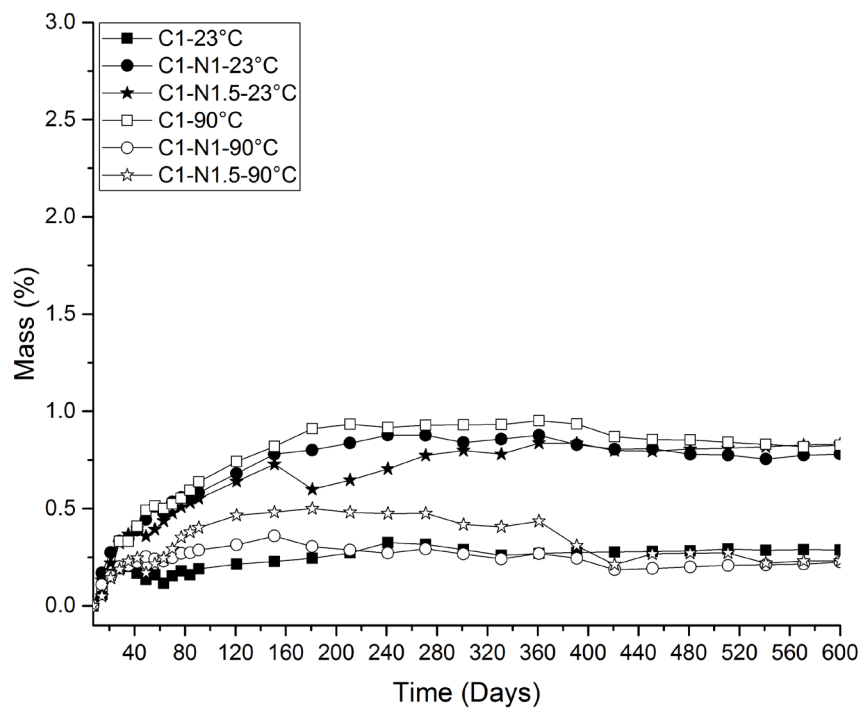


Figure 7.7 Mass changes of Cement 1 mortars with increasing alkali content cured at 23°C and 90°C

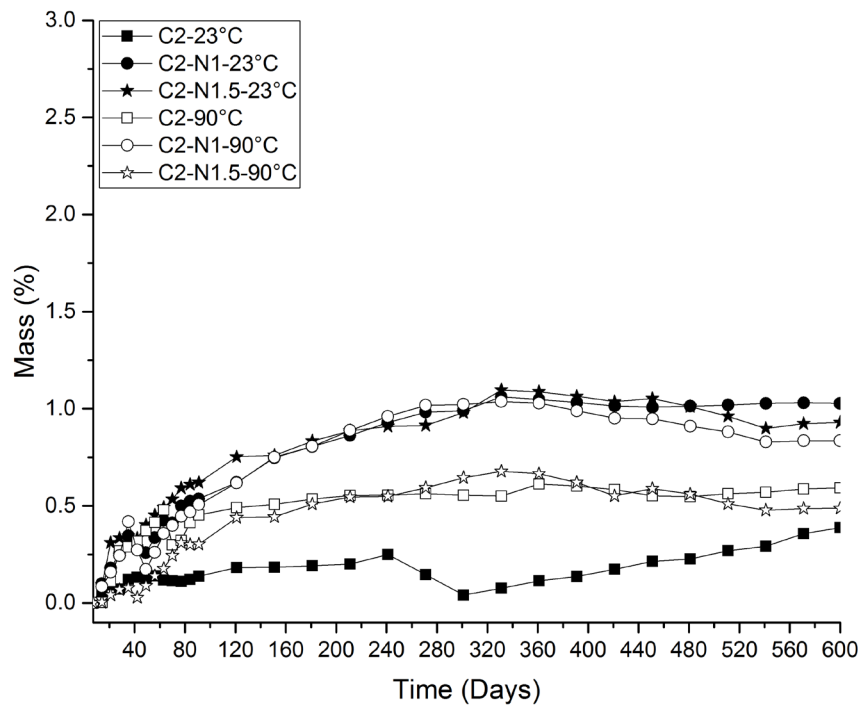


Figure 7.8 Mass changes of Cement 2 mortars with increasing alkali content cured at 23°C and 90°C

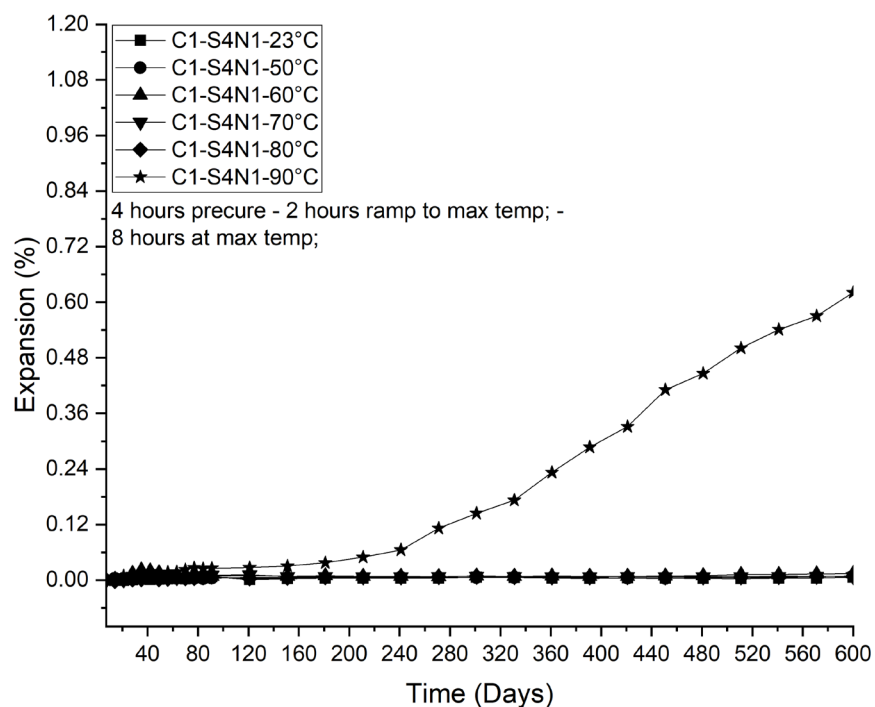


Figure 7.9 Linear expansive behaviour of Cement 1 mortars with SO_3 -4% + $\text{Na}_2\text{O}_{\text{eq}}$ - 1% cured at 23°C-90°C

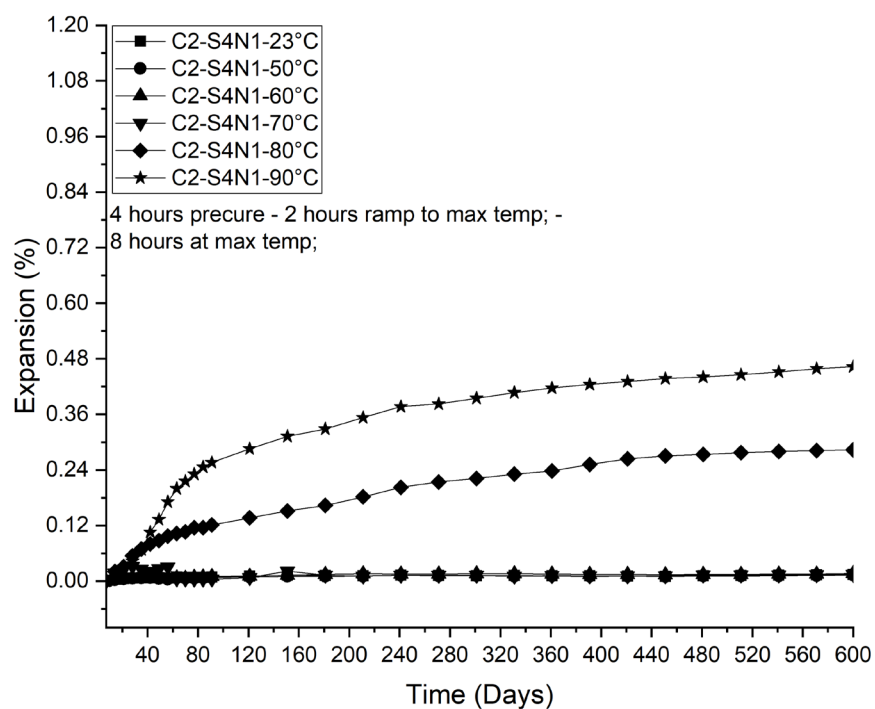


Figure 7.10 Linear expansive behaviour of Cement 2 mortars with SO_3 -4% + $\text{Na}_2\text{O}_{\text{eq}}$ - 1 cured at 23°C-90°C

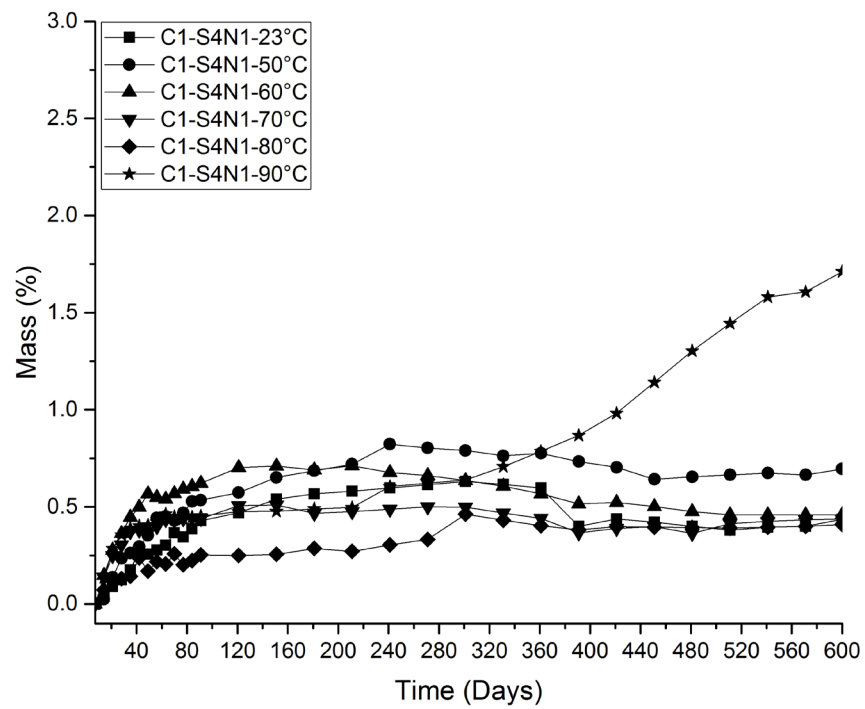


Figure 7.11 Mass changes of Cement 1 mortars with SO_3 -4% + $\text{Na}_2\text{O}_{\text{eq}}$ - 1 cured at 23°C-90°C

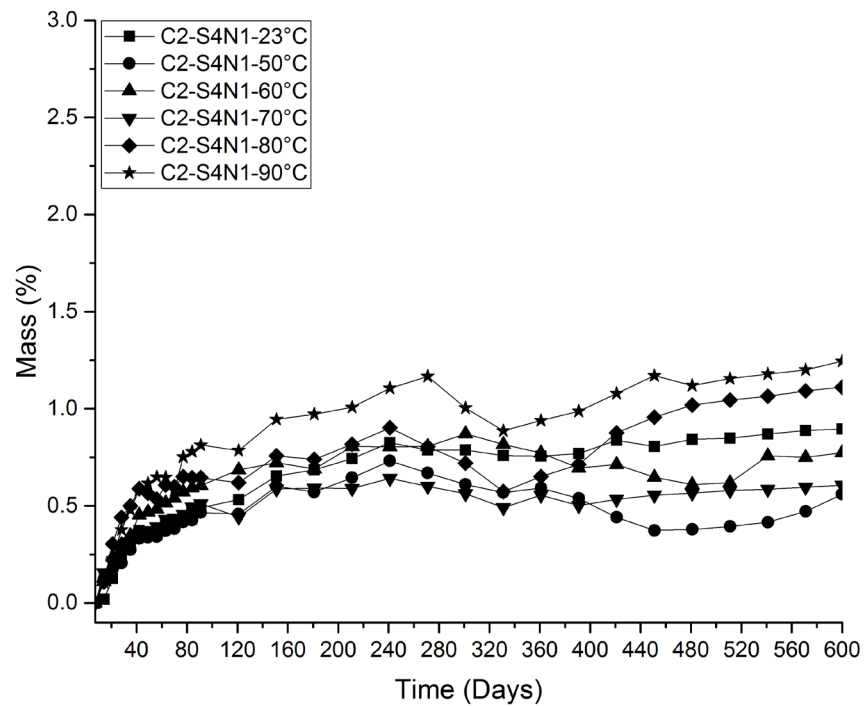


Figure 7.12 Mass changes of Cement 2 mortars with SO_3 -4% + $\text{Na}_2\text{O}_{\text{eq}}$ -cured at 23°C-90°C

The maximum expansion observed was 0.621% at the end of 600 days, which is well above the 0.2% threshold (Chapter 6 Section 6.1) to be labelled as expansive DEF. As expansion was above 0.4%, microstructural damage is expected for this level of expansion. In the case of C2, significant expansion was observed from 80°C onward, showing a difference between C1 and C2 in terms of the critical temperature for expansive DEF. At the end of 600 days, C2 gave a maximum expansion of 0.283% and 0.462% for 80°C and 90°C curing respectively. Comparatively, the C1 mortar expanded more than the C2 despite a lower C₃A content in C1 (Table 3.2). However, the role of higher C₃A in C2 is more pronounced in the rate of expansion. The C2 mortar reached 0.1% expansion at about 40 days, whereas C1 expanded much slower to reach 0.1% at ~260 days. The expansion reached saturation in C2 mortars, whereas the C1-S4N1-90°C mortar at the age of 600 days was still expanding, suggesting it is tedious to fix an arbitrary time frame for DEF tests as it may well vary for different cements.

As discussed earlier, the mass gain correlated well with the expansion results (Figure 7.11 and Figure 7.12). In the case of C1, the mass gain of the expanding mortar stands out from the rest of non-expanding mortars and correlates with the rate of expansion, which supports the results obtained by Zhang, Olek & Diamond (2002a). In C2, an increase in mass gain was not proportional to curing temperature until 70°C. In other words, no proper correlation was seen between mass gain and curing temperature in non-expanding mortars. However, in expanding mortars, the relationship between curing temperature (80°C-90°C) and mass gain exists. Further, the typical drop in mass at a certain age and recovery is observed in C2 mortars (80°C-90°C), indicating the possible occurrence of DEF (Shao et al. 1997).

7.2 Electrical resistivity

From the above discussions, only the $\text{SO}_3 - 4\% + \text{Na}_2\text{O}_{\text{eq}} - 1$ containing mortars show any difference in terms of expansion when heat cured. As such, mortars of that cement system were considered for EIS tests. Nyquist plots obtained by EIS (Section 4.2.6) are given in Figure 7.13 and Figure 7.14. The impedance arcs decrease in size as the heat curing temperature increases for C1 mortars; there is almost an overlap of spectra observed for C1 mortars cured at 60-80°C. In the case of C2 mortars, all non-expanding mortars cured at 23°C-70°C show relatively minor differences in the impedance arcs. The expanding mortars, cured at 80°C-90°C, show a clear contrast with the non-expanding mortars with smaller impedance arcs. However, among the expanding mortars, no apparent differences in impedance arcs are noted, probably due to the slight increase in expansion (0.283% & 0.462%) between the two mortars. The smallest impedance arc among all the mortars (C1 and C2) was for the 90°C cured C1 mortar, which gave the maximum expansion (0.621%), indicating the relationship between expansion and EIS data.

As discussed in Section 6.34, the mortar-electrode intersection impedance value from the EIS spectra was taken and used to calculate the electrical resistivity of mortars using the equation (4) given in Section 4.26. Electrical resistivity calculations eliminate any differences (or overlaps) that occur due to minor dimensional differences among specimens. The results of the electrical resistivity of C1 and C2 mortars are provided in Figure 7.15 and Figure 7.16. These show the reduction in resistivity of specimens as the curing temperature increases, indicating damage due to porosity changes. The increased porosity due to heat curing may have created the favourable conditions for ion transportation, which encourages DEF.

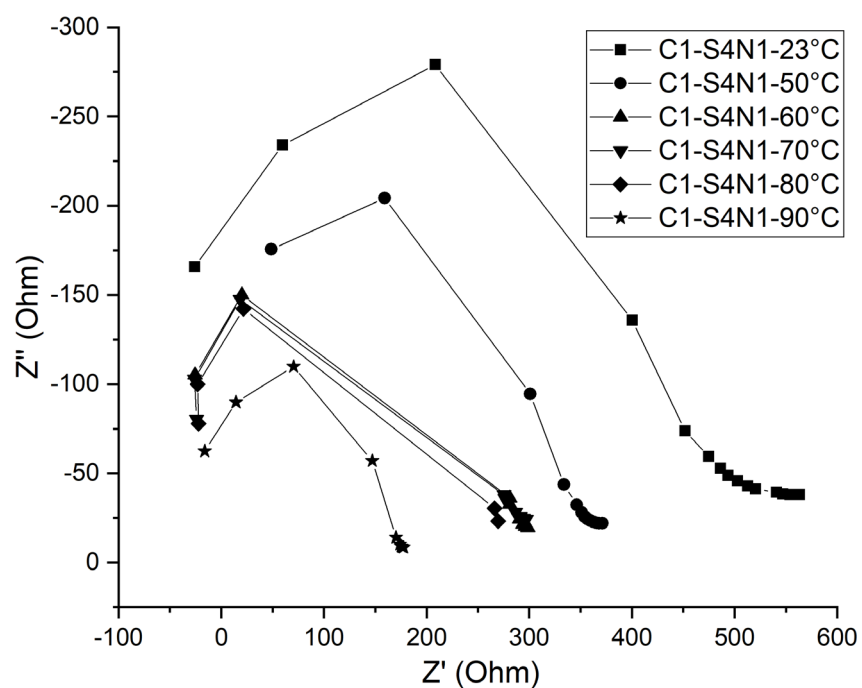


Figure 7.13 Nyquist plots of C1 mortars with SO_3 -4% + $\text{Na}_2\text{O}_{\text{eq}}$ – 1 showing the effect of heat-curing temperature – 500 days

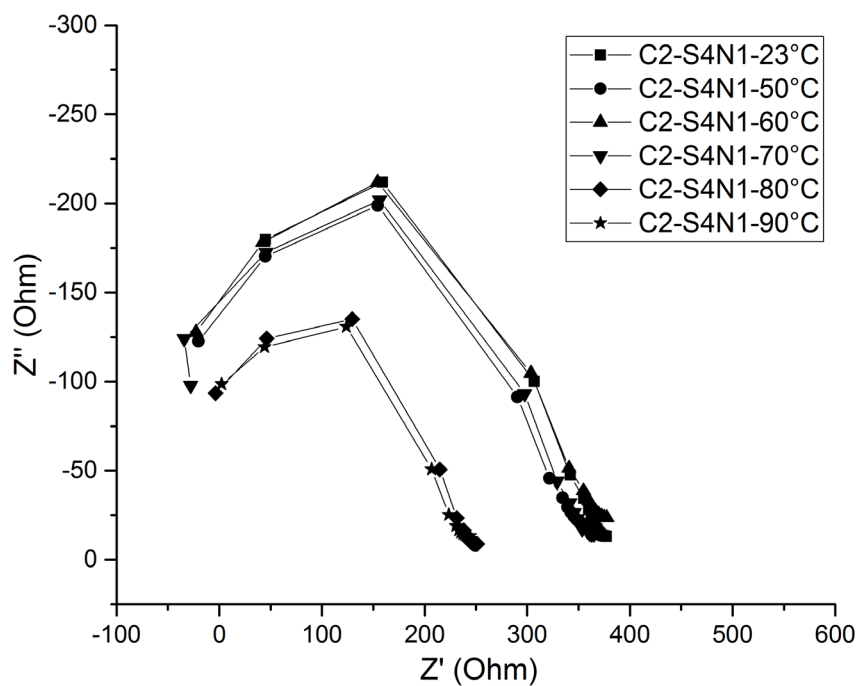


Figure 7.14 Nyquist plots of C2 mortars with SO_3 -4% + $\text{Na}_2\text{O}_{\text{eq}}$ – 1 showing the effect of heat-curing temperature – 500 days

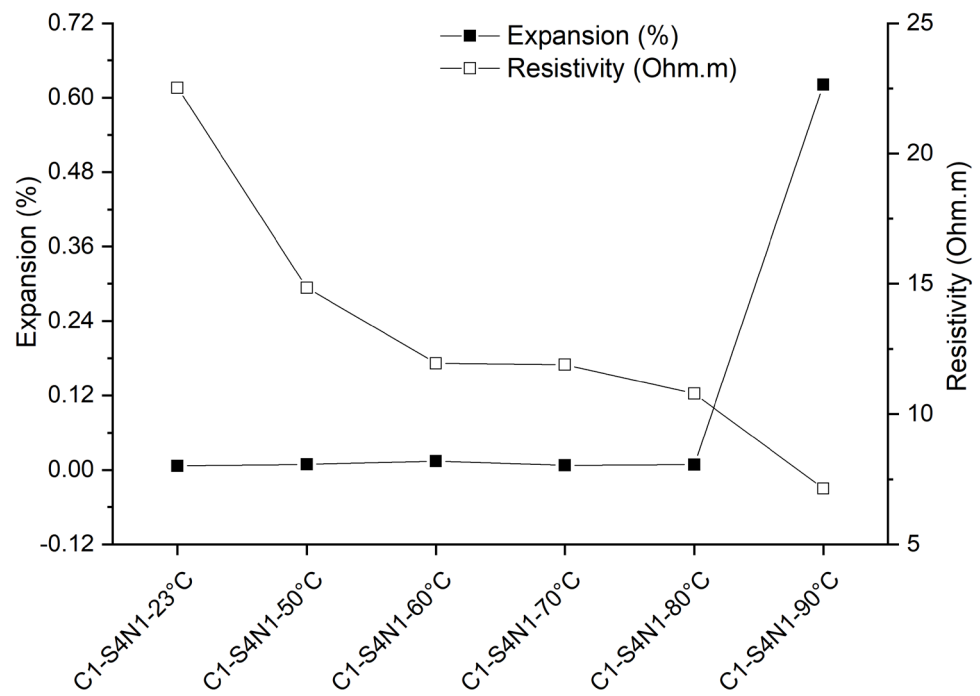


Figure 7.15 Relationship between expansion and electrical resistivity in modified C1 mortars with respect to curing temperature

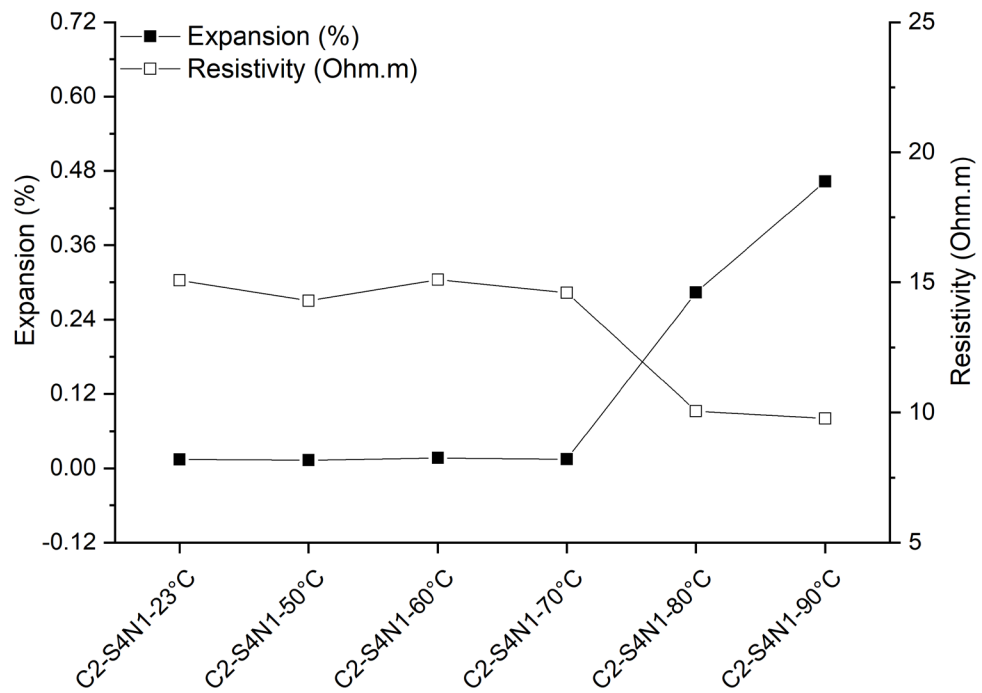


Figure 7.16 Relationship between expansion and electrical resistivity in modified C2 mortars with respect to curing temperature

7.3 Summary

From the results, not all chemically modified cement systems are prone to expansive DEF when heat cured. On the basis of an 8-hour heat-cure with C1 and C2 standard cement mortars, there is very little likelihood of DEF for a standard cement mix with 7.4-11.2% C_3A , $< 0.6\%$ Na_2O_{eq} and $< 3.5\%$ SO_3 , even with elevated temperature curing. Even separately modifying the cements to have SO_3 up to 6% or Na_2O_{eq} up to 1.5% did not show any expansive DEF. However, the cements modified to have 4% SO_3 with 1% Na_2O_{eq} showed signs of expansive DEF, suggesting a pessimum cement composition required to cause DEF when heat cured.

The identified pessimum cement composition (SO_3 -4% and Na_2O_{eq} -1%) will be carried forward for the next chapter to investigate the impact of heat-curing duration and pre-cure time on DEF.

Chapter 8 Effect of heat-curing time and pre-curing time on chemically modified cement systems

In the previous chapter, expansive DEF was observed at the pessimum cement composition of 4% SO_3 with 1% $\text{Na}_2\text{O}_{\text{eq}}$ (C1-S4N1, C2-S4N1) and subjected to heat curing at 80-90°C for 8 hours. Cement composition of 4-6% SO_3 (with unaltered $\text{Na}_2\text{O}_{\text{eq}}$) and $\text{Na}_2\text{O}_{\text{eq}}$ 1.0 to 1.5% (with unaltered SO_3) showed no indication of expansive DEF. Among these, alkali-modified systems show shrinkage and lower mass gain than unaltered standard cement systems and so were excluded from further studies. As SO_3 -4% cement systems give a ($\text{SO}_3/\text{Al}_2\text{O}_3$) molar ratio of about 1%, which is the pessimum condition for DEF, these were retained for further research with two alkali levels. Further, increasing the duration of heat curing and reducing the pre-cure time has been reported to increase the vulnerability of DEF in literature. Studying the impact of combining the DEF pessimum cement composition with more rigorous heat curing regimes is the objective of this chapter. Hence, in this chapter cement systems with 4% SO_3 (C1-S4, C2-S4) and 4% SO_3 + 1% $\text{Na}_2\text{O}_{\text{eq}}$ (C1-S4N1, C2-S4N1) only were considered to study the impact of increased heat-curing (at 90°C) duration from 8 to 12 hours and reduced pre-cure duration from 4 to 0 hours. Refer Table 4.6 and Table 4.7 for the detailed description of mixes studied in this chapter. Linear expansions were recorded to up to 600 days to differentiate expansive and non-expansive DEF occurrence in heat-cured mortars. Mass changes in mortar prisms were noted up to 600 days. Changes in the dissolution of different ions due to additional sulphates, alkalis and heat curing were studied by analysing pore solutions extracted from cement pastes. Further, the development of crystalline phases in heat-cured systems was studied using FTIR, TGA and XRD. XRD semi-quantitative analysis was used to study changes in ettringite precipitation due to heat curing. Microstructural changes, in particular ettringite deposition within cementitious

systems, were investigated using BSE-SEM imaging and EDS mapping. The electrical resistivity of selected mortars was studied using EIS to understand the changes in porosity properties of mortars due to heat curing. Results of commercial cements from Chapter 6 were used in graphs as a reference, wherever necessary.

8.1 Linear expansion and mass changes

8.1.1 Effect of heat-curing time

Figure 8.1 and Figure 8.2 illustrate the linear expansion differences in Cement1 and Cement 2 mortars due to the increased heat curing duration in different cementitious systems. Irrespective of heat curing duration, reference mortars made with commercial cements do not show expansion, as discussed in Section 6.1.

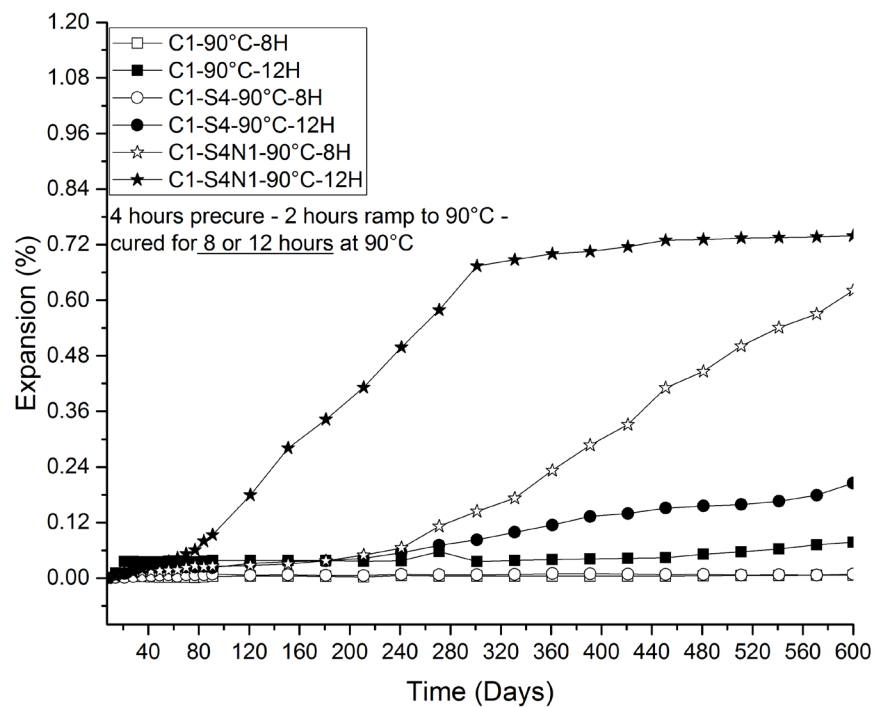


Figure 8.1 Effect of increase in heat-curing duration (8 to 12 hours) in linear expansive behaviour of Cement1 mortars

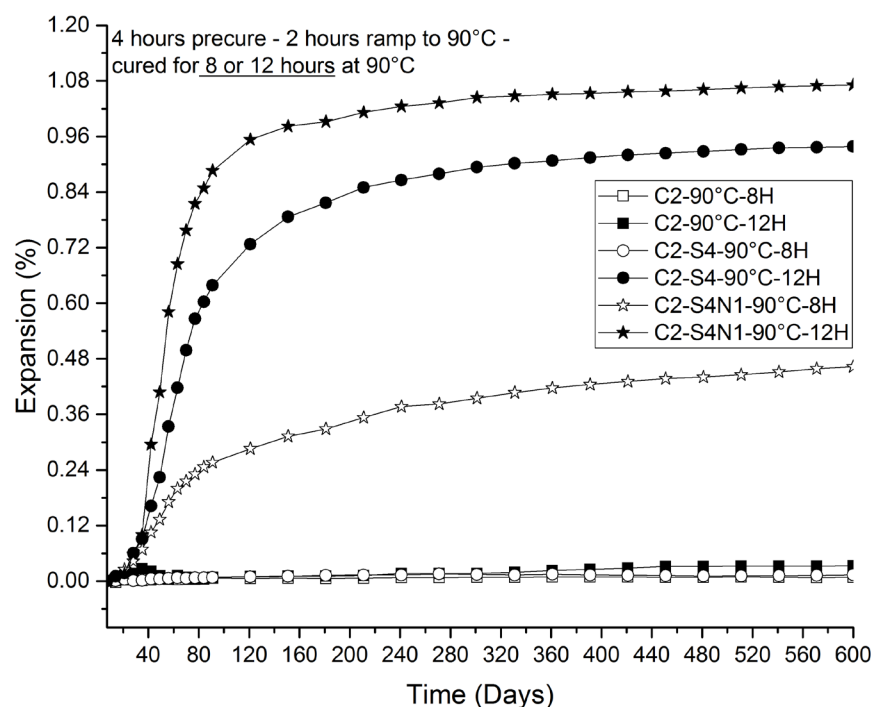


Figure 8.2 Effect of increase in heat-curing duration (8 to 12 hours) in linear expansive behaviour of Cement2 mortars

In the case of mortars made with 4% SO_3 cements, i.e., C1-S4 and C2-S4, an increase in ultimate expansion from 0.008% to 0.205 % and 0.013% to 0.938% was noted, corresponding to the increase in heat-curing time from 8 to 12 hours. The additional 4 hours of 90°C curing transform the 4% SO_3 cement mortars from innocuous to expansive DEF (Section 6.1), thus proving the composition of cement is not the only factor affecting DEF. Similar results of comparable cement composition (3-4% SO_3 , 0.6% $\text{Na}_2\text{O}_{\text{eq}}$) and heat curing around 90-100°C for 10-12 hours have been obtained by other researchers (Fu, Ding & Beaudoin 1997; Pavoine, Divet & Fenouillet 2006; Yang et al. 1999; Yang & Sharp 2001a). The C2-S4 specimen had an expansion of 0.938%, which is well above 0.4% (see Section 6.1) and so microstructural damage is expected. The increase curing duration, caused SO_3 alone increased system C2-S4 to expand but not in C1-S4, shall be attributed to the high alumina content in Cement 2. In the case of mortars made with SO_3 - 4% + $\text{Na}_2\text{O}_{\text{eq}}$ -1% cements, i.e., C1-S4N1 and C2-S4N1, mortars had an increase in

expansion from 0.621% to 0.738% and 0.463% to 1.071% respectively, for the additional 4 hours of heat curing. Due to prolonged heat curing, the period to attain expansive DEF that may potentially cause deterioration (i.e., 0.2% expansion) was reduced from 345 to 128 days and 64 to 39 days for C1-S4N1 and C2-S4N1 respectively. Thus in chemically modified cements, increasing the heat curing duration increases both the degree and rate of expansion thus increasing DEF risk (Famy 1999). The mass gain trends given in Figure 8.3 Figure 8.4 show a higher mass gain for 12 hour heat-cured mortars than 8 hours for a given cement system and correlate well with the expansion data. Cement 2 mortars appears to have strong correlation between expansion and mass trends than C1, suggesting the change with respect to DEF needs to be much higher to establish proper correlation between linear expansion and mass gain data. Water absorption by the specimens during storage was responsible for the mass gain (Ekolu, Rakgosi & Hooton 2017; Santhanam 2001; Zhang, Olek & Diamond 2002a).

Researchers have contradicting opinions on how water absorption occurs. Ekolu, Rakgosi & Hooton (2017) suggest that heat-cured specimens have more affinity to absorb water to compensate the lost moisture during the heat curing process. However, mass gain occurs in ambient-cured specimens too, as in the case of external sulphate attack (Santhanam 2001). Further, Ekolu, Rakgosi & Hooton (2017) reported non-expanding specimens gained greater mass than expanding ones, which is again conflicting as mass gain correlates well with the expansion, loss in mechanical properties and microstructural damage occurring in the specimens (Santhanam 2001; Zhang, Olek & Diamond 2002a). The higher water absorption and the associated mass gain will be considered to be linked with cracked or damaged, more porous microstructures resulted from a combination of accelerated hydration due to heat curing and DEF.

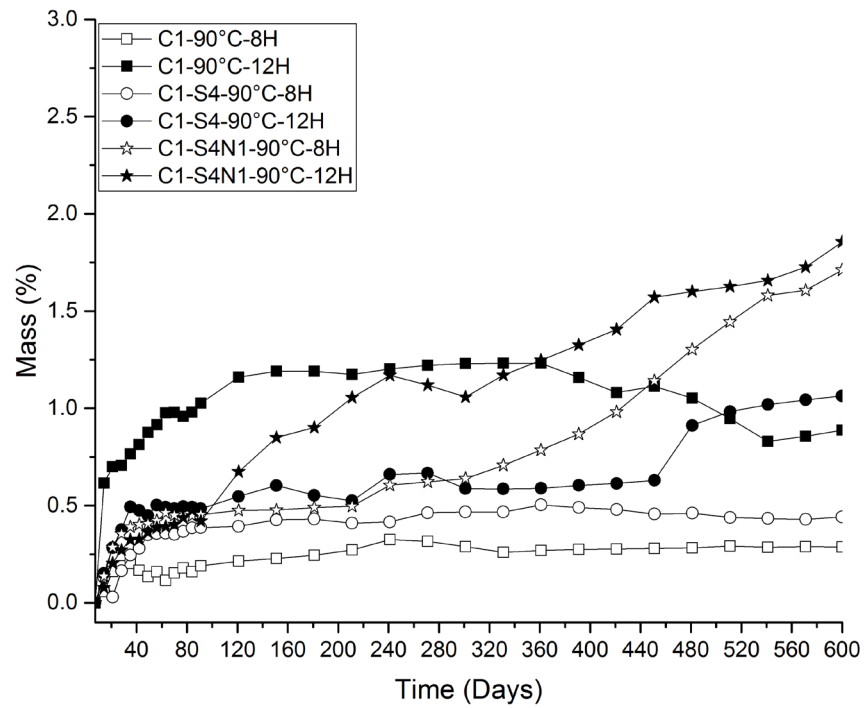


Figure 8.3 Effect of increase in heat-curing duration (8 to 12 hours) in mass changes of Cement 1 mortars

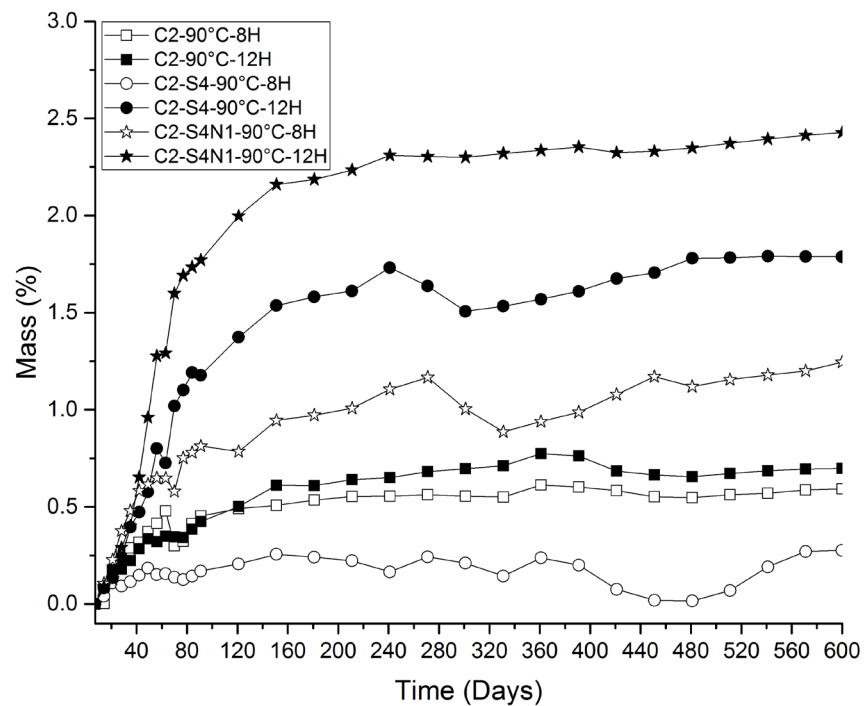


Figure 8.4 Effect of increase in heat-curing duration (8 to 12 hours) in mass changes of Cement 2 mortars

Among 12-hour heat-cured S4N1 mixes, C2-S4N1 had a higher degree of expansion and mass gain compared to C1-S4N1. As all the other cement parameters and experimental conditions being the same, the higher C_3A in C2 (11.2%) than C1 (7.4%) is appear to be the most significant factor in increasing the increasing the DEF expansion, as it can contribute to more ettringite precipitation by reacting with available sulphates.

8.1.2 Effect of pre-curing time

Linear expansion differences between Cement 1 and Cement 2 mortars with two different pre-cure times i.e. 4 and 0 hours cured at 90°C for 12 hours are illustrated in Figure 8.5 and Figure 8.6. As discussed in Section 6.1, commercial GP cements (C1, C2) did not show any difference in expansion, irrespective of pre-cure time. In C1-S4 and C1S4N1 mortars, significantly lesser expansion resulted in 0-hour pre-cure specimens than 4 hour pre-cure specimens contradicting with other studies (Azzam 2002; Fu, Ding & Beaudoin 1997; Sylla 1988). The mortars cured at 0-hour pre-cure, did not had enough time at ambient temperature to crystallise significant quantity of primary ettringite, thereby reducing the chance of expansion related to ettringite reformation (Famy 1999). On the contrary C2-S4 and C2-S4N1 mortars cured with 0-hour pre-cure expanded much the same as the 4-hour pre-cure mortars. The reduction in pre-curing time (from 4 to 0 hours) showed a marginal increase in ultimate expansion for C2-S4 and C2-S4N1 mortars, from 0.938% to 1.085 % and 1.071 % to 1.088 % respectively. This suggests that pre-cure time has less impact on DEF expansion than other parameters. Like the discussion in Section 8.1.1, the higher C_3A content in C2 (11.2%) compared to C1 (7.2%) contributed to the DEF expansion, as other cement parameters and experimental conditions were constant. The mass changes given in Figure 8.7 and Figure 8.8 correlate well with the linear expansion results. The degree and rate of mass gain were lower for 0-hour pre-cure C1 mortars compared to 4-hour pre-cure mortars. In the case of C2 expanding mortars C2-

S4 and C2-S4N1, the mass gain was marginally higher for 0-hour pre-cure than 4-hour pre-cure mortars, indicating that the reduction in pre-cure time increases the chance of deterioration due to DEF. Although the pre-cure time is essential and its reduction has led to some detrimental effects in C2 mortars, the reason for a lack of expansion in C1 mortars was not apparent. As heat curing at 90°C has been proven to suppress early age ettringite completely and favours subsequent reformation of ettringite at a later age (refer Section 6.2.2), there is no doubt about the occurrence of DEF in 0-hour pre-cure mortars. However, the non-expansive nature of 0-hour pre-cured C1 mortars suggests supplementary test methods should be used along with expansion study to understand the detrimental effects of DEF.

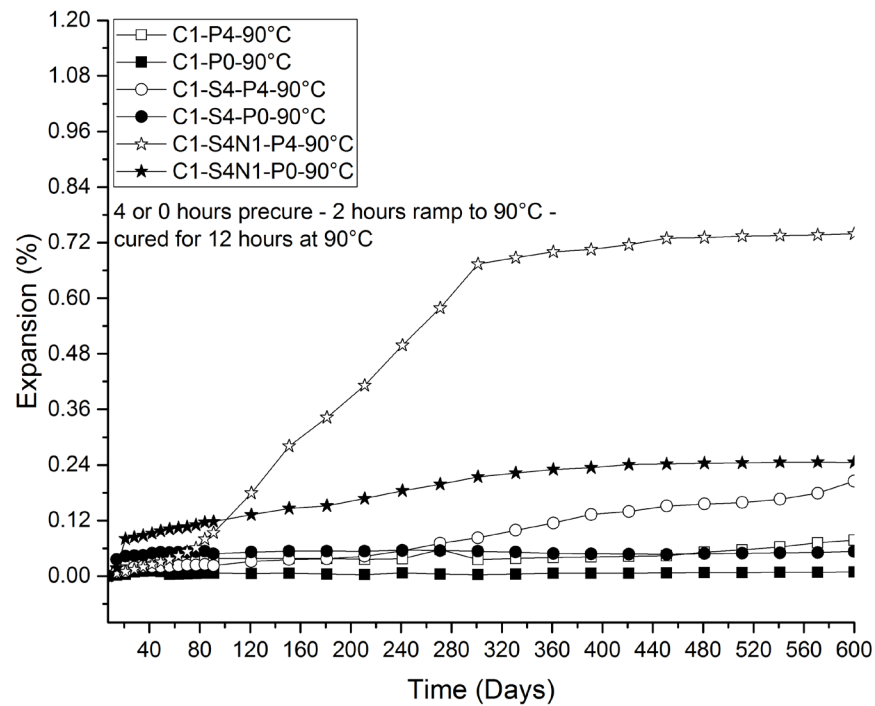


Figure 8.5 Effect of reduction in heat-curing duration (4 to 0 hour) in linear expansive behaviour of Cement 1 mortars

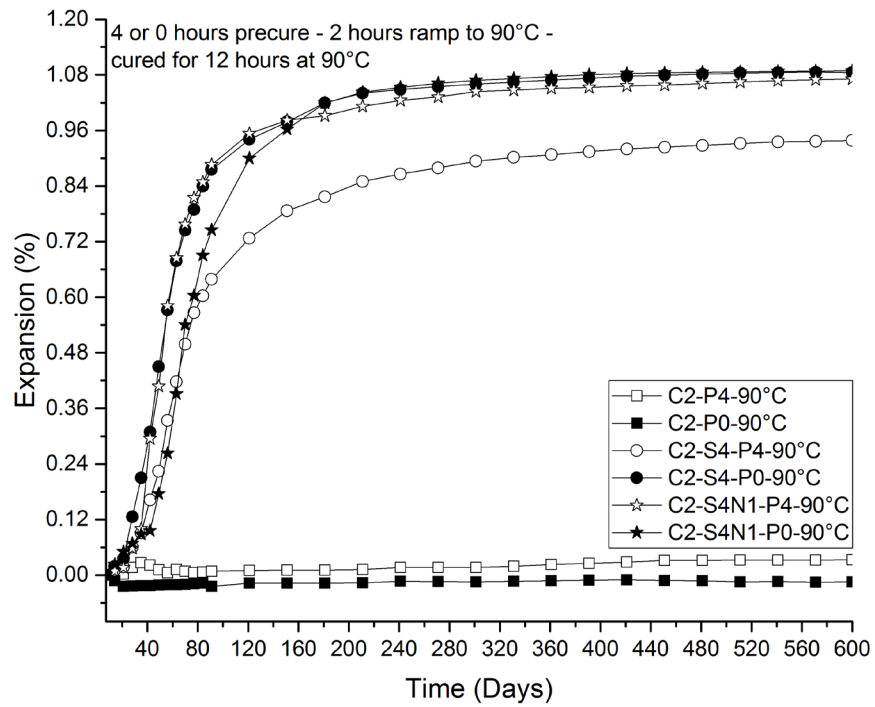


Figure 8.6 Effect of reduction in heat-curing duration (4 to 0 hour) in linear expansive behaviour of Cement 2 mortars

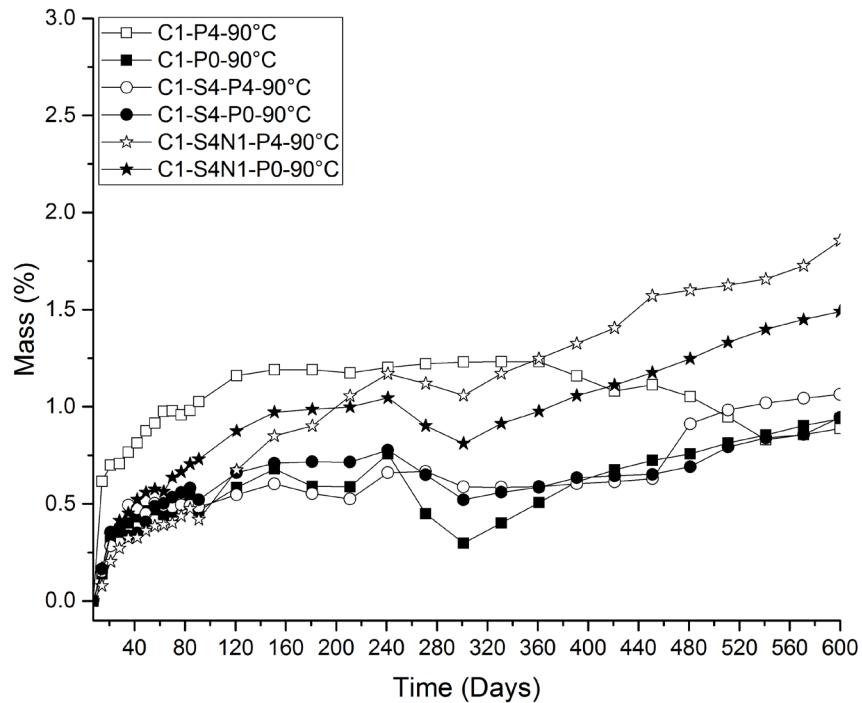


Figure 8.7 Effect of reduction in heat-curing duration (4 to 0 hour) in mass changes of Cement 1 mortars

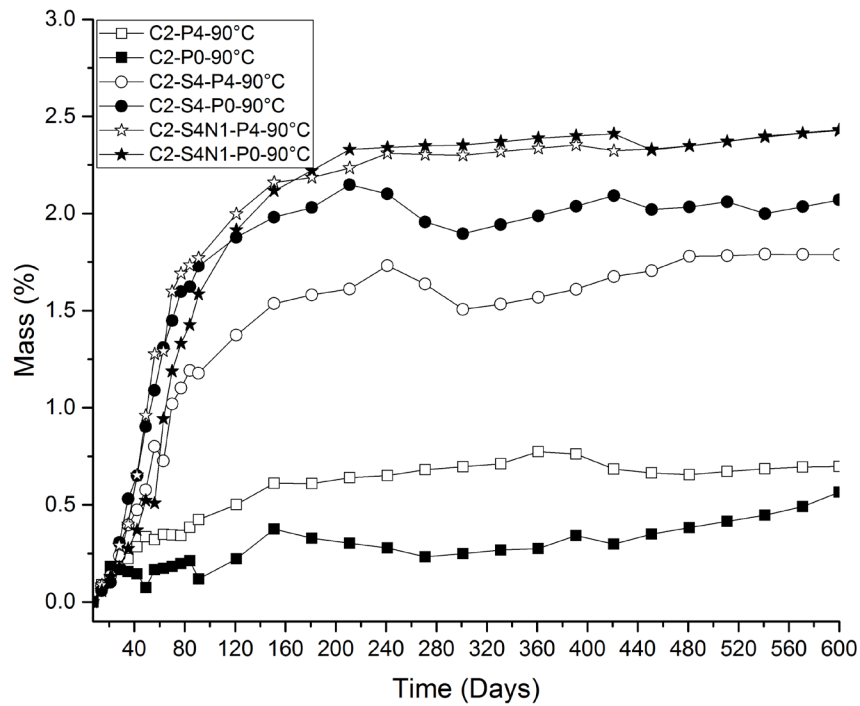


Figure 8.8 Effect of reduction in heat-curing duration (4 to 0 hour) in mass changes of Cement 2 mortars

8.2 Evolution of ionic pore solution characteristics and crystalline phases

From the expansion and mass change studies, it is well understood that 12-hour heat curing at 90°C shows a higher risk of DEF in modified cement systems than the 8-hour curing. Hence in this section, changes in pore solution chemistry and evolution of crystalline phases of expansive cement systems cured at 90°C for 12 hours are discussed.

8.2.1 GP cement systems with 4% sulphate cured at 90°C for 12 hours

Ionic concentrations of pore solutions from C1-S4 and C2-S4 pastes cured at 90°C for 12 hours are shown in Figure 8.9Figure 8.10. No visible changes were noticed in the concentrations of Al and Si ions throughout the testing time. At the end of heat-curing (day 1), due to the added gypsum, 4% SO₃ -4% cements showed an increase in SO₂ ion concentration (measured as sulphur); C1- 63.72 to 67.47 mmol/L; C2 - 23.26 to 57.42 mmol/L. However, the added gypsum only marginally raises the Ca ion concentration in

C1 (5.83 to 5.95 mmol/L). On the contrary, additional gypsum in C2 raised the Ca ion concentration from 3.17 to 11.41 mmol/L; this could be due to combination of additional calcium from gypsum, and additional sulphate from gypsum retarding C₃A reactions. However, the reason for the increase in K ions (C1 - 91.92 to 171.66 mmol/L; C2 - 62.16 to 126.66 mmol/L) in sulphate added cements remains unclear, considering no additional alkali was added to the system and curing conditions were the same. As discussed in Section 6.22, high alkali concentration in the pore solution increases the solubility of sulphates decomposing the ettringite and matches with the ettringite absence in the day 1 TGA mass loss curves (refer to Table 4.9 for various mass loss peaks) presented in Figure 8.11 Figure 8.12. The gradually decreasing concentration of alkalis during the storage period is due to leaching into the storage water.

Table 8.1 Measured pH and calculated OH⁻ ion concentrations of modified C1 & C2 pastes cured at 90°C for 12 hours

Mix ID	pH		OH ⁻ (mmol/L)	
	1 day	30 day	1 day	30 day
C1-S4-90°C	13.2	12.5	147.9	32.4
C2-S4-90°C	13.2	12.4	144.5	26.9
C1-S4N1-90°C	13.4	12.6	269.1	40.7
C2-S4N1-90°C	13.6	12.5	416.9	31.6

Although alkali concentration in storage water was not tested, the drop in pH and alkalinity ([OH⁻] ions concentration) (Table 8.1) of pore solution over the storage period could be due to leaching of alkalis as other studies which tested storage water of similar storage conditions reports leaching of alkalis from similar sized specimens (Aubert & Escadeillas 2013; Barbarulo et al. 2005; Lindgård, Sellevold, et al. 2013; Scrivener & Taylor 1993; Thomas et al. 2006; Tosun & Baradan 2010). Reduction in alkalinity through leaching of alkalis favours sulphate to react with aluminates to precipitate ettringite and can be (Diamond 1996) apparently seen from day 7 to day 600 in the TGA

results (Figure 8.11 and Figure 8.12), corresponding to the drop in sulphate ion concentration (Figure 8.9 Figure 8.10). However, the same mechanism of reactions occurred in heat-cured commercial GP cements (Section 6.2.2) but did not result in expansion. By comparing Figure 8.13 Figure 8.14, 4% SO₃ cements (C1-S4, C2-S4) have higher sulphate ion concentrations in pore solutions than commercial GP cements at the end of heat curing.

Analysing the early age (24 hours) pore solution chemistry and later age expansion (day 600) gives insights about expansive and non-expansive DEF. Table 8.2 shows, the marginal increase in pore solution S ion concentration ($\Delta\uparrow$) in early age resulted in a small expansion increase ($\phi\uparrow$) in C1-S4 systems at the later age. Whereas in case of C2-S4, the difference in S ion concentration ($\Delta\uparrow$) was drastically high resulted in much higher degree of expansion difference ($\phi\uparrow$).

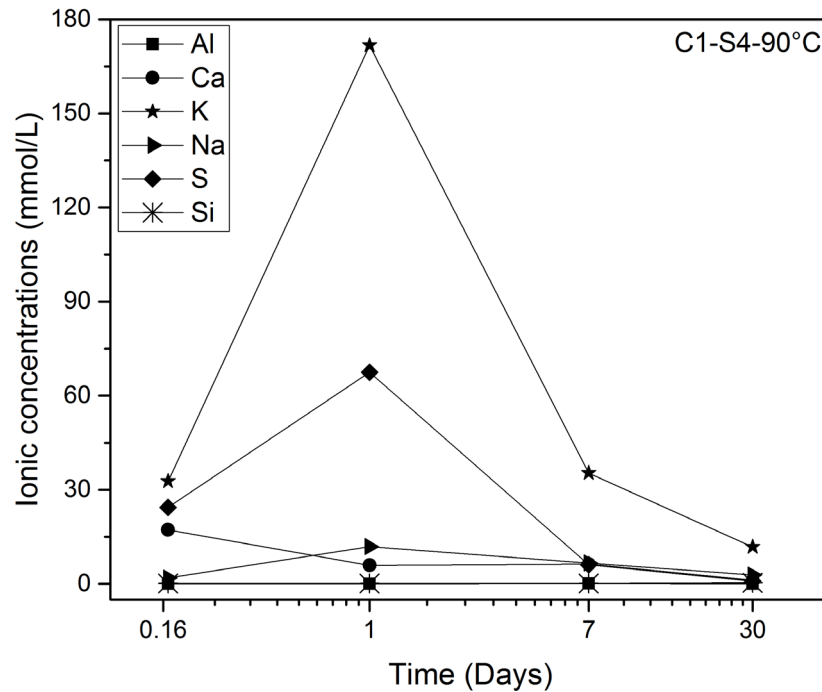


Figure 8.9 Ionic concentrations of pore solution from C1-S4 cement paste cured at 90°C for 12 hours

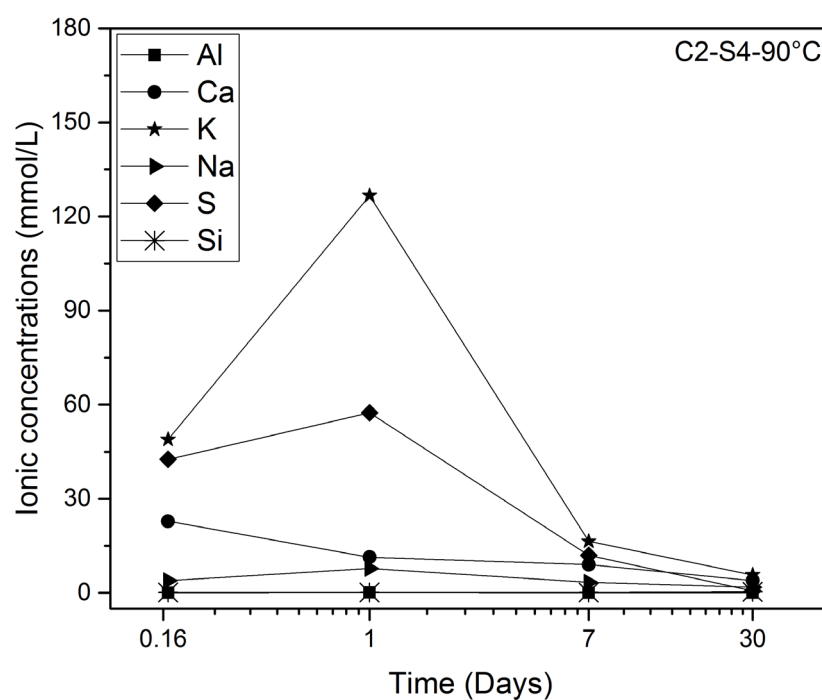


Figure 8.10 Ionic concentrations of pore solution from C2-S4 cement paste cured at 90°C for 12 hours

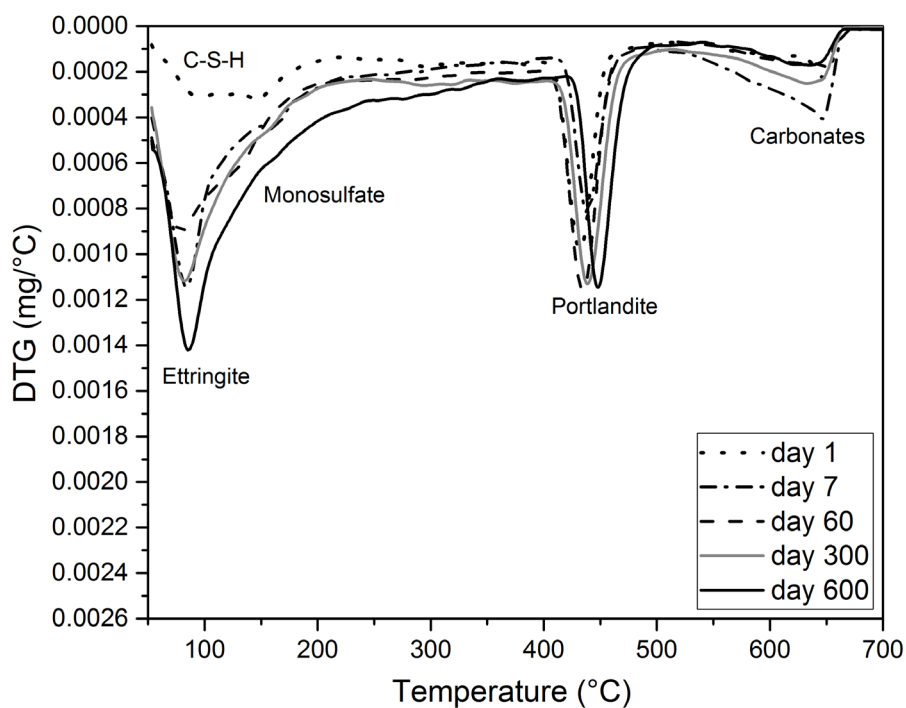


Figure 8.11 TGA mass loss curves of C1-S4 paste cured at 90°C for 12 hours – day 1 to day 600

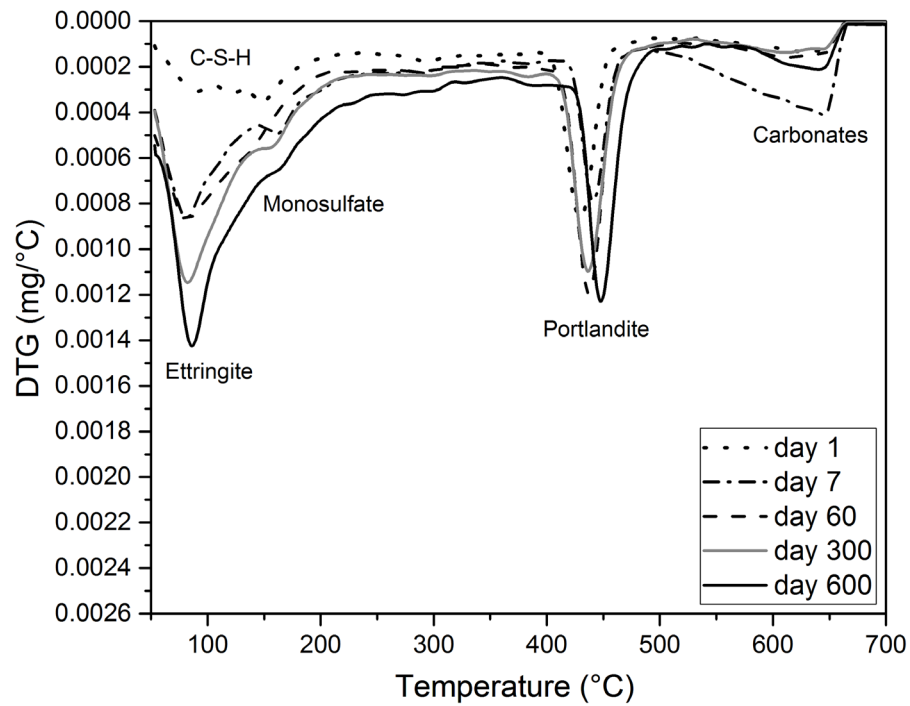


Figure 8.12 TGA mass loss curves of C2-S4 paste cured at 90°C for 12hours – day 1 to day 600

Table 8.2 Early age S ion concentration and later age expansion comparison of sulphate modified cement systems

Mix ID	Early age (24 hours) S ion concentration (mmol/L)	S ion difference ($\Delta\uparrow$) in mmol/L	Later age expansion at 600 days (%)	Expansion difference ($\phi\uparrow$) in %
C1-90°C	63.7	3.8	0.008	0.197
C2-S4-90°C	67.5		0.205	
C1-90°C	23.7	33.7	0.013	0.925
C2-S4-90°C	57.4		0.938	

These results suggest that the higher sulphate content in the pore solution, induced by heat curing, is responsible for more ettringite formation at the later age and subsequently increases the level of expansion. However, the entire scenario of expansion/non-expansion in heat-cured systems cannot be explained with pore solution data alone. Sulphates in the aqueous state account only for 10 % of total sulphates in cementitious systems (Thomas, Hooton & Ramlochan 2010).

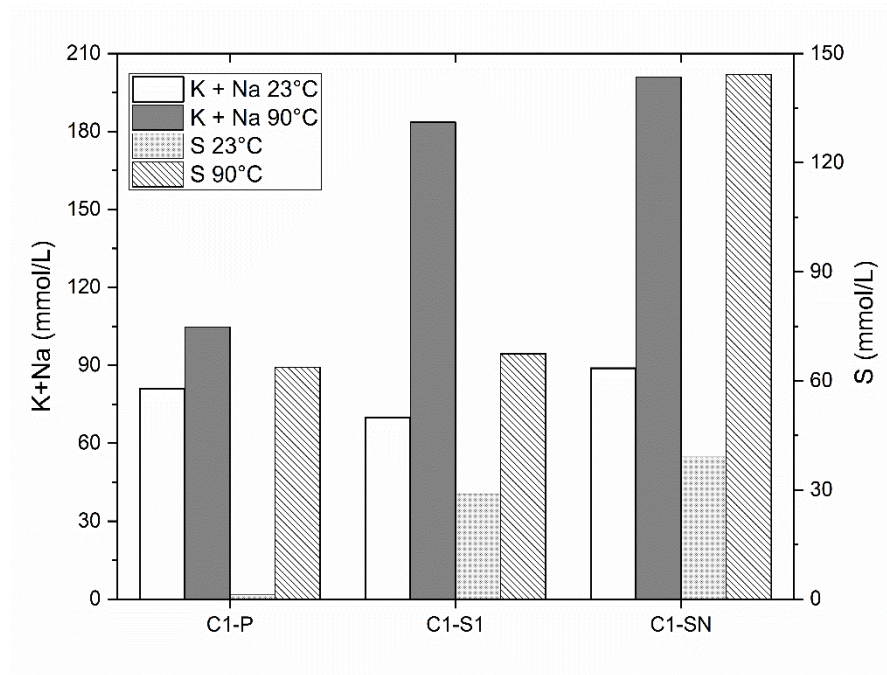


Figure 8.13 Sulphur and total alkali concentration in pore solution extracted from C1 pastes at 24 hours

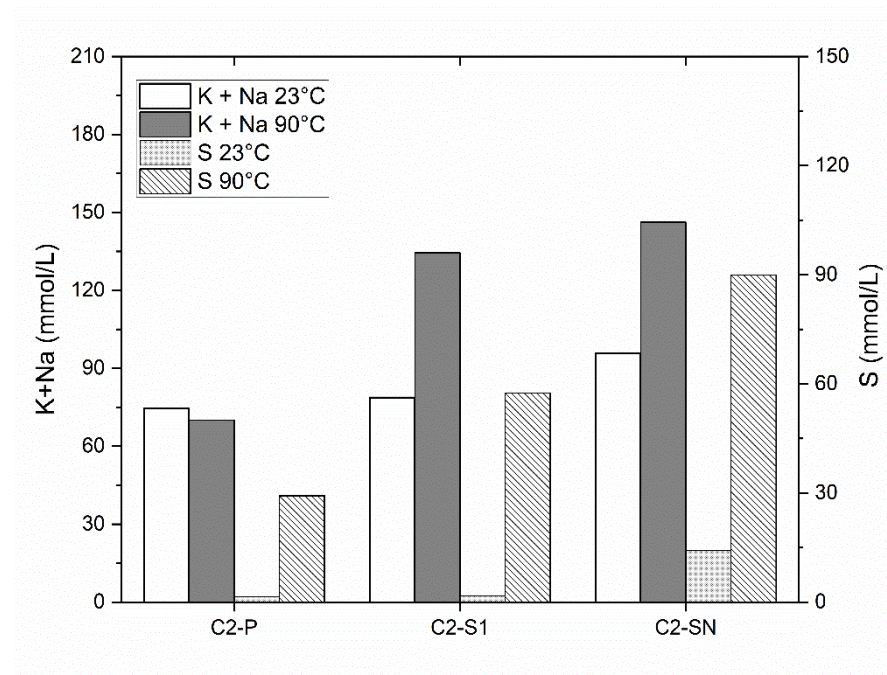


Figure 8.14 Sulphur and total alkali concentration in pore solution extracted from C2 pastes at 24 hours

Hence the sulphates adsorbed to C-S-H during heat curing (Barbarulo, Peycelon & Leclercq 2007; Divet & Randriambolo 1998) and their release at a later stage are vital for DEF expansion.

To understand the differences in aqueous sulphates and sulphates bound in solid phases, the sulphate (S-O) band intensity from the FTIR spectrum (Figure 8.15) is analysed along with the pore solution data given in Figure 8.13Figure 8.14. The S-O stretch occurs at 1115 cm^{-1} (refer to Table 4.10 for various wavenumbers of cement hydrates) and the intensity of the same can be studied by taking the transmittance (%) ratio between 1056 cm^{-1} (S_i) (where the stretch begins) and 1115 cm^{-1} (S_o) (the end of the stretch). The ambient cured cement pastes have S_i/S_o ratios of 1.52 for C1-S4-23°C and 1.32 for C2-S4-23°C. These values are higher than those of the heat-cured pastes (C1-S4-90°C - 1.21, C2-S4-90°C - 0.98), suggesting that heat curing increases the bonded or adsorbed sulphates to hydrates such as C-S-H, thus reducing the S-O band intensity assigned for ettringite ($1115\text{--}1110\text{ cm}^{-1}$). Further, the reduced solid phase S-O band correlates well with the increased sulphate ion concentration in the pore solution compared to ambient cured pastes, where the primary ettringite precipitation is steady. Similar research on the influence of heat curing on O-H bands (but not S-O bands) in FTIR spectra was conducted and reported by Ballester et al. (2009).

8.2.2 GP cement systems with 4% sulphate and 1% alkali cured at 90°C for 12 hours

The maximum DEF expansion and mass gain were obtained for mortars made with cements having 4% $\text{SO}_3 + 1\% \text{Na}_2\text{O}_{\text{eq}}$ and heat cured at 90°C for 12 hours (C1-S4N1, C2-S4N1). The possible reasons for the expansion are discussed here in this section with the help of various characterisation techniques. The pore solution chemistry of C1-S4N1 and C2-S4N1 when subjected to heat curing at 90°C for 12 hours is given in Figure 8.16 Figure 8.17. At the end of 4 hours, before the onset of heat curing, in C1-S4N1 and C2-

S4N1 systems S ions in the pore solution spiked to 97.19 mmol/L and 158.48 mmol/L respectively when compared to 27.15 and 10.80 mmol/L in commercial GP cements, C1 and C2

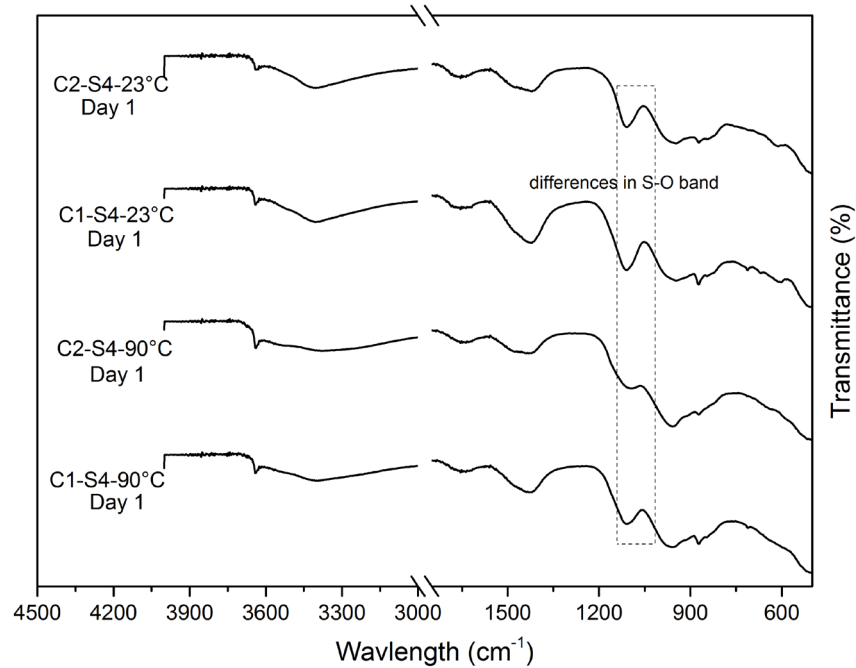


Figure 8.15 FTIR spectrum of C1-S4 & C2-S4 pastes cured at 23°C and 90°C for 12 hours – day 1

The substantial increase in the dissolution of sulphates into the pore solution can be entirely attributed to the increased alkali (1%) content in cements, as it occurred during the pre-cure time, before the starting of heat curing. Heat curing at 90°C increased the dissolution of alkalis. K and Na ions as rose from 36.40 to 169.61 mmol/L and from 19.11 to 31.33 mmol/L respectively for C1-S4N1 at the end of heat curing. Similarly, for C2-S4N, K and Na ions rose from 44.67 to 113.84 mmol/L and from 30.65 to 32.38 mmol/L respectively. The increase in curing temperature and higher alkali content in the pore solution increased the dissolution of sulphates, thus preventing the ettringite precipitation. From Figure 8.13 and Figure 8.14, at the end of day 1 sulphate and alkali ions in the pore

solution were much higher than ambient cured cement and other heat-cured cementitious systems, indicating an increased risk of expansive DEF.

FTIR spectra of the C1-S4N1 and C2-S4N1 cementitious system are presented in Figure 8.18, comparing the differences between heat-cured and ambient-cured pastes at the age of day 1. Results show the S_i/S_o ratios were lower for heat-cured pastes (C1-S4N1 - 1.04; C2-S4N1 - 0.93) than ambient cured pastes (C1-S4N1 - 1.11; C2-S4N1 - 1.12). This suggests that the reduced intensity of the S-O band (1115 cm^{-1}) associated with ettringite was due to the increase in sulphate ions adsorbed to C-S-H. This again, as discussed in Section 8.2.1, confirms the contribution of solid-phase sulphates to DEF. As above (Section 6.2.2), due to solubility of sulphate under a high-alkaline and high-temperature environment, a complete absence of ettringite was noticed in TGA mass loss curves at day 1 (Figure 8.19 and Figure 8.20). Similar to Section 8.2.1, the drop in K and Na ion concentrations (Figure 8.16 and Figure 8.17) and reduction in pH and alkalinity (Table 8.1) during the storage time in saturated lime water confirms the leaching of alkalis. As the alkalis leach, a drop in sulphate and calcium concentrations was noticed. Concurrently, ettringite precipitation occurs (Figure 8.19 and Figure 8.20) in the hardened cementitious system causing the expansion and mass gain as discussed in Section 8.1.1.

It is understood from the above discussions that among heat-cured cementitious systems the non-expansive and expansive nature is identifiable by the differences in the pore solution concentration of S ions. However, it is an indirect measure and suffers shortcomings such as the lower distribution of sulphates in aqueous form. To check the direct relevance to quantity of ettringite and expansion in different cementitious systems, semi-quantitative XRD was used, and the results are presented in Figure 8.21 Figure 8.24.

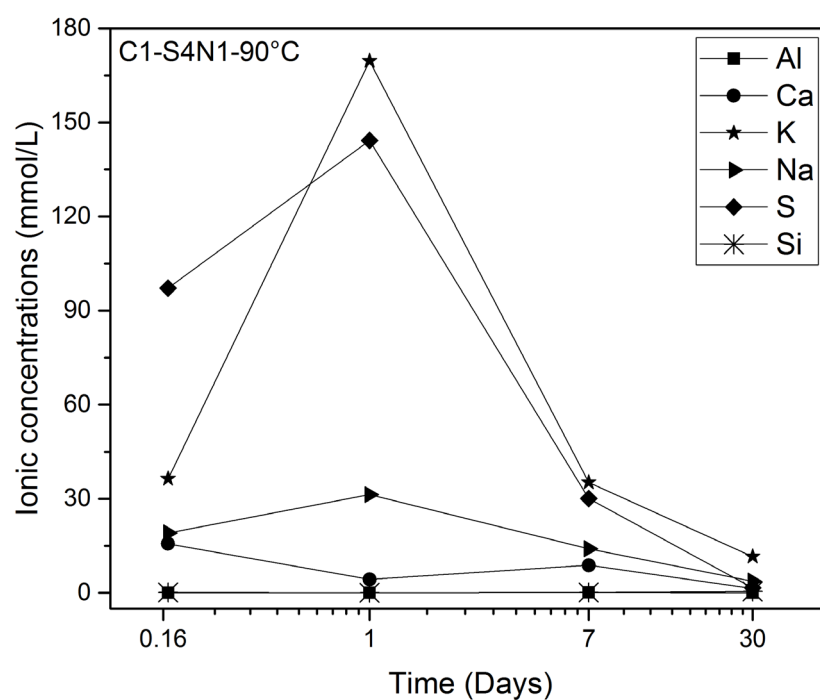


Figure 8.16 Ionic concentrations of pore solution from C1-S4N1 cement paste cured at 90°C for 12 hours

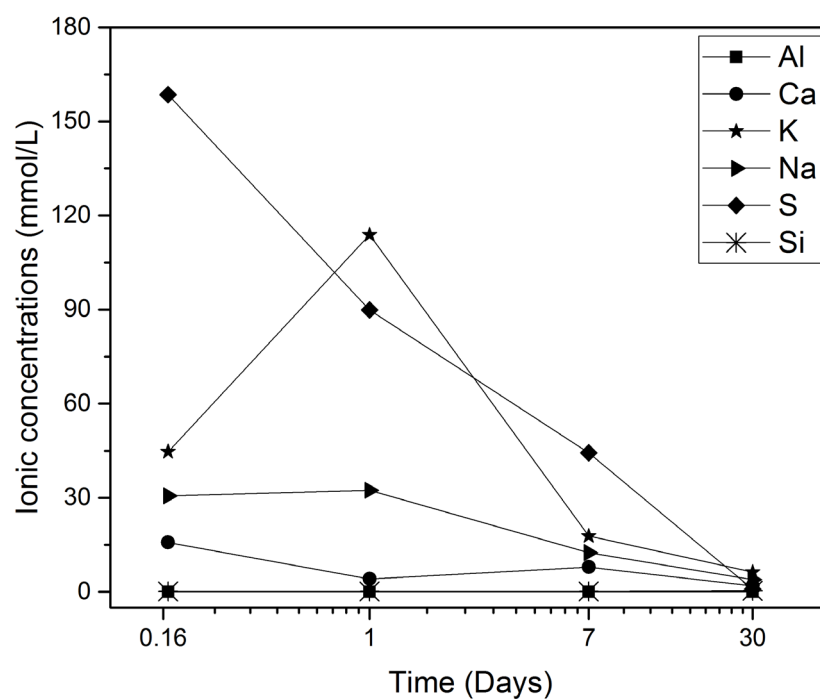


Figure 8.17 Ionic concentrations of pore solution from C2-S4N1 cement paste cured at 90°C for 12 hours

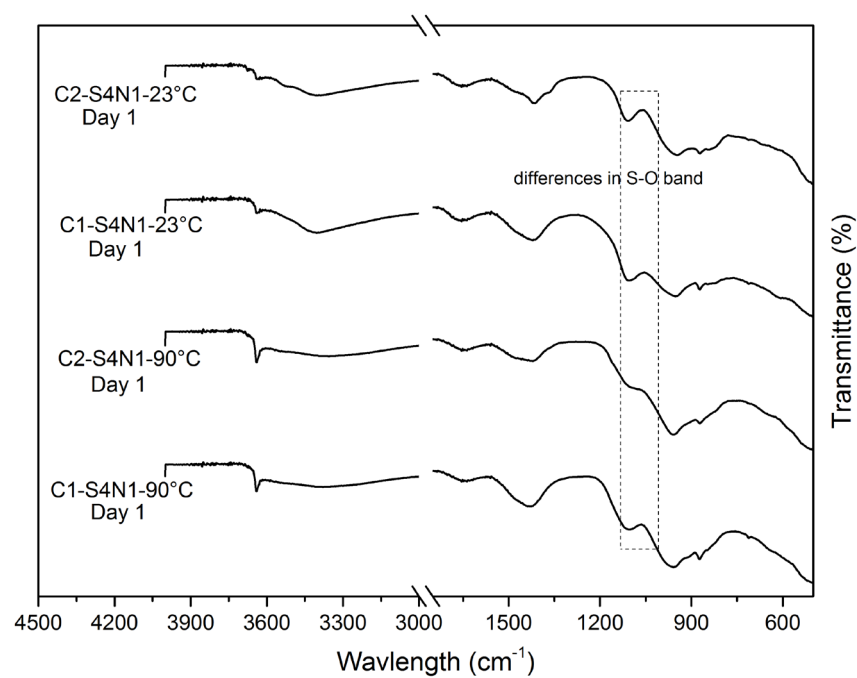


Figure 8.18 FTIR spectrum of C1-S4N1 & C2-S4N1 pastes cured at 23°C and 90°C for 12 hours – day 1

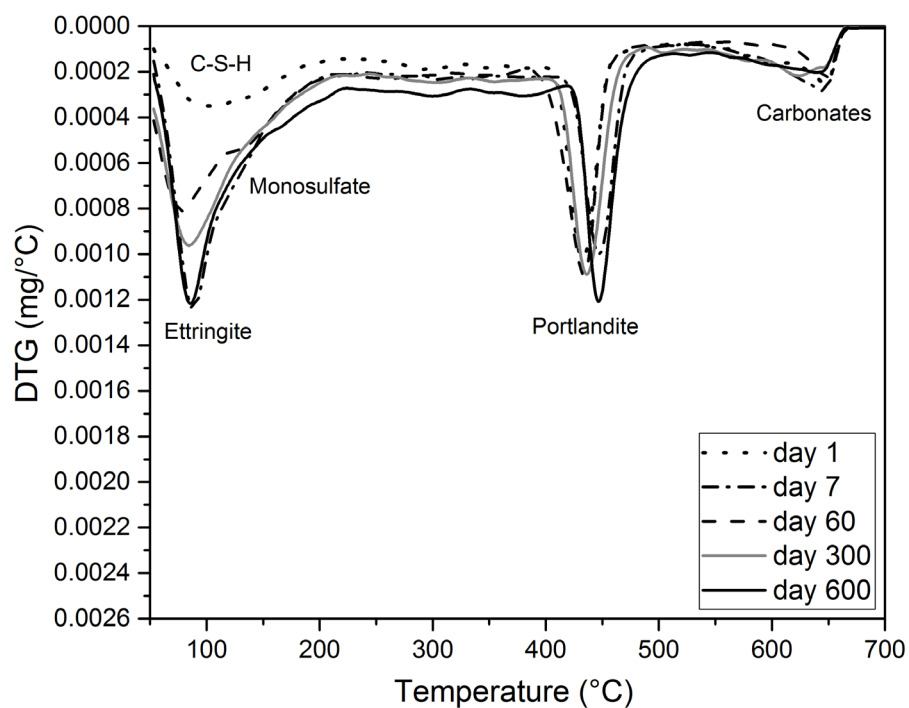


Figure 8.19 TGA mass loss curves of C1-S4N1 paste cured at 90°C for 12hours – day 1 to day 600

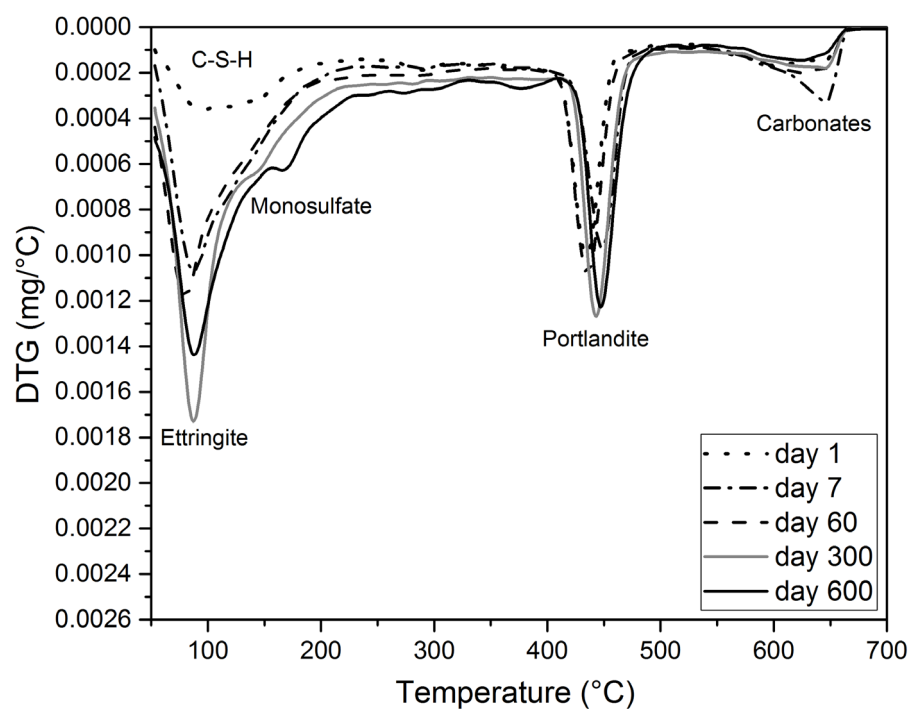


Figure 8.20 TGA mass loss curves of C2-S4N1 paste cured at 90°C for 12hours – day 1 to day 600

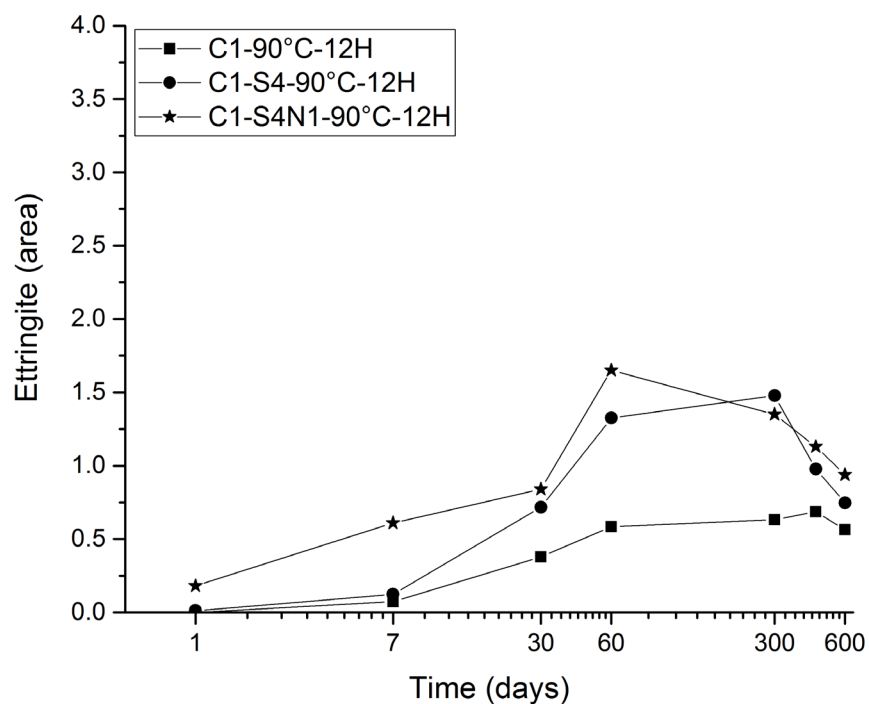


Figure 8.21 Ettringite evolution over time of different C1 cementitious system cured at 90°C-12 hours

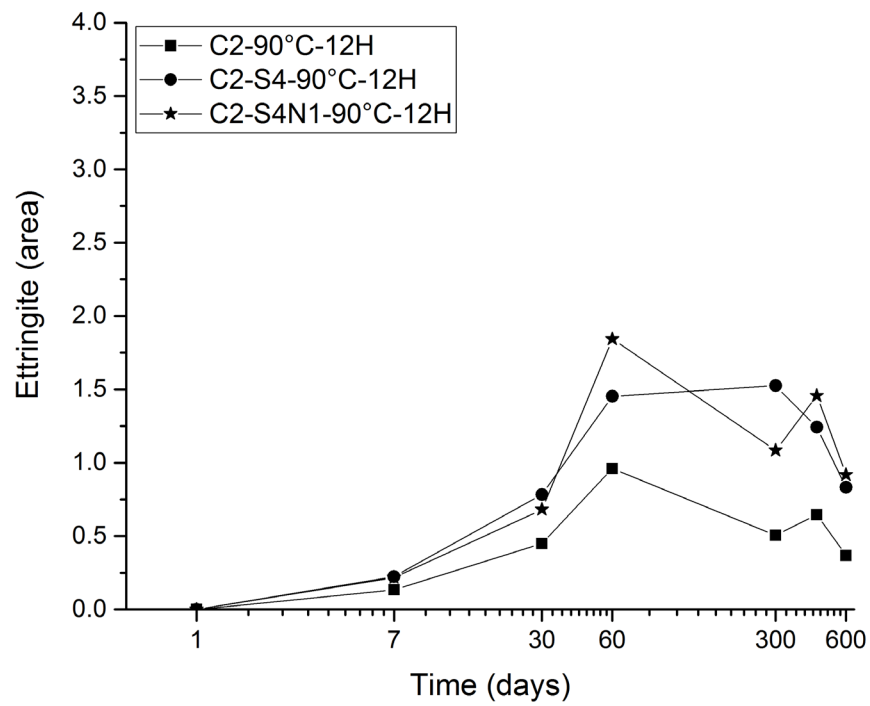


Figure 8.22 Ettringite evolution over time of different C2 cementitious system cured at 90°C-12 hours

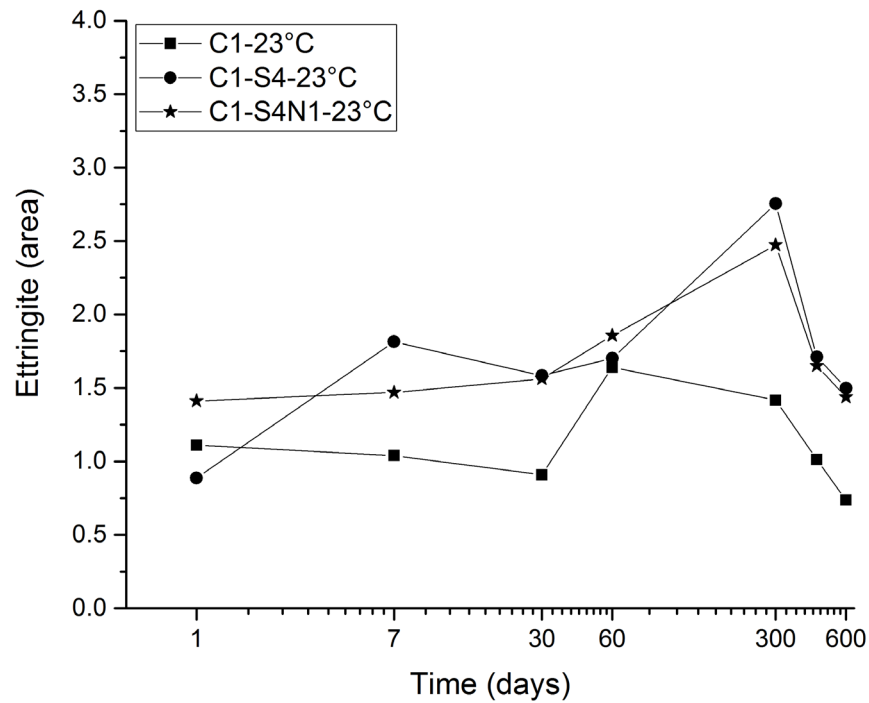


Figure 8.23 Ettringite evolution over time of different C1 cementitious system cured at 23°C

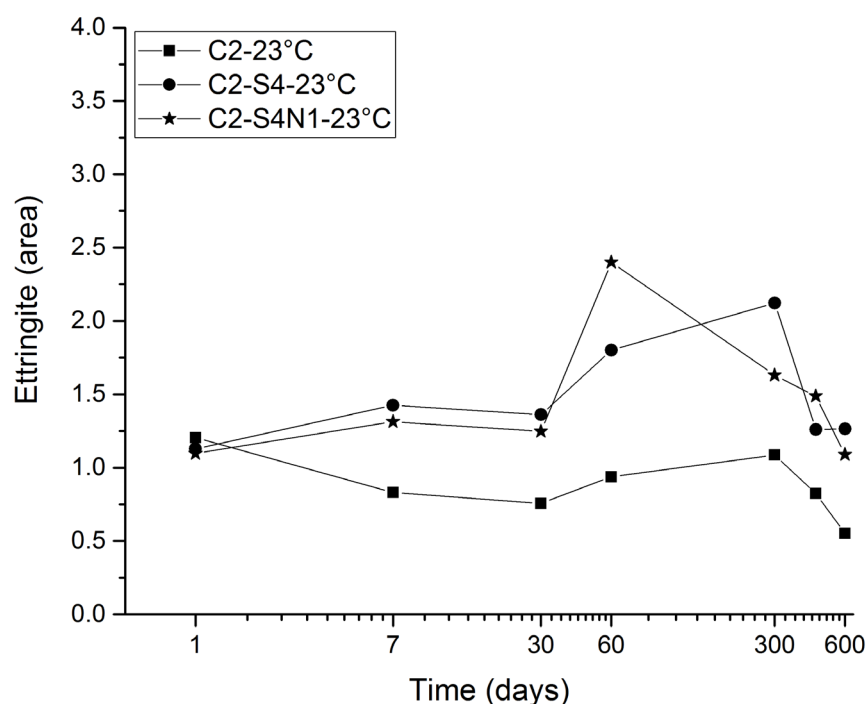


Figure 8.24 Ettringite evolution over time of different C2 cementitious system cured at 23°C

Figure 8.21 Figure 8.22 show significant regrowth of ettringite at 7 days, which again confirms the same trends from the TGA mass loss curves. The commercial GP cement mixes (C1, C2) showed far less ettringite than the modified cementitious systems, which explains the non-expansive behaviour of commercial GP cement mixes despite being subjected to high-temperature curing at 90°C for a long period of 12 hours. Among the modified cementitious systems, the SO₃ and Na₂O increased systems (C1-S4N1, C2-S4N1) had higher (though marginally so) ettringite precipitation over time than the SO₃ alone modified systems (C1-S4, C2-S4). This correlates well with the higher expansion experienced in the C1-S4N1 and C2-S4N1 systems (Figure 8.1Figure 8.2) compared to other systems. The reduction in ettringite at later ages is due to the precipitation of ettringite reaching a saturation level due to a lack of available sulphates. Since ettringite is an unstable hydrate, it converts into other alumino-ferrite phases.

The evolution of ettringite in ambient-cured cementitious systems is given in Figure 8.23 Figure 8.24 for reference purposes. The quantity of ettringite formed in the ambient-cured cementitious systems was always more than heat-cured cementitious systems, thus suggesting the relation between degree of expansion and quantity of ettringite relevant only within the heat-cured systems. Further, the results also suggest that precipitation of ettringite in the hardened cementitious systems is more critical than the amount of ettringite. In the ambient cured cementitious systems also ettringite precipitation occurred in hardened cementitious systems, as is apparent from Figure 8.23 Figure 8.24 in the day 7 to 300 trend. This raises a valid question of why ettringite precipitation in ambient-cured systems did not result in any expansion despite the quantity being higher than heat-cured systems. The possible answer could be that in the ambient-cured systems, precipitation of ettringite occurs uniformly throughout. In the case of heat-cured systems, precipitation of ettringite occurs after sulphate ions are transported through the pore solution and desorbed from C-S-H at different microstructural locations within a cementitious system. Therefore, both the quantity and the location of ettringite precipitation are vital for expansive DEF. To experimentally validate this statement, microstructural studies were completed and the results are discussed in Section 8.3.

8.3 Microstructural investigation by SEM

An increase in the degree of expansion and mass gain was noted when the heat curing time was increased from 8 to 12 hours. The role and impact of extended heat curing duration in the microstructure, especially ettringite deposition locations, are discussed in the section.

8.3.1 GP cement systems with 4% sulphate and 1% alkali cured at 90°C for 8 hours

The micrograph of C1-S4N1 mortar cured at 90°C for 8 hours and subsequently cured at room temperature under saturated lime water for 500 days is shown in Figure 8.25. The unhydrated or partially hydrated cement grains are reduced when compared with ambient-cured specimens (Figure 6.20 & 6.23) at 500 days. Cracks are visible in the aggregate-paste interface (ITZ). The cracks were developed due to the loss of adhesion between aggregates and the paste during heat curing. The cracks are free from ettringite and empty. This observation is in concord with results obtained by Escadeillas et al. (2007); Leklou, Aubert & Escadeillas (2009) and Pavoine, Divet & Fenouillet (2006). A calcium hydroxide (CH) (portlandite) rim is found in the ITZ and it is not expansive. Cavities can also be seen throughout the micrograph. The two-tone C-S-H, with inner (darker) and outer (lighter) products have been identified, which is common in heat-cured cementitious systems (Famy 1999; Scrivener & Taylor 1993; Yang & Sharp 1996).

Even though the mortar expanded by about 0.62%, it presents the characteristic features of non-expanding heat-cured mortars such as empty cracks, cavities and portlandite near the ITZ. At a comparable degree of expansion (0.4 to 0.6%), other research works (Leklou, Aubert & Escadeillas 2009; Silva et al. 2010a; Yang et al. 1999; Yang & Sharp 2001b) show heat-cured concrete specimens with ettringite band formation within the cement matrix and around aggregates which contradicts with the results obtained in this research. The ettringite may have been lost during the sample preparation process or not visible due to the limitations of the technique used (Leklou, Aubert & Escadeillas 2009). Evidence of ettringite presence can be inferred from atomic ratio plots and EDS. The atomic plots of S/Ca vs Al/Ca in Figure 8.26 show significant ettringite points in the microstructure, especially near the ITZ.

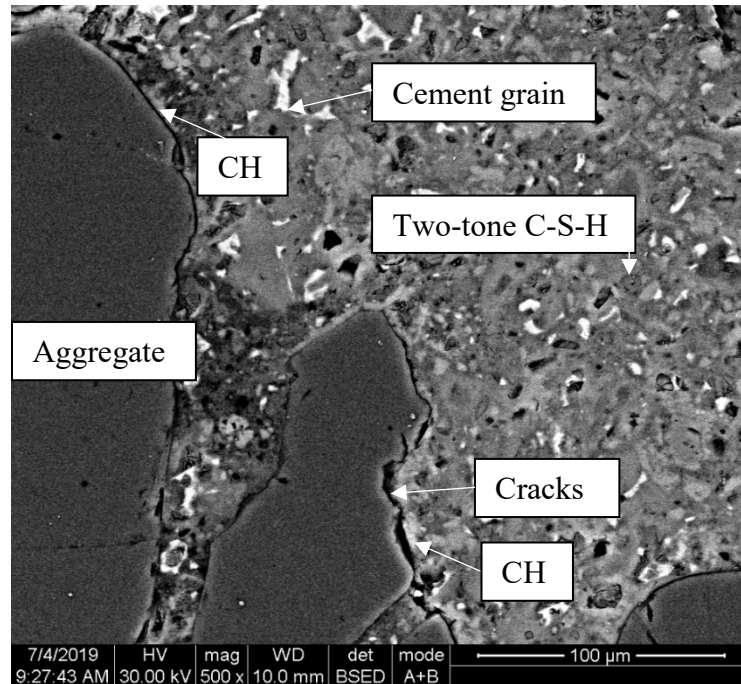


Figure 8.25 Microstructure of C1-S4N1 mortar cured at 90°C for 8 hours and subsequently stored in saturated lime water for 500 days

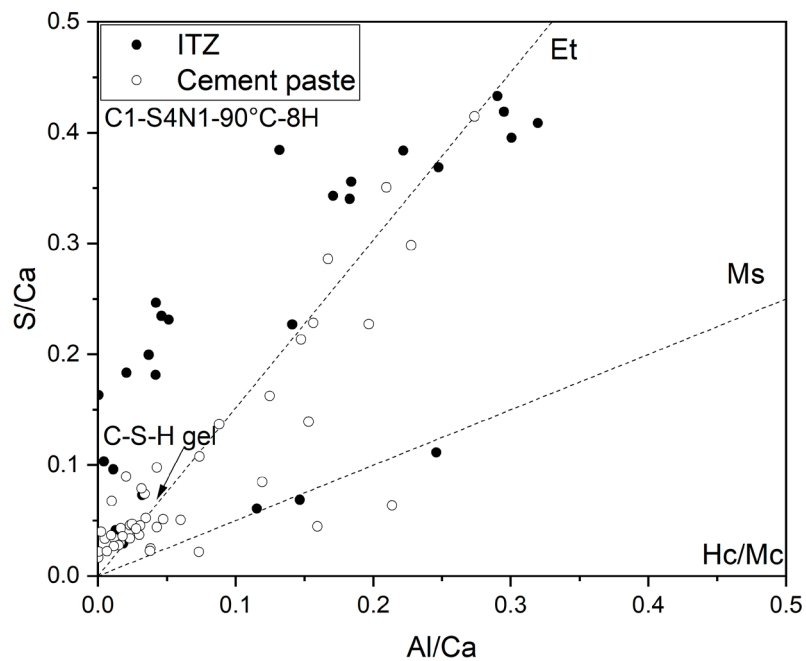


Figure 8.26 Atomic ratio plots of S/Ca vs Al/Ca of C1-S4N1 mortar cured at 90°C for 8 hours and subsequently stored in saturated lime water for 500 days

The EDS plot in Figure 8.27 again confirms the presence of ettringite near the ITZ from the overlapping regions of calcium, aluminium and sulphur. Further, within the marked

area (Figure 8.27), the absence of alumina confirms the presence of free sulphates that may continue to react and precipitate ettringite. Furthermore, the same can be confirmed from the atomic ratio plots of S/Ca vs Al/Ca in Figure 8.26 as they show unreacted sulphur near the ITZ, indicating ettringite may continue to precipitate and deposit near there. It should be noted that the mortar did not reach a plateau like earlier specimens (Figure 8.1), indicating that expansive reactions were still taking place; the EDS and atomic ratio plot evidence supports this.

The micrograph of C2-S4N1-90°C mortar cured at 90°C for 8 hours illustrated in Figure **8.28** presents similar characteristics to the C1-S4N1-90°C mortar, such as cracks near the ITZ, microstructural cavities, two-tone C-S-H and the presence of CH near the ITZ. Unlike C1-S4N1-90°C, the C2-S4N1-90°C has some visible ettringite precipitated in the ITZ. However, ettringite within the cement paste was not visible. The atomic ratio plots (Figure 8.29) demonstrate that more ettringite spots are near the ITZ than in the cement paste, and free sulphates are also present. Further, EDS confirms the presence of ettringite near the ITZ with the overlap of calcium, alumina and sulphur regions (Figure 8.30). Ettringite precipitation in the ITZ is always an indication of DEF and results in expansion, irrespective of the debateable argument whether ettringite contributed to expansion or preferably precipitated in the spaces already expanded due to heat-curing.

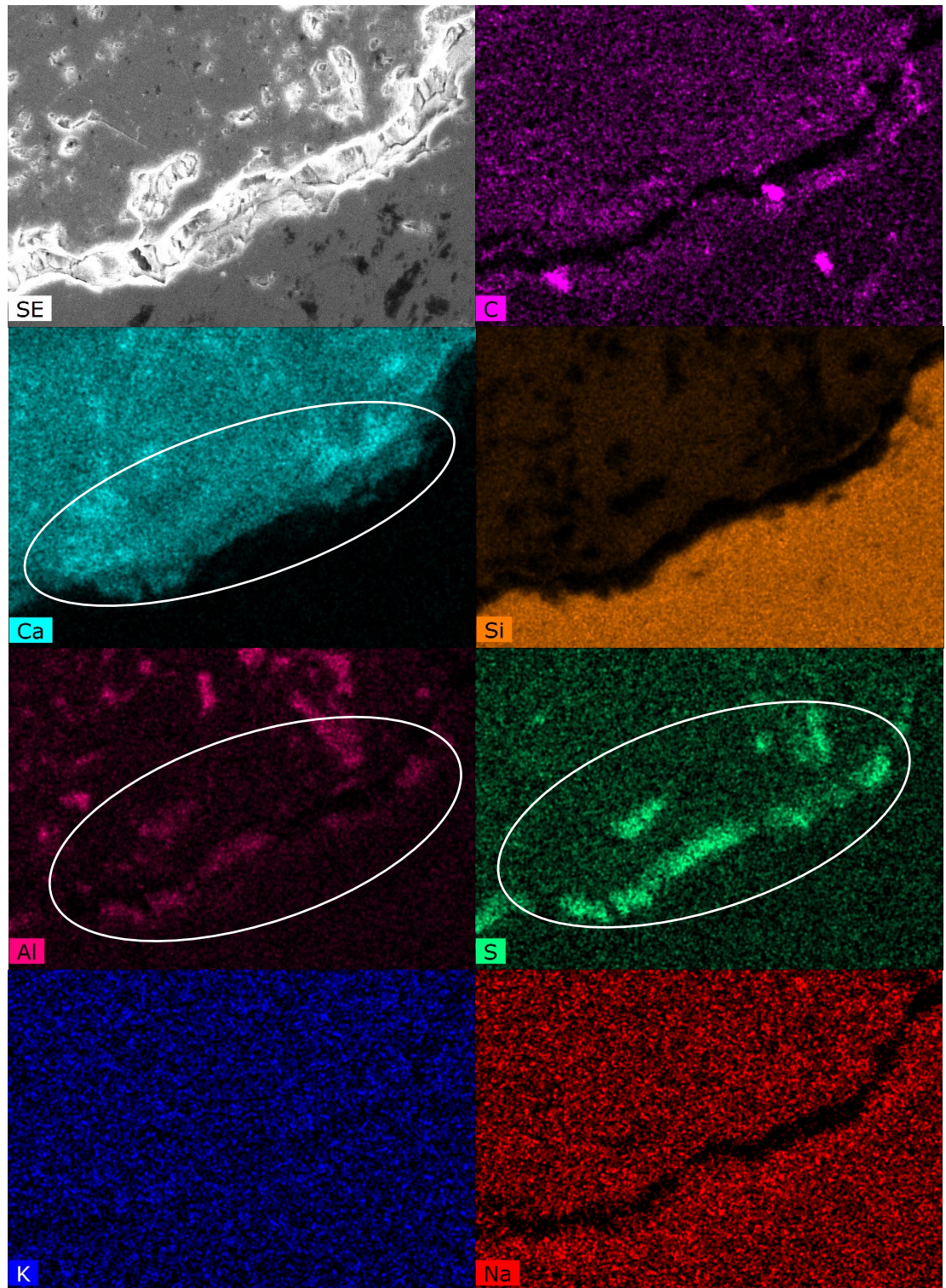


Figure 8.27 Elemental mapping of C, Ca, Si, Al, S, K, Na of C1-S4N1 mortar cured at 90°C for 8 hours and subsequently stored in saturated lime water for 500 days

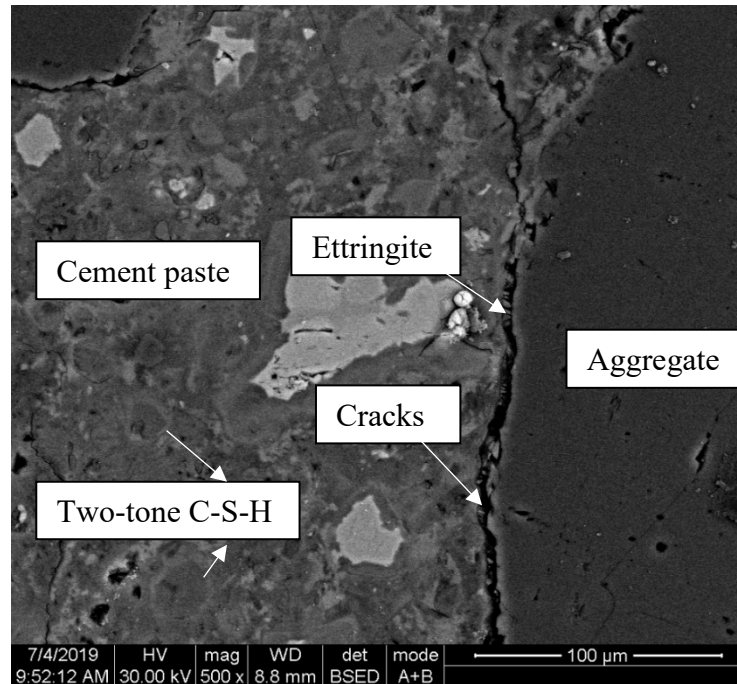


Figure 8.28 Microstructure of C2-S4N1 mortar cured at 90°C for 8 hours and subsequently stored in saturated lime water for 500 days

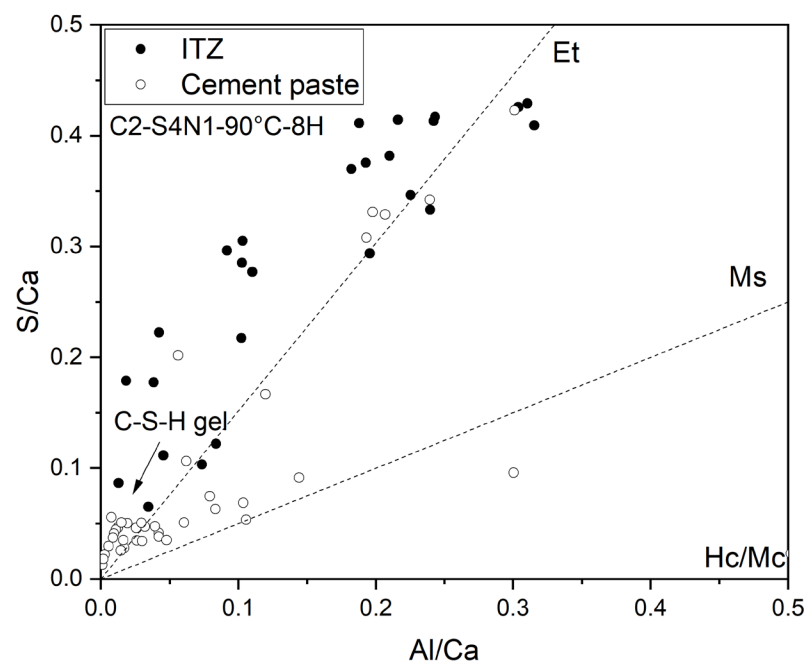


Figure 8.29 Atomic ratio plots of S/Ca vs Al/Ca of C2-S4N1 mortar cured at 90°C for 8 hours and subsequently stored in saturated lime water for 500 days

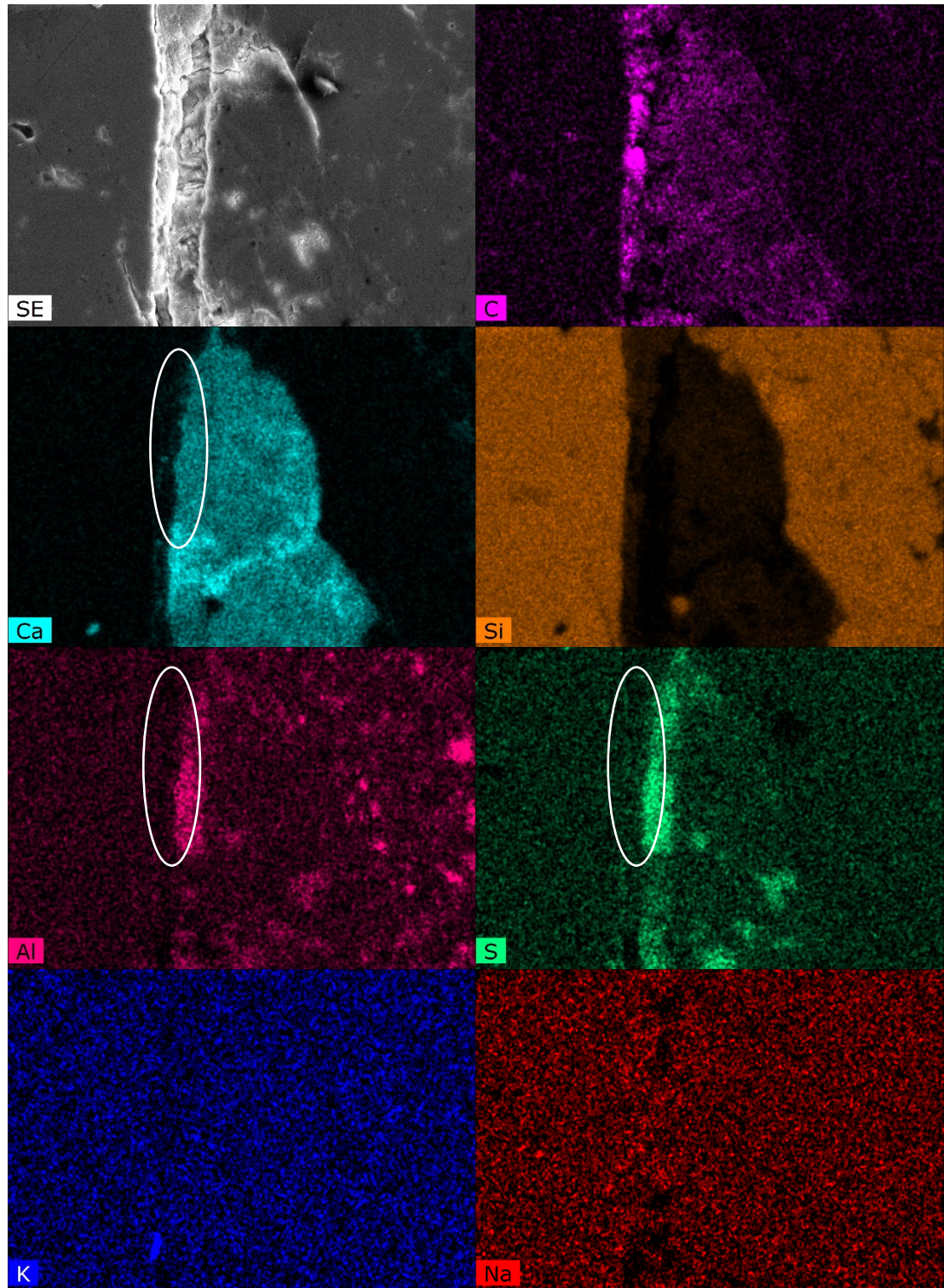


Figure 8.30 Elemental mapping of C, Ca, Si, Al, S, K, Na of C2-S4N1 mortar cured at 90°C for 8 hours and subsequently stored in saturated lime water for 500 days

8.3.2 GP cement systems with 4% sulphate and 1% alkali cured at 90°C for 12 hours

The impact of extended heat curing hours on the microstructure of C1-S4N1 and C2-S4N1 mortars is discussed in this section. Figure 8.31 illustrates the micrograph of the C1-S4N1-90°C mortar, heat-cured for 12 hours. The level of unreacted or partially reacted cement grains are reduced in the 12-hour heat-cured specimen compared to the 8-hour (Figure 8.25), indicating a higher degree of hydration due to additional heat-curing hours. Further, a band of ettringite precipitation is noted in the ITZ for the 12-hour heat-cured C1-S4N1 mortar, unlike the empty cracks in the 8-hour heat-cured specimen. Moreover, the ettringite precipitates are perpendicular to the aggregate and paste matrix, suggesting it could be expansive. A layer of CH is present near the ettringite deposit location, suggesting expansive ettringite pushed the CH in the process of precipitation. The atomic ratio plot of S/Ca vs Al/Ca shown in Figure 8.32 further confirms more ettringite spots in the ITZ than in the cement paste matrix. In addition, EDS again confirms the strong band of ettringite (Figure 8.33) precipitation in the ITZ from the overlap of calcium, alumina and sulphate. Identical results were obtained for C2-S4N1 12-hour heat-cured mortar (Figure 8.34 Figure 8.35), the only exception being that in addition to the ITZ, significant ettringite deposits were found within the cement paste as noted from the EDS (Figure 8.36). The degree of ultimate expansion of C1-S4N1 and C2-S4N1 mortars increased from 0.62 to 0.74% and 0.46 to 1.07% respectively with the additional 4 hours heat-curing. The increase in expansion correlates well with the abundant presence of ettringite.

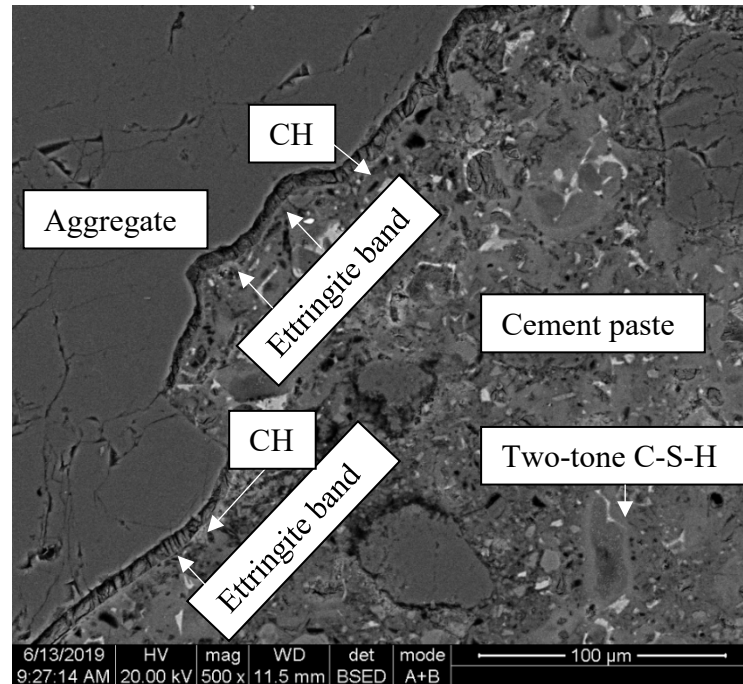


Figure 8.31 Microstructure of C1-S4N1 mortar cured at 90°C for 12 hours and subsequently stored in saturated lime water for 500 days

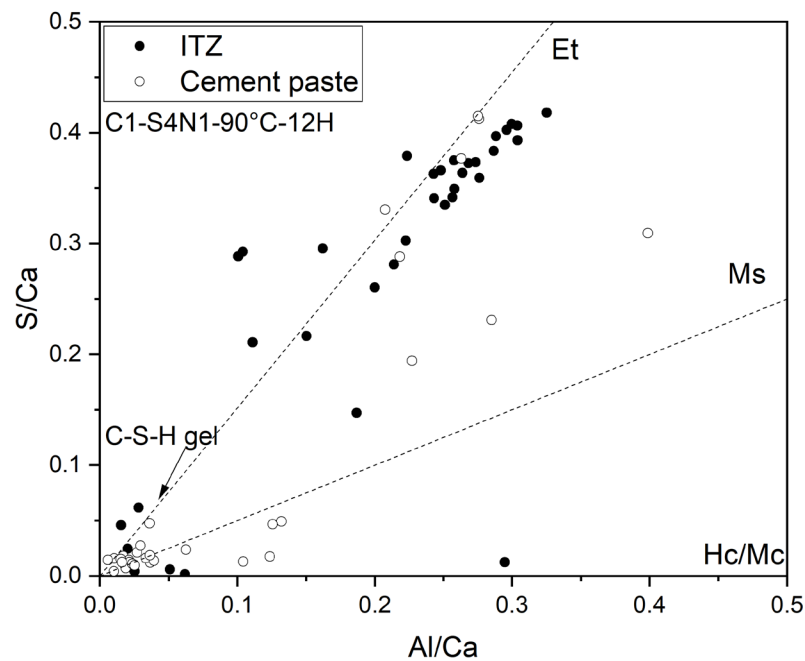


Figure 8.32 Atomic ratio plots of S/Ca vs Al/Ca of C1-S4N1 mortar cured at 90°C for 12 hours and subsequently stored in saturated lime water for 500 days

However, is this correlation the same as causation? Over three decades of DEF research, prominent researchers in this field have taken opposite stands while discussing the

causation of expansion occurring in DEF-affected laboratory specimens. Thaulow & Skalny (1993); Scrivener & Taylor (1993); Taylor, Famy & Scrivener (2001) and Scrivener, Damidot & Famy (1999) believe in the uniform paste expansion theory, where the precipitation of microcrystalline ettringite in the outer (lighter) porous C-S-H is considered to cause expansion. As evidence, these researchers often show the EDS microanalysis, where sulphate and alumina concentrations in the outer C-S-H are higher than the inner C-S-H. After causing expansion, ettringite is believed to decompose and re-precipitate at the ITZ. Hence the ettringite seen at ITZ is the effect of expansion, not the cause; a mere artefact (Barbarulo et al. 2005). On the other hand, Diamond (1996); Leklou, Aubert & Escadeillas (2009) and Yang & Sharp (2001b) believe the crystal growth theory. According to these researchers, the high pressure produced due to the precipitation of substantial ettringite over time at the ITZ is the cause of expansion. With the results available here, this research work supports the latter view. The supporting arguments are as follows: In the first place, the uniform dispersion of ettringite also occurs in the ambient-cured cement matrix, though more finely intermixed in the outer C-S-H (Yang & Sharp 1996). Secondly, the quantity of ettringite in the ambient-cured cementitious system is always higher than in the heat-cured (Figure 8.21 to Figure 8.24) (Yang & Sharp 1996, 2001b). Further, the precipitation of ettringite in hardened cementitious systems also occurs in ambient-cured specimens (Figure 8.23Figure 8.24). Combining these three statements, if the uniform paste expansion theory is true, the ambient cured-systems also should expand considering ettringite continue to precipitate in hardened cement system until 300 days; however, that is not the case (Section 6.1).

The uniform paste expansion theory suggests that ettringite precipitation occurs throughout the system; if this is true, then the more dispersed ettringite distribution may not collectively have the required stress to cause expansion (Yang & Sharp 2001b).

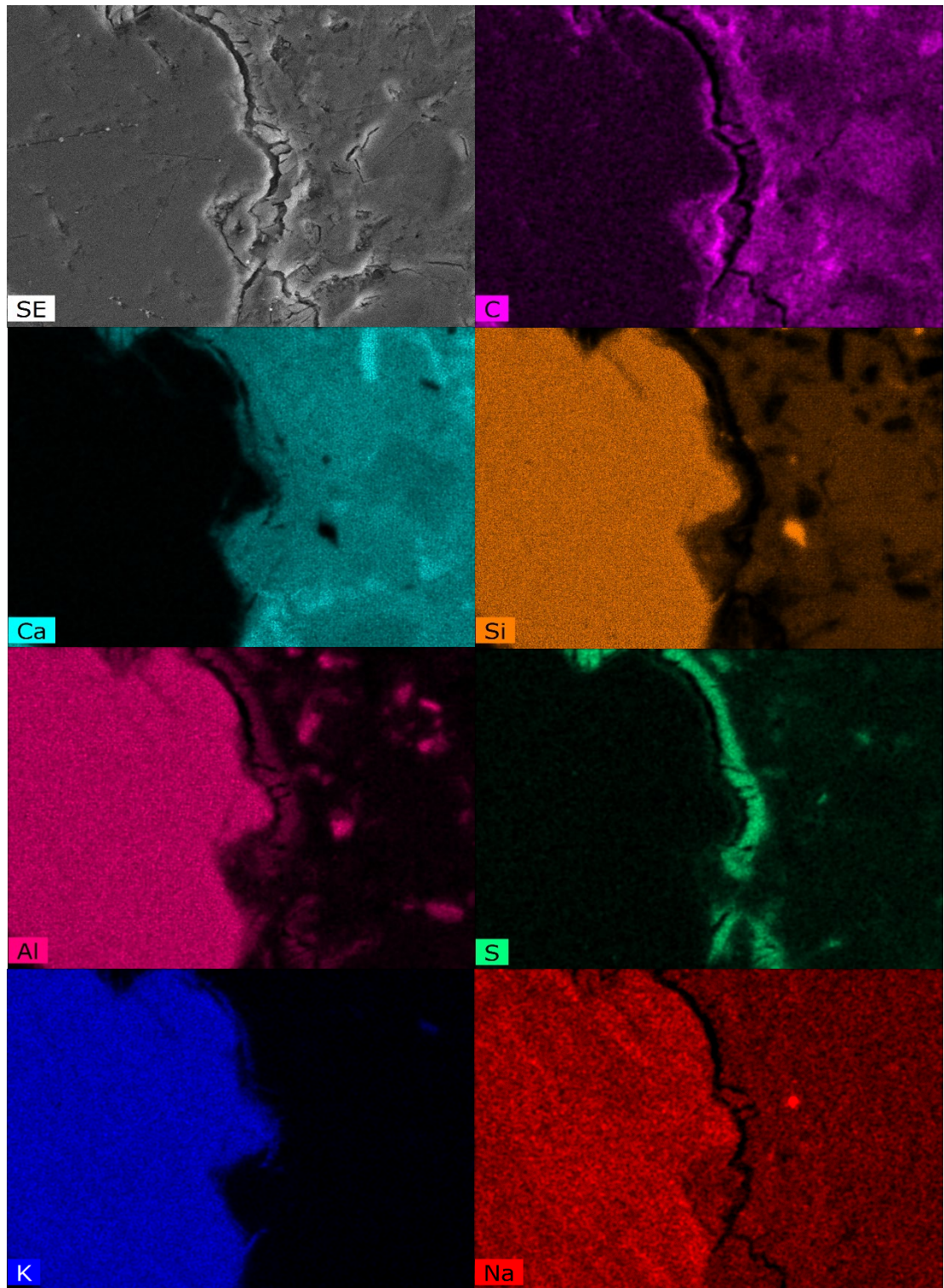


Figure 8.33 Elemental mapping of C, Ca, Si, Al, S, K, Na of C1-S4N1 mortar cured at 90°C for 12 hours and subsequently stored in saturated lime water for 500 days

The expansive stress will only generate when crystals (in this case ettringite) can grow within a crack against a restraint force offered by other microstructural elements (in this

case the aggregate-paste interface, cracks within cement matrix and voids), as concrete is a quasi-brittle material (Diamond 1996).

If the cracks at the ITZ, in the cement matrix or simply at voids are filled with ettringite and precipitation continues to occur, then expansion will result (Ekolu, Rakgosi & Hooton 2017), which is termed 'ice ettringite' (Lee et al. 2005). Further, localised ettringite accumulation is required to generate expansion, as Yang & Sharp (1996) found ettringite bands are more prominent at the edge of a specimen than in the centre, which cannot be explained through uniform expansion theory. Hence the ettringite deposit location in the microstructure is more important (Yang & Sharp 2001a) than uniform precipitation throughout the system. Moreover, the results show no visible ettringite in the ITZ of non-expansive ($< 0.2\%$) heat-cured mortars (Figures 6.26 and 6.29), EDS detectable ettringite in mild but significantly expanded (0.46-0.62%) mortars (Figure 8.27 Figure 8.30) and a substantial amount of ettringite in highly expanded (0.7-1.07%) mortars (Figure 8.31 and Figure 8.34). Furthermore, the negligible quantity of ettringite found in the cement matrix from atomic ratio plots of expanding mortars (Figure 8.26, Figure 8.29, Figure 8.32 Figure 8.35), suggests localised ettringite formation in significant quantity is more responsible for the expansion experienced by the mortars. The substantial amount ettringite in the ITZ of expanding DEF-affected heat-cured mortars supports the crystallisation theory as confirmed by many other researchers (Ekolu, Rakgosi & Hooton 2017; Escadeillas et al. 2007; Leklou, Aubert & Escadeillas 2009; Leklou, Nguyen & Mounanga 2017a; Pavoine, Divet & Fenouillet 2006; Silva et al. 2010a; Yang et al. 1999; Yang & Sharp 1996).

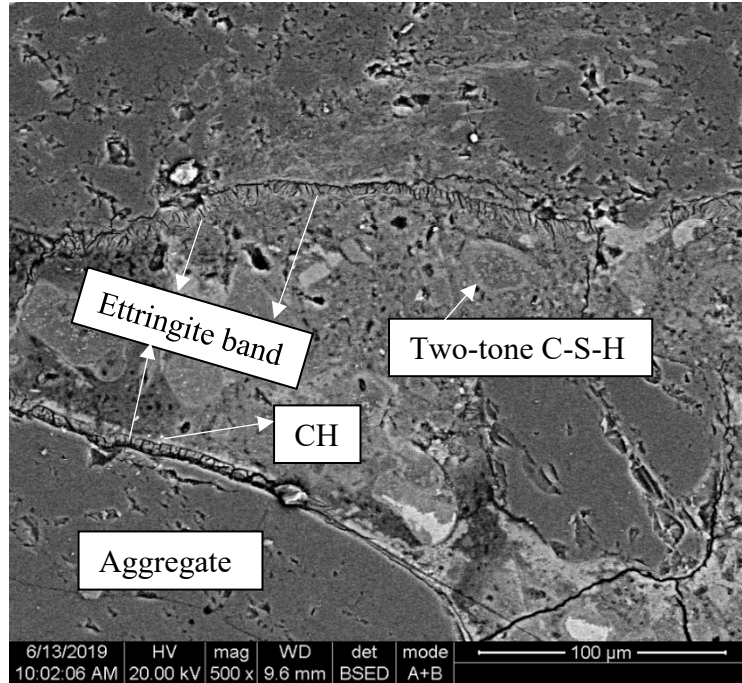


Figure 8.34 Microstructure of C2-S4N1 mortar cured at 90°C for 12 hours and subsequently stored in saturated lime water for 500 days

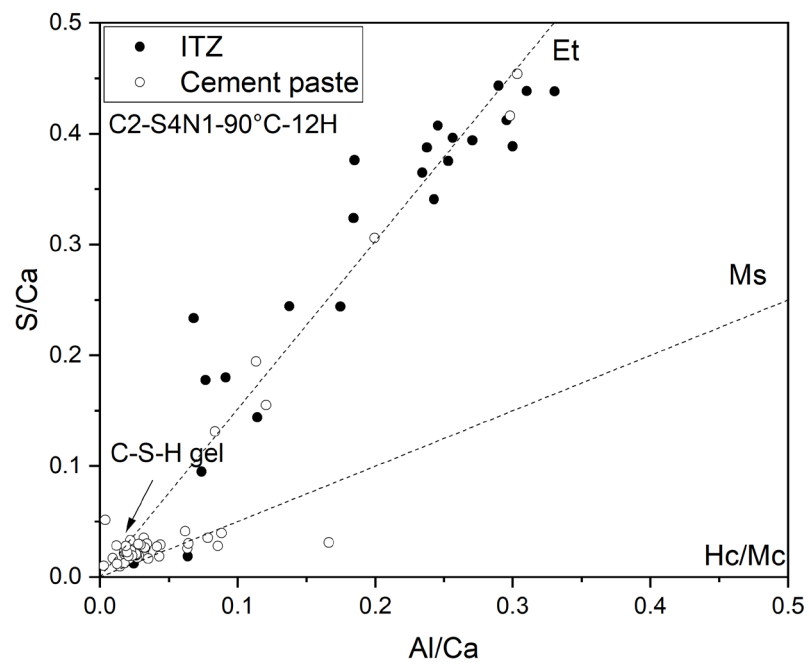


Figure 8.35 Atomic ratio plots of S/Ca vs Al/Ca of C2-S4N1 mortar cured at 90°C for 12 hours and subsequently stored in saturated lime water for 500 days

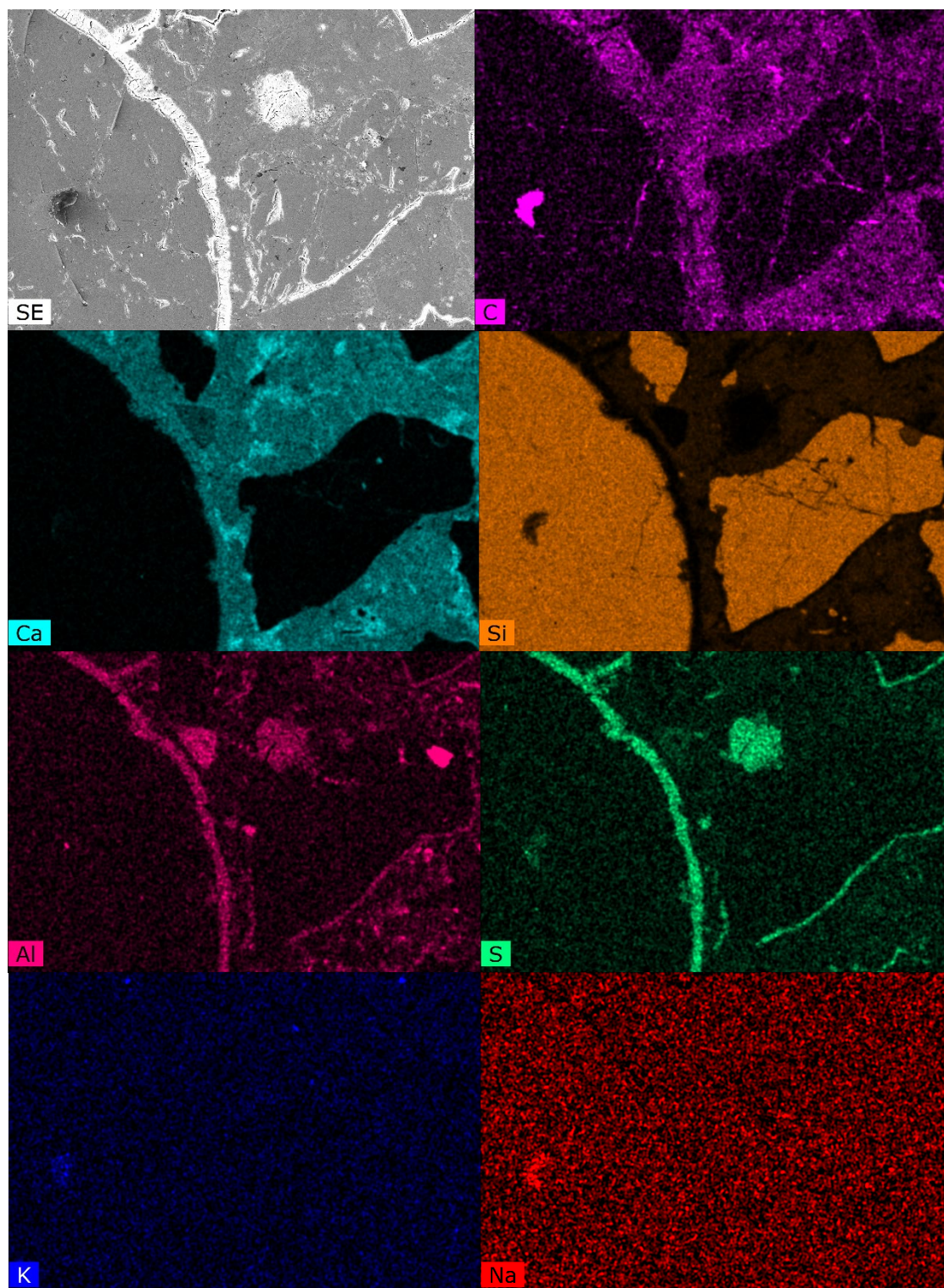


Figure 8.36 Elemental mapping of C, Ca, Si, Al, S, K, Na of C2-S4N1 mortar cured at 90°C for 12 hours and subsequently stored in saturated lime water for 500 days

8.4 Electrical resistivity

Whichever theory the DEF expansion does follow, the impact heat-curing leaves on cementitious systems is important as it can have a significant effect on durability. Only the chemically modified cement systems (S4, S4N1) with 12-hour heat curing at 90°C resulted in expansive DEF, so these were considered for electrical resistivity comparison with the reference mortars. From Figure 8.37 and Figure 8.38, the Nyquist plots of 4-hour pre-cured C1 and C2 mortars suggests that as impedance spectra arcs are getting smaller this corresponds to an increase in the severity of DEF. Similar trends observed in 0-hour pre-cured C1 and C2 mortars suggest (Figure 8.39 and Figure 8.40) that the duration of heat curing and the chemical composition of cement is far more important than the pre-cure time. The resistivity calculated from the mortar-electrode intersection impedance was compared with the ultimate expansion at 500 days (Figure 8.41 Figure 8.42). From these results, C1 mortars (Figure 8.41) show an inconsistency in the resistivity and expansion relationship in 0 pre-cure mortars; however, in other samples, resistivity decreases with the increase in expansion. In the case of C2 mortars (Figure 8.42), the increase in DEF deterioration and expansion due to composition and heat curing regimes consistently reduced the electrical resistivity.

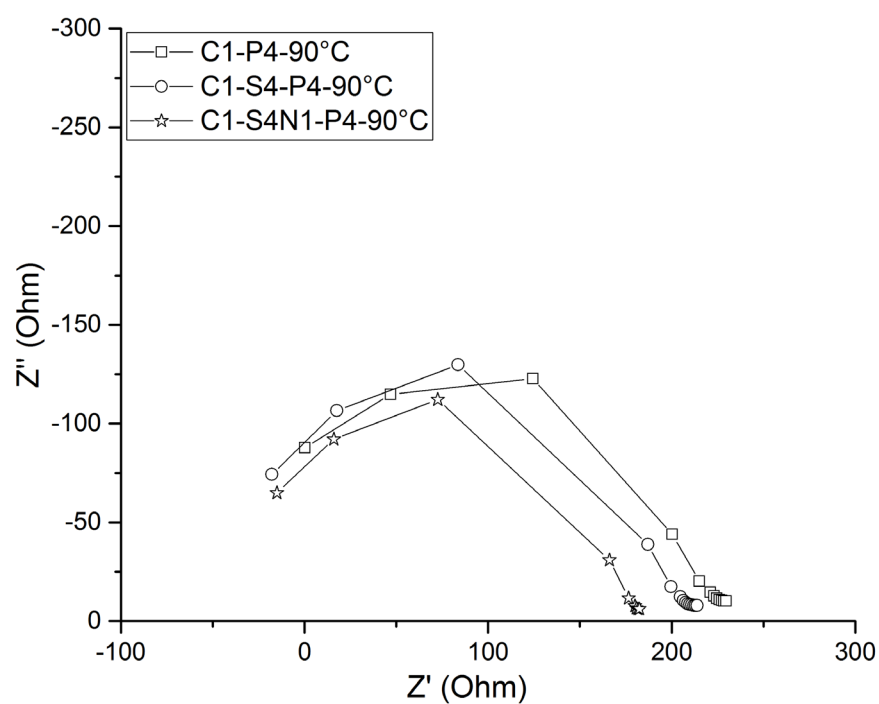


Figure 8.37 Nyquist plots of C1 mortars cured 90°C-12 hours with 4 hours pre-cure– 500 days

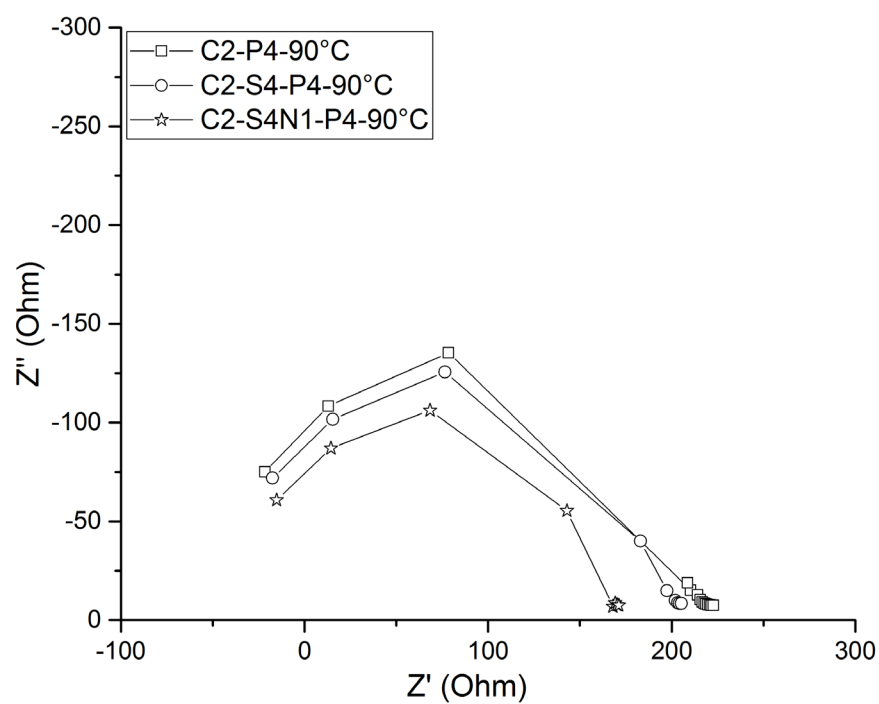


Figure 8.38 Nyquist plots of C2 mortars cured 90°C-12 hours with 4 hours pre-cure– 500 days

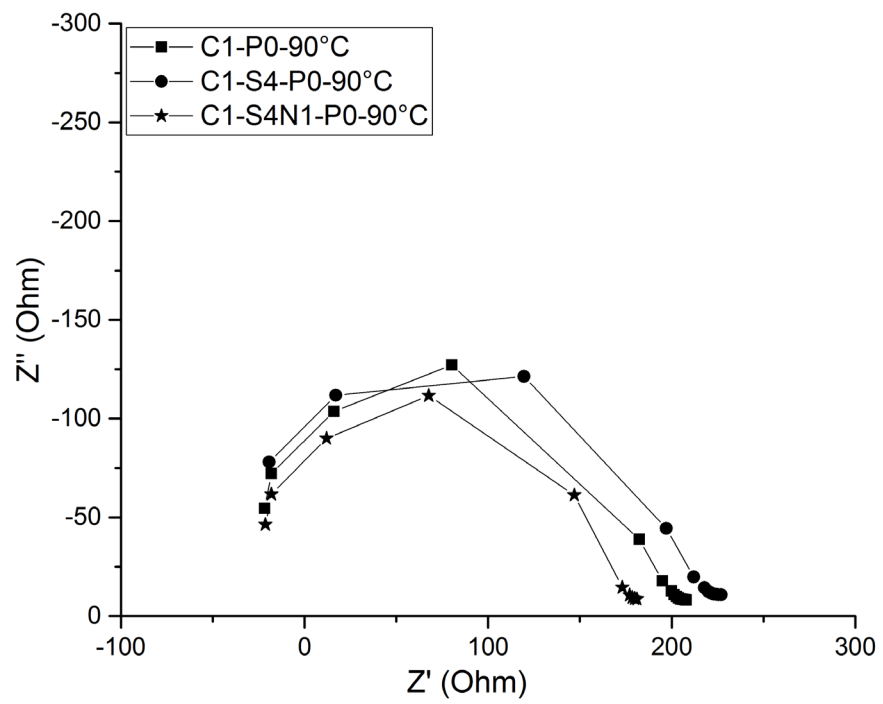


Figure 8.39 Nyquist plots of C1 mortars cured 90°C-12 hours with 0 hours pre-cure– 500 days

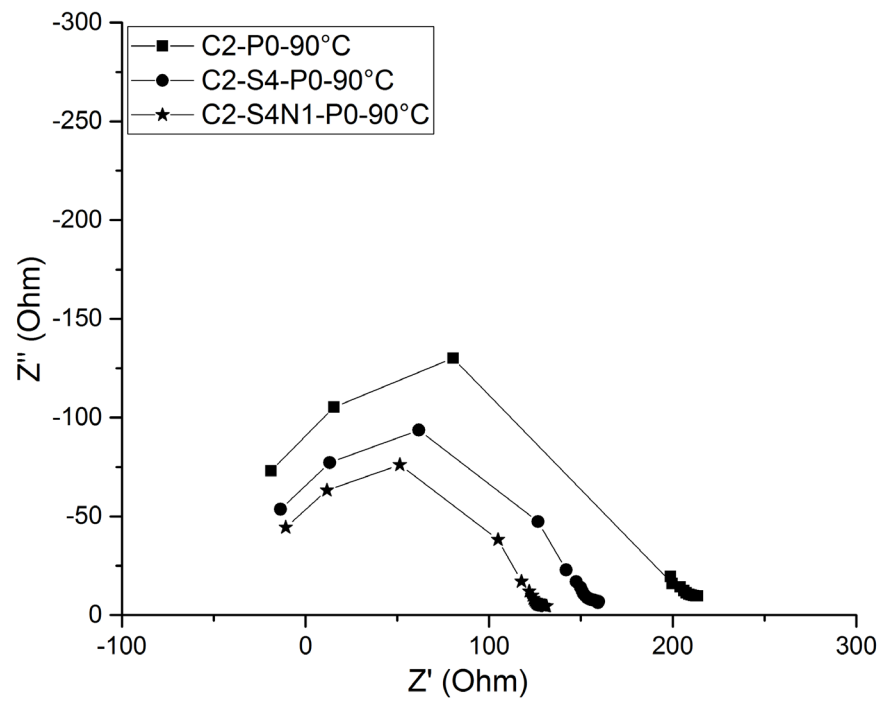


Figure 8.40 Nyquist plots of C2 mortars cured 90°C-12 hours with 0 hours pre-cure– 500 days

As heat curing led to porous C-S-H and other hydrates (Patel, Bland & Poole 1996), an increase the pore volume (Gu et al. 2019) and cracks in cementitious systems caused a significant rise in permeability (Ramezaniapour, Khazali & Vosoughi 2013). As a consequence, this can favour increased transportation of ions through the pore solution (Dhandapani, Scrivener & Santhanam 2017) and can result in lower electrical resistivity (Guangling 2000). Comparing the literature with the obtained results, the heat-curing resulted in lower resistivity in general when compared to ambient cured mortars (Figure 6.34), suggesting the transportation of reactants to precipitate DEF occurred through the increased pore space and cracks in the heat-cured mortars. The differentiation of non-expansive and expansive DEF can be attributed to the quantity of ettringite precipitation which is directly related to cement composition.

Guangling (2000) suggests that if the transport of ions through the solution is partly or wholly blocked by hydrates or aggregates, the electrical resistivity should improve. However, the systems with empty ITZ cracks in C1-P4-90°C and C2-P4-90°C (Figures 6.26 and 6.29) and systems C1-P4-S4N1-90°C and C2-P4-S4N1-90°C (Figure 8.31 & Figure 8.34) with ettringite precipitated in the ITZ did not result in an increase in electrical resistivity and in fact showed a decrease (Figure 8.41). Further, a reduction in pore volume due to pore filling by DEF was reported by Gu et al. (2019); if this holds true then it should result in increased electrical resistance. No such improvement in electrical resistance was noticed in this study.

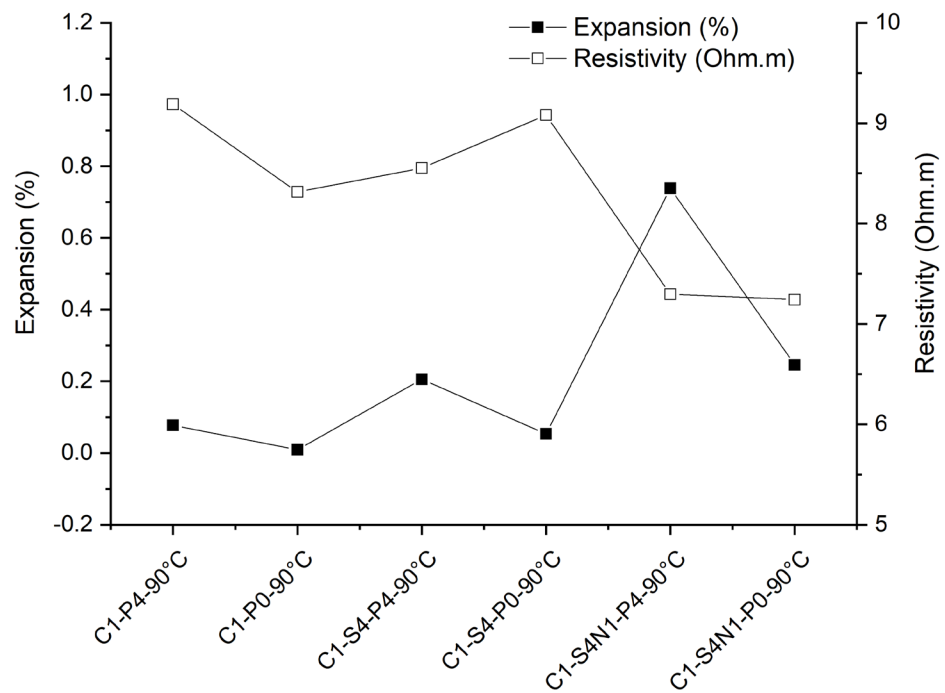


Figure 8.41 Impact of pre-cure time differences in C1 mortars at 500 days - electrical resistivity and expansion comparison

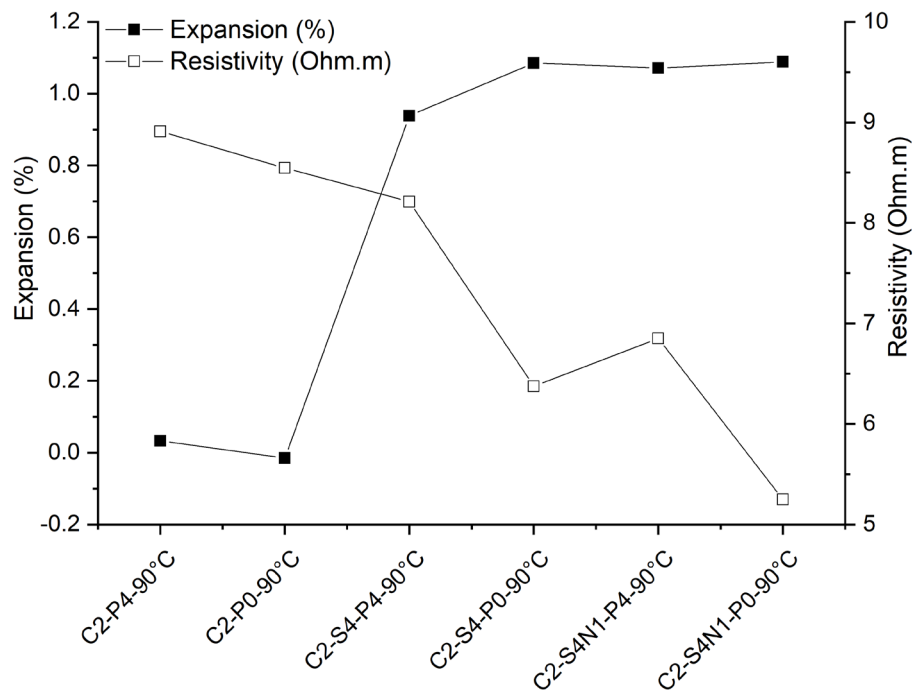


Figure 8.42 Impact of pre-cure time differences in C2 mortars at 500 days - electrical resistivity and expansion comparison

8.5 Summary

The impact of prolonging the heat curing duration (8 to 12 hours) and reducing the pre-cure time (4 to 0 hours) in three different cementitious systems was discussed. Although, there are some inconsistencies, the results for the C2 mortars suggest that reducing pre-cure time has a significant effect on expansion. . Increasing heat-curing duration, clearly increased the risk of DEF as it resulted in a significant and systematic increase in DEF expansion, mass gain and a reduction in electrical resistivity. Since the 12-hour 90°C curing produced the maximum expansion, the impact in pore solution chemistry was studied. The results suggested that the sulphate and alkali ion concentrations peaked at the end of 12 hours at 90°C, and thus impeded ettringite formation. Also, a higher sulphate and alkali ion concentration was found in the pore solution at the end of day 1 for the mortar systems which gave maximum expansion in the long run. Further storage in saturated lime water favoured the leaching of alkalis and ettringite precipitation, which was confirmed by TGA and XRD results. Moreover, the FTIR results gave a hint about sulphate adsorption after heat curing. Heat-cured mortar specimens showed higher expansion, which correlated with the quantity of ettringite precipitated. Microstructural studies revealed that both the quantity and deposition location within microstructure are important. Further, the SEM results suggest that the scale of expansion correlated well with the abundance of ettringite precipitation at the ITZ. These findings support the crystal growth theory of expansion. Cements with $\text{SO}_3 - 4\% + \text{Na}_2\text{O}_{\text{eq}} - 1$ likely to be the most vulnerable to deleterious DEF when heat cured for 12 hours.

Chapter 9 Efficacy of fly ash in mitigating expansive DEF in heat-cured cement systems

From Chapter 6, the insusceptibility of Australian commercial GP cements to deleterious expansive DEF, despite curing at 90°C for 12 hours, was evident. The chemically modified cements containing $\text{SO}_3 - 4\% + \text{Na}_2\text{O}_{\text{eq}} - 1\%$ (C1-S4N1, C2-S4N1) were proven to be vulnerable to deleterious DEF expansion when heat cured at 90°C (Chapter 7), and the extent of vulnerability increased when curing hours were extended from 8 to 12 (Chapter 8). Hence, the efficacy of fly ash (FA) in mitigating deleterious DEF was tested in the most DEF-vulnerable cement systems (C1-S4N1, C2-S4N1) by curing at 90°C for 12 hours. Though notable research have already been completed in incorporating FA in cementitious systems to mitigate DEF by Leklou, Nguyen & Mounanga (2017); Ramlochan, Thomas & Hooton (2003) and Silva et al. (2010), the current research in this project differs in the following ways; (1) efficacy of FA is tested in the pessimum conditions for DEF as stated above, (2) the impact of dilution of ($\text{SO}_3/\text{Al}_2\text{O}_3$) by alumina from FA was minimised by increasing SO_3 to 4% along with 1% alkali (which may increase the dissolution of sulphate), thus encouraging substantial C_3S hydration before C_3A hydration dominates (Section 5.3), (3) Further, FA addition was done in two different ways; (i) without increasing the total cementitious content of the mix, i.e. partial substitution of cement by 25% with FA (C1-S4N1-FR, C2-S4N1-FR), ii) increasing the total cementitious material in the mix, i.e. FA added to the mix by 25% weight of cement (C1-S4N1-FF, C2-S4N1-FF). Mixes without FA were labelled as C1-S4N1-F0 and C2-S4N1-F0. Refer Table 4.8 for detailed description of mixes studied in this chapter. Length and mass changes were monitored for 600 days similar to other chapters. The influence of FA in the dissolution of cement ions, primarily sulphates and alkalis, was studied using pore solution chemistry analysis. The impact of FA in ettringite precipitation and other

crystalline phase evolution was studied using TGA, XRD and FTIR. Microstructural analysis was done using BSE-SEM imaging and EDS mapping. Electrical resistivity of FA included mortars was studied to understand the changes in porosity properties due to alterations at the microstructural level. Results from previous chapters were used in graphs as a reference, wherever necessary.

9.1 Linear expansion and mass changes

Figure 9.1 and Figure 9.2 illustrate the linear expansion differences of cement mortars with and without FA. It is obvious that FA-incorporated mortars show a complete elimination of expansion. The maximum expansion among FA added mortars was 0.01% for C2-S4N1-FF at the end of 600 days. The expansion results obtained are in agreement with other studies (Famy 1999; Leklou, Nguyen & Mounanga 2017b; Ramlochan, Thomas & Hooton 2003; Silva et al. 2010b). Further, a reduction in mass gain was noted (Figure 9.3 Figure 9.4), suggesting reduced water absorption. The elimination of DEF expansion and reduced mass gain suggests that the dimensional stability and mechanical properties of FA-added mortars were tremendously improved. The mitigation of deleterious DEF expansion could be attributed to the combined effect of dilution of cementitious systems with the inclusion of FA, and the changes occurred in the crystalline phases; this is discussed further in the following section.

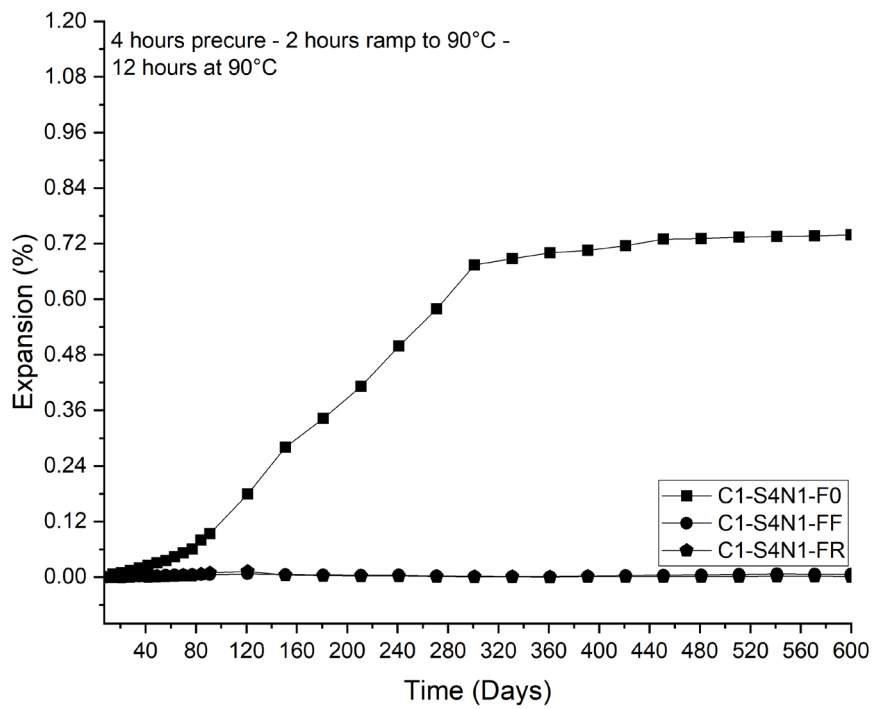


Figure 9.1 Effect of fly ash in linear expansive behaviour of heat-cured C1-S4N1 mortars

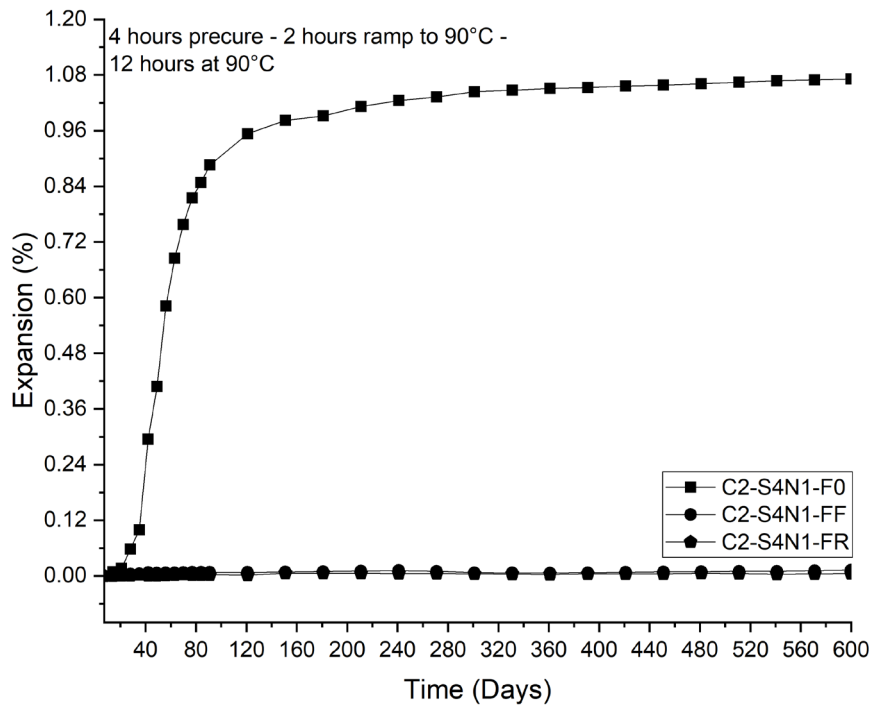


Figure 9.2 Effect of fly ash in linear expansive behaviour of heat-cured C2-S4N1 mortars

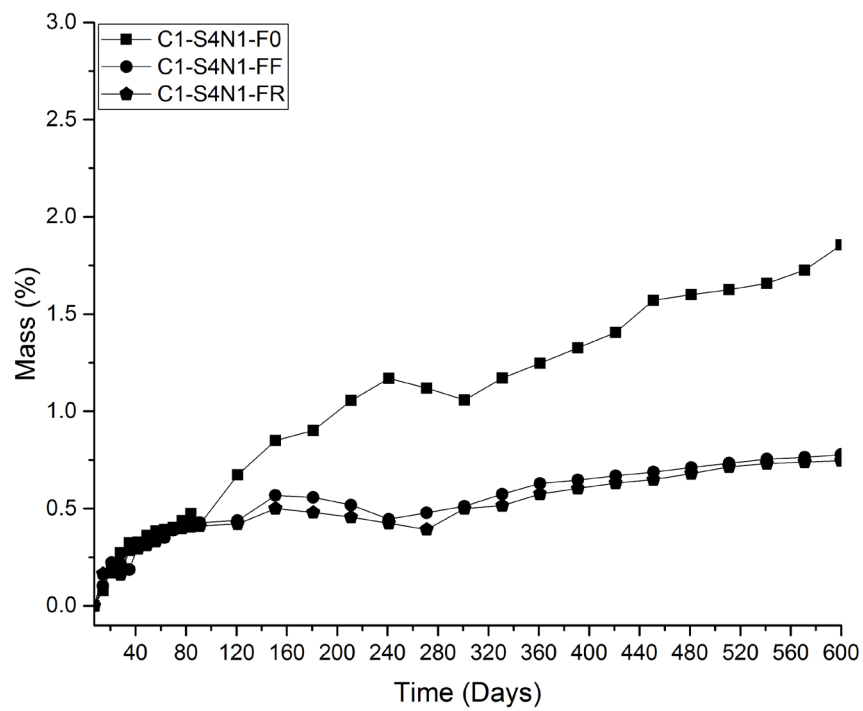


Figure 9.3 Effect of fly ash in mass changes of heat-cured C1-S4N1 mortars

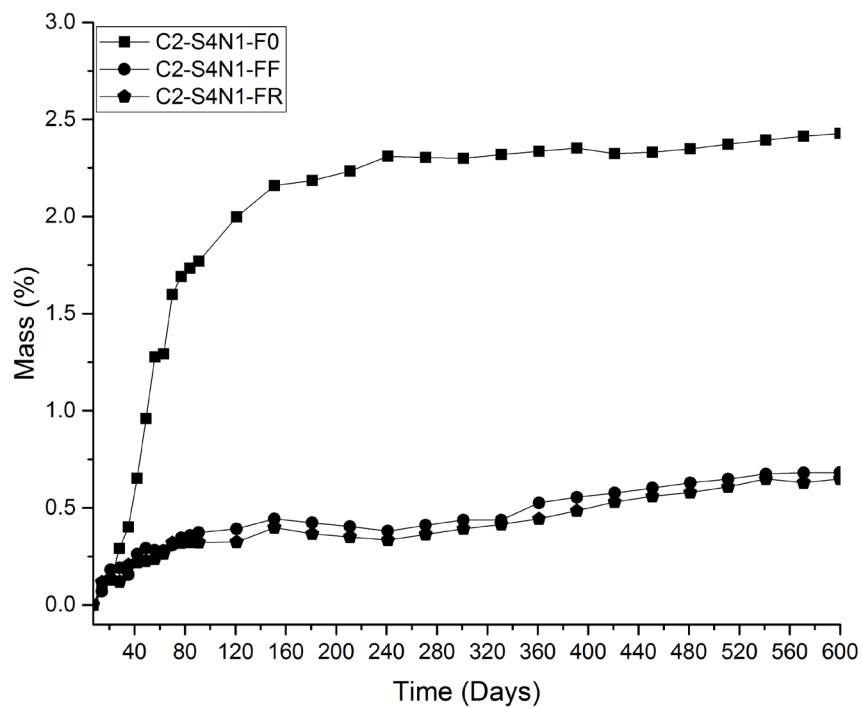


Figure 9.4 Effect of fly ash in mass changes of heat-cured C2-S4N1 mortars

9.2 Evolution of ionic pore solution characteristics and crystalline phases

The ionic concentrations of pore solutions from C1-S4N1-FR and C2-S4N1-FR cement pastes cured at 90°C for 12 hours are given in Figure 9.5 Figure 9.6. No visible changes were noticed in the concentrations of Al and Si ions throughout the testing time due to the saturation of these ions in the pore solution. Compared to FA-free systems, at the end of pre-cure time (0.16 day), (Compare Figure 8.16 with 9.5, and Figure 8.17 with 9.6) a significant drop in K (C1-S4N1 36.40 to 30.26 mmol/L, C2-S4N1 44.67 to 34.05 mmol/L), Na (C1-S4N1 19.11 to 16.21 mmol/L, C2-S4N1 30.65 to 23.51 mmol/L) and S (C1-S4N1 97.19 to 71.96 mmol/L, C2-S4N1 158.48 to 86.87 mmol/L) ion concentrations was noticed with the inclusion of FA, indicating the dilution effect (Figures 8.17, 8.18, 9.5 and 9.6). At the end of day 1, dissolution of S ions increased to 86.34 from 71.96 mmol/L in C1-S4N1-FR, due to the decomposition of primary ettringite and the dissolution of gypsum under high temperature and high alkali conditions. In the case of C2-S4N1-FR, sulphate ions faced a drop to 77.95 from 86.87 mmol/L, possibly due to a combination of reasons such as higher aluminate hydration in Cement 2 and increased adsorption of sulphate into C-S-H while heat curing. The sulphate concentrations at the end of day 1 in non-expansive FA-added cement systems (C1-S4N1-FR 86.34 mmol/L & C2-S4N1-FR 77.95 mmol/L) were much lower than the expansive systems (C1-S4N1-F0 144.23 mmol/L & C2-S4N1-F0 89.89 mmol/L). Further, the rate of alkalinity reduction in FA-added mixes was found to be much slower than FA-free mixes, leaving more alkalis in the pore solution after of 7 and 30 days, as shown in Table 9.1. Hence the pore solution of FA-added mixes had a marginally higher pH and higher alkali content for a longer period of time, thus impacting the sulphate consumption to form ettringite (Table 9.1).

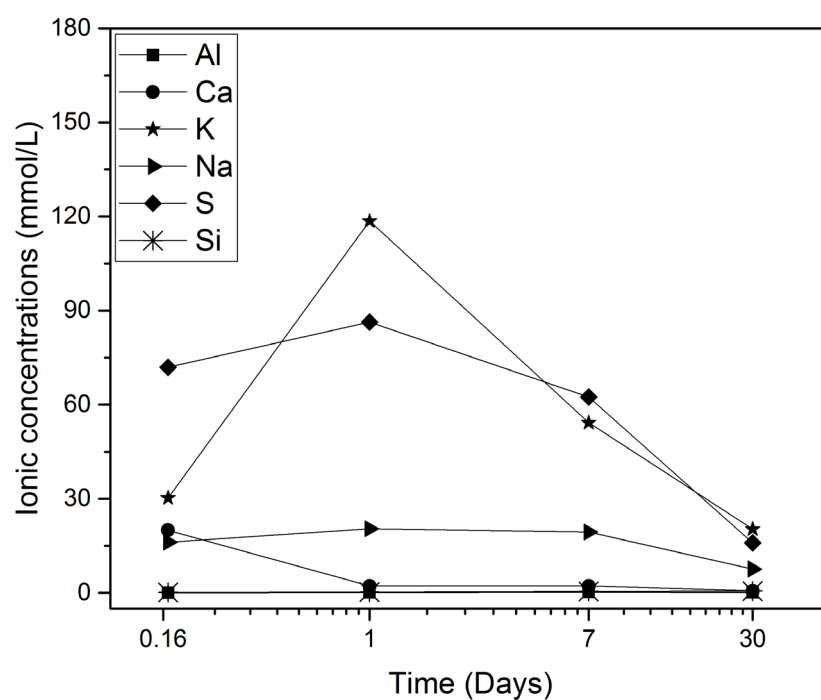


Figure 9.5 Ionic concentrations of pore solution from C1-S4N1-FR cement paste cured at 90°C for 12 hours

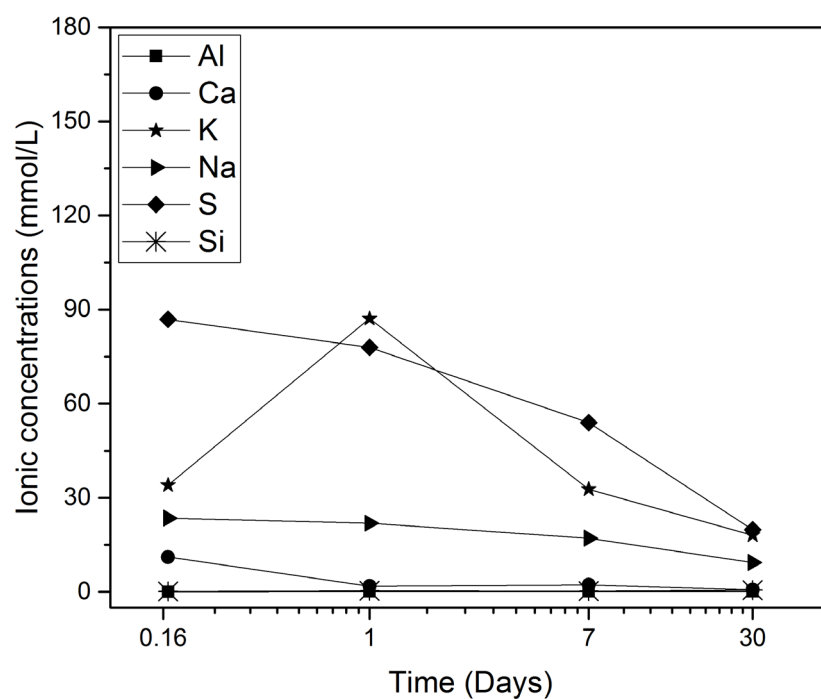


Figure 9.6 Ionic concentrations of pore solution from C2-S4N1-FR cement paste cured at 90°C for 12 hours

Table 9.1 Differences in total alkali concentrations in FA added mixes and its impact on pH, OH⁻ and S ion concentrations over time

Mix ID	K+Na (mmol/L)		pH		OH ⁻ (mmol/L)		S (mmol/L)	
	7 days	30 days	7 days	30 days	7 days	30 days	7 days	30 days
C1-S4N1-F0	49.4	15.3	13.1	12.6	134.9	40.7	30.1	1.8
C2-S4N1-F0	30.4	10.2	13.0	12.5	112.2	31.6	44.3	0.9
C1-S4N1-FR	73.6	27.9	13.1	12.7	141.2	49.0	62.5	16.0
C2-S4N1-FR	49.9	27.5	13.2	12.7	169.8	51.3	54.0	19.8

The increased retention of alkalis can be attributed to the reduced diffusivity in FA-added cement systems (Ramlochan, Thomas & Hooton 2004). Corresponding to the increase in S ion concentration at the end of day 1 after heat-curing, an absence of ettringite was noted from the TGA mass loss curves and XRD patterns (Figure 9.7 to Figure 9.10). Although FA-added mixes are non-expansive, non-deleterious DEF occurred during storage, as noted from the day 7 TGA mass loss curves (Figure 9.7 to Figure 9.8). It appears from the TGA results that the ettringite precipitation continued until day 600 in C1-S4N1-FR but only until day 300 in C2-S4N1-FR. XRD results, however, show no appreciable difference in ettringite formation (Figure 9.9 and Figure 9.10).

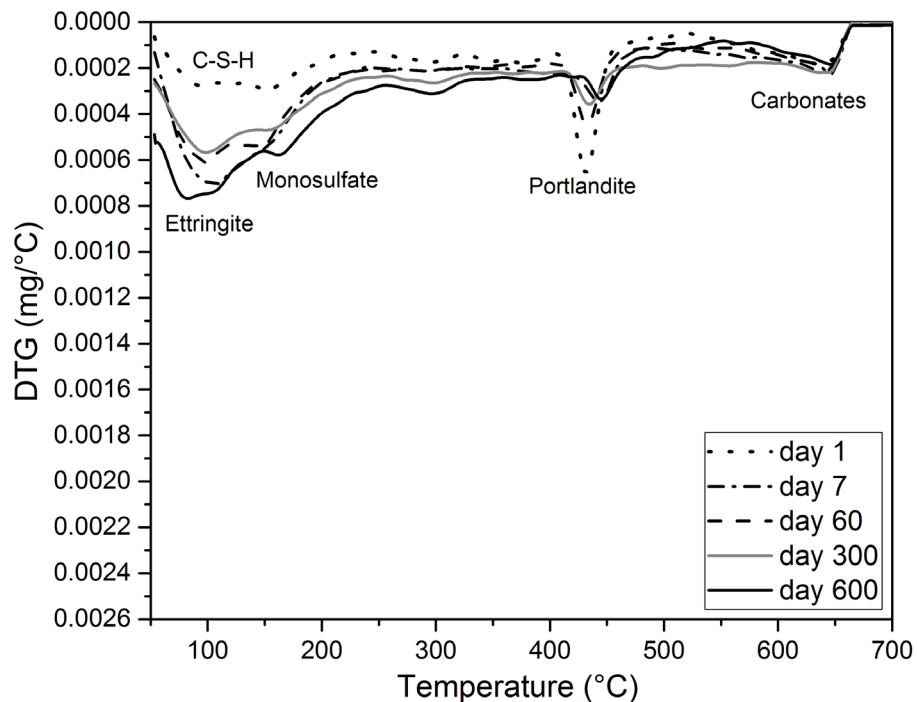


Figure 9.7 TGA mass loss curves of C1-S4N1-FR paste cured at 90°C for 12hours – day 1 to day 600

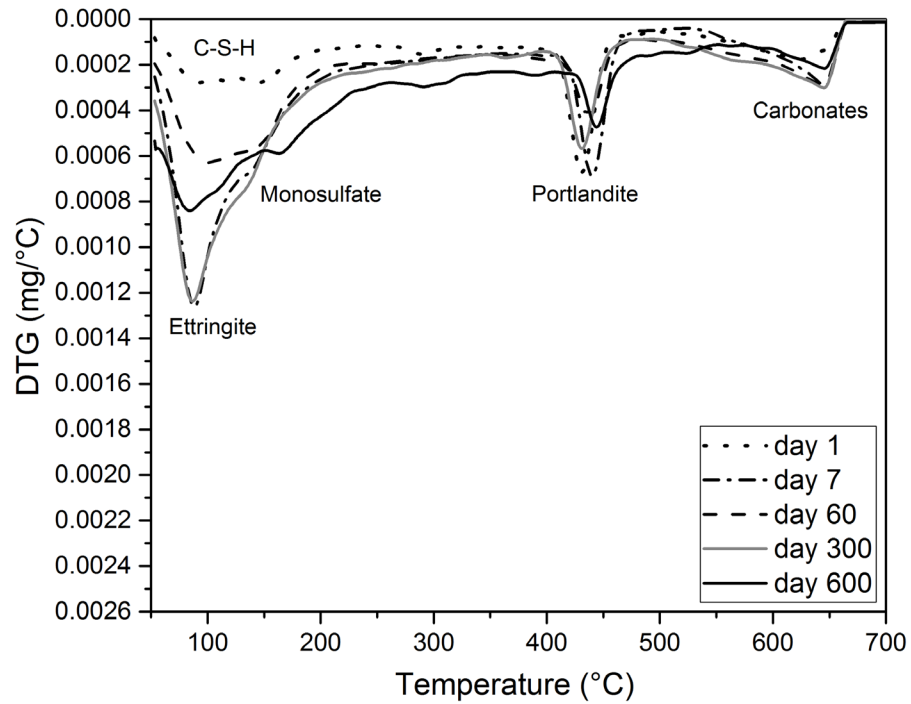


Figure 9.8 TGA mass loss curves of C2-S4N1-FR paste cured at 90°C for 12hours – day 1 to day 600

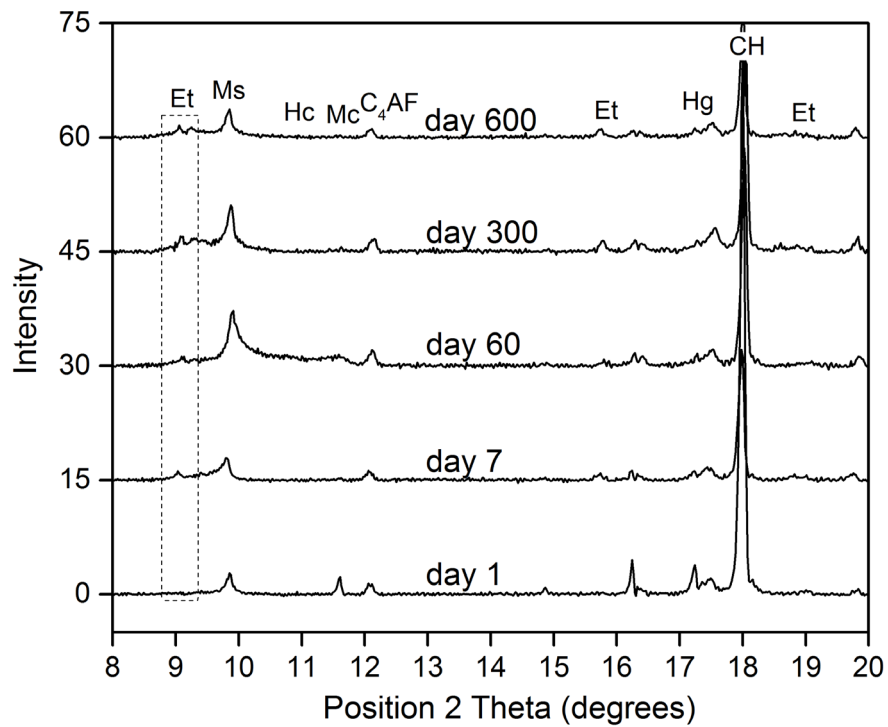


Figure 9.9 XRD patterns of C1-S4N1-FR paste cured at 90°C for 12 hours – day 1 to day 600

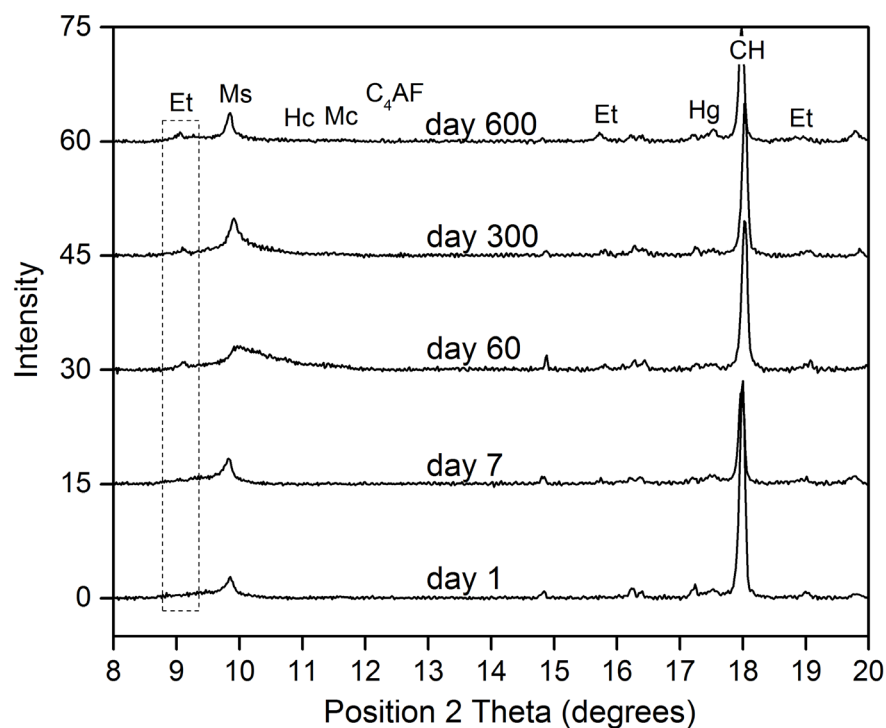


Figure 9.10 XRD patterns of C2-S4N1-FR paste cured at 90°C for 12 hours – day 1 to day 600

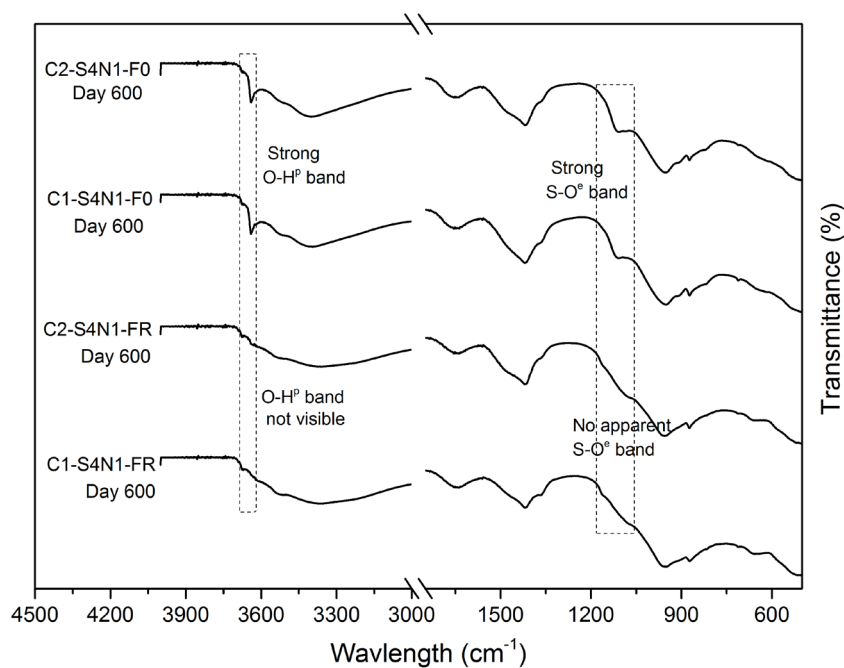


Figure 9.11 FTIR spectrum of C1-S4N1-FR & C2-S4N1-FR pastes cured at 90°C for 12 hours – day 1 & day 600

The presence of monosulphate and hydrogarnet were noted throughout the FA cement systems in all ages. At later ages, the lack of abundant sulphates due to the restricted transportation of ions in the improved impermeable environment could be attributed to the formation of monosulphate, rather than higher sulphate demanding ettringite precipitation. Furthermore, more precipitation of less voluminous monosulphate (interlayer spacing 8.9 Å) instead of ettringite (interlayer spacing 11.23 Å) – as discussed in Section 6.2.1 -- contributes to the non-expansive nature of FA-added mortars. The lower ettringite precipitation noted from the TGA and XRD results correlates well with the FTIR transmittance spectrum as it shows (Figure 9.11) a near absence of the S-O^e band associated with ettringite (refer to Table 4.9 for various FTIR bands associated with cement hydrates and its notation).

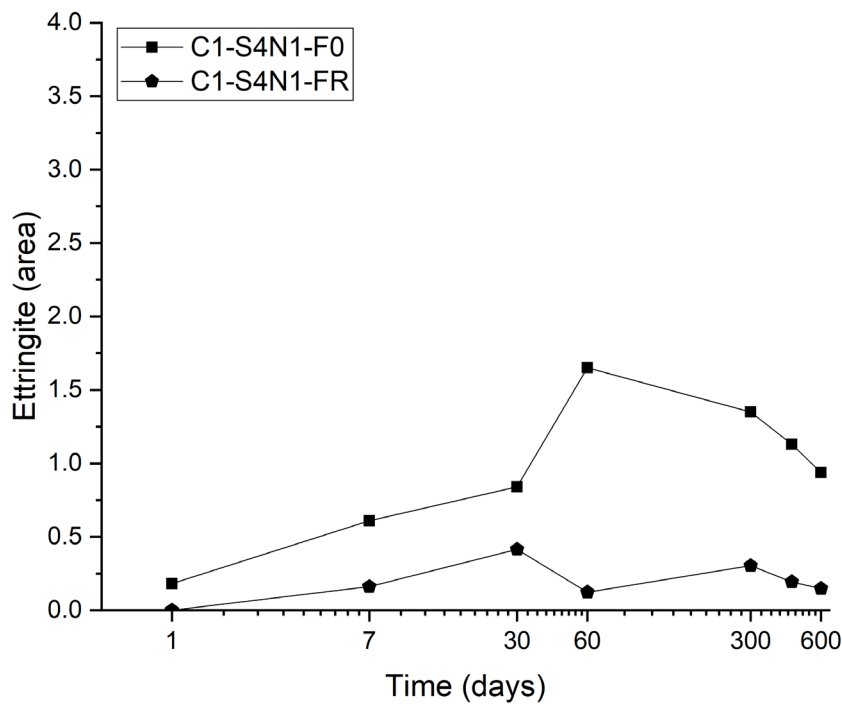


Figure 9.12 Impact of fly ash in ettringite evolution over time C1 cementitious system cured at 90°C-12 hours

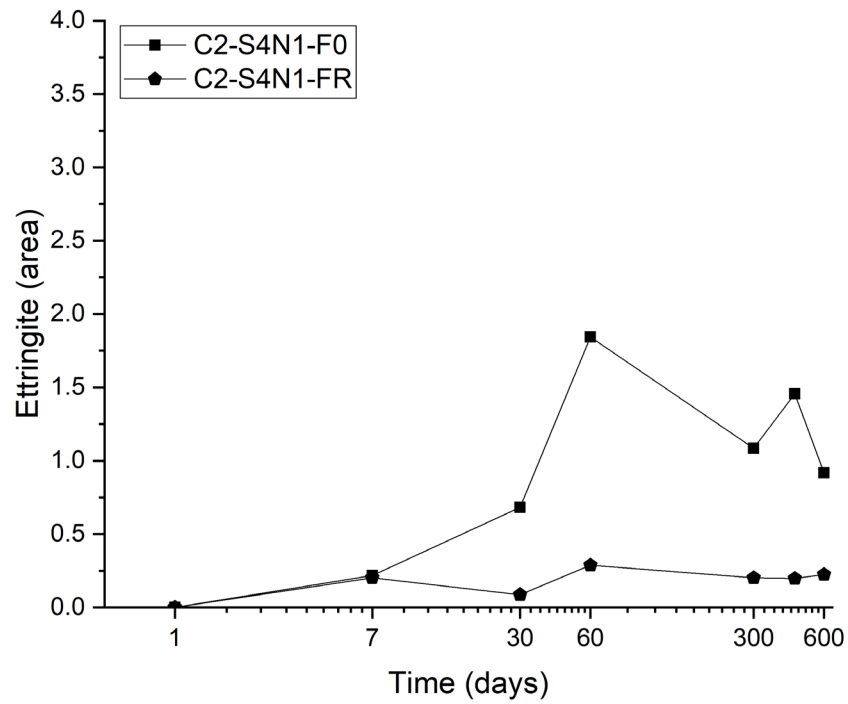


Figure 9.13 Impact of fly ash in ettringite evolution over time C2 cementitious system cured at 90°C-12 hours

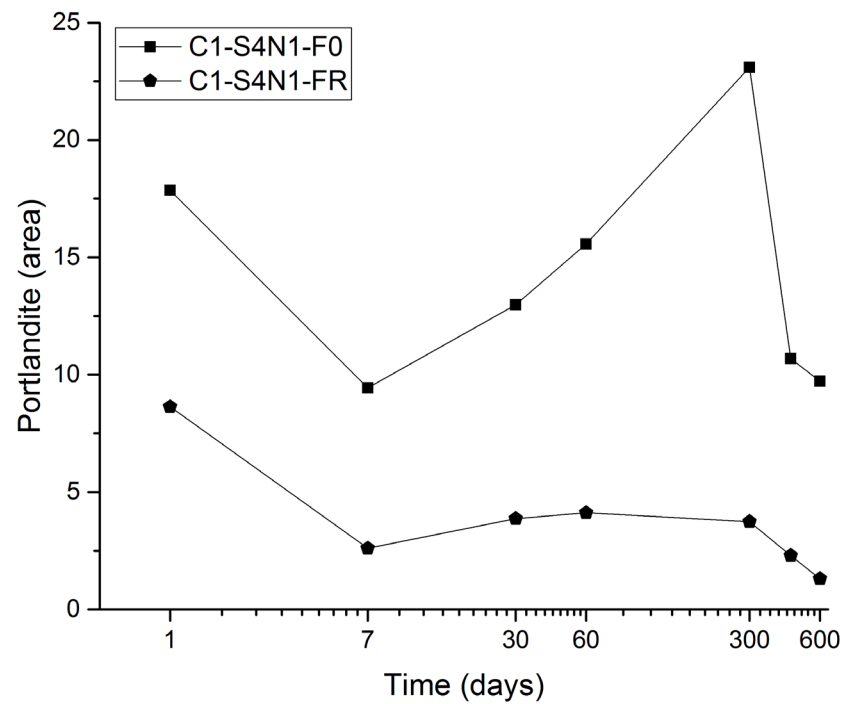


Figure 9.14 Impact of fly ash in portlandite evolution over time C1 cementitious system cured at 90°C-12 hours

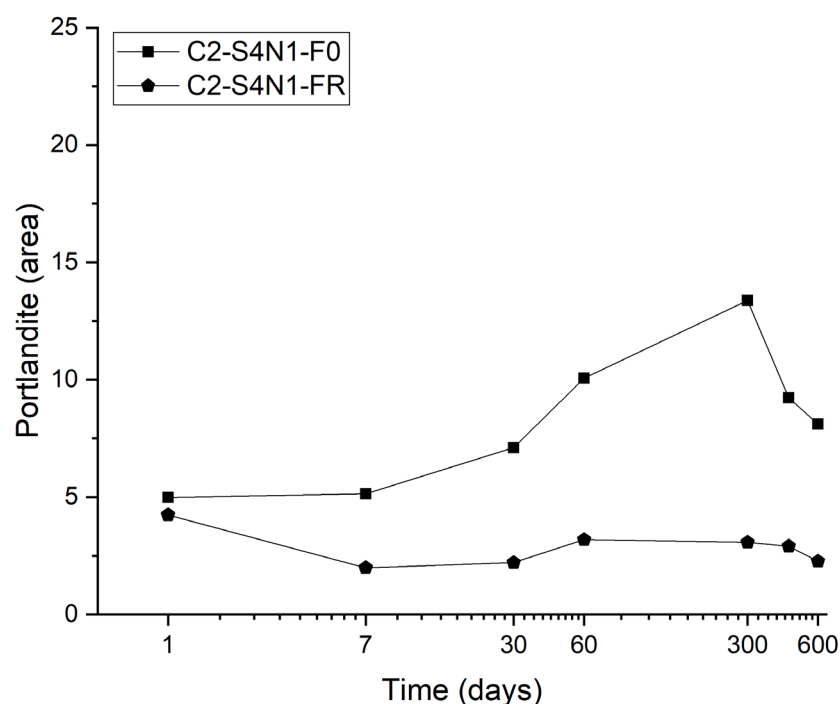


Figure 9.15 Impact of fly ash in portlandite evolution over time C2 cementitious system cured at 90°C-12 hours

The differences in the quantity of ettringite precipitation between expansive (C1-S4N1-F0, C1-S4N1-F0) and non-expansive FA-added mixes (C1-S4N1-FR, C2-S4N1-FR) are compared in Figure 9.12 and Figure 9.13. It is evident from the semi-quantitative analysis that FA-added mixes had far less ettringite in their systems, and thus no expansion was experienced in these mortars (Figure 9.1 Figure 9.2). Further, strong O-H^p band vibrations that had been seen in C1-S4N1 and C2-S4N1 essentially vanished in the FTIR spectra of the FA-added mixes (Figure 9.11), indicating the consumption of CH by silica from FA to form C-S-H. The quantity of CH is compared between expansive (C1-S4N1-F0, C1-S4N1-F0) and non-expansive FA-added mixes (C1-S4N1-FR, C1-S4N1-FR) in Figure 9.14Figure 9.15. It is evident that CH precipitation was greatly reduced in non-expansive FA mixes due to a pozzolanic reaction resulting in higher C-S-H formation, thereby semi-quantitatively confirming the qualitative FTIR results. The conversion of CH to C-S-H due to the pozzolanic reactivity of FA does refine the pore structure by reducing capillary

pores and increasing gel pores (Thomas 2013a), thus improving impermeability and encouraging monosulphate precipitation instead of ettringite, as discussed earlier.

9.3 Microstructural investigation by SEM

The impact of FA on the microstructure of heat-cured mortars C1-S4N1-FR and C2-S4N1-FR is presented in this section. Figure 9.16 shows the micrograph of C1-S4N1-FR mortar cured at 90°C for 12 hours. The empty cracks formed during the sample preparation are visible in the micrograph. Although the unhydrated or partially hydrated cement grains are difficult to distinguish, the unreacted FA is easily spotted in a few locations. The CH rim noticed in expansive mortars (Figures 8.31 and 8.34) was not easily identifiable in the non-expansive C1-S4N1-FR mortar. Unlike the expansive DEF mortars, no ettringite precipitation was found in the ITZ despite heat curing. However, from the atomic ratio plots in Figure 9.17, ettringite within cement paste with different alumina levels was detected at fewer locations. Further, the atomic ratio plot shows a slight shift in C-S-H gel towards the right due to the incorporation of alumina. The presence of more monosulphate in the XRD and TGA results was again confirmed by the atomic ratio plot. However, the monosulphates show varying alumina and calcium levels.

In addition to the atomic ratio plots, the composition of C-S-H was analysed by taking an average of 20 EDS points (in total) from three different micrographs, presented in Table 9.2. The FA inclusion lowered the Ca/Si ratio, and the alumina intake into C-S-H was clear from the Ca/(Si+Al) ratio. Further, the alumina intake was responsible for the increased alkali binding in the C-S-H for FA-added mortars. Adsorption of sulphates in the C-A-S-H solid phases was higher for FA added mortars, again contributing to the lower availability of the same for ettringite precipitation, even at the age of 500 days.

The elemental mapping in Figure 9.18 corroborates the absence of an ettringite band. Further, within the cement paste an intermix of calcium, alumina and sulphate was not readily distinguished. The sparsely intermixed calcium with sulphate and calcium with alumina suggests the presence of monosulphate and hydrogarnet in the system, which matches well with the XRD results discussed in the previous section. The unreacted FA was easy to distinguish with bright alumina and silica spots in the elemental maps. As the aggregates used are mildly reactive (Section 3.3) the presence of alkalis in the aggregate was observed in the elemental mapping (encircled); nevertheless, no traces of alkali-silica reaction (ASR) gel were found.

As in the C1-S4N1-FR mortar, in C2-S4N1-FR no traces of CH rim or ettringite band were found near the ITZ (Figure 9.19). The presence of unreacted FA and two-tone C-S-H was noted at some locations. Further, within cement pastes, few spots of ettringite were identified from atomic ratio plots (Figure 9.20) as identical to C1-S4N1-FR. Among the FA added mortars, C2-S4N1-FR had lower Ca/Si and Ca/(Si+Al) ratios, suggesting increased C-A-S-H phase formation. The corresponding alkali binding was also increased (Table 9.2). The elemental mapping (Figure 9.21) again confirms the absence of an ettringite band in the ITZ and having the presence of only sparsely formed ettringite, carboaluminates, monosulphates and hydrogarnet in the system. No traces of mild reactive aggregate particles were found within the boundaries of the micrograph.

Table 9.2 Influence of flyash on the composition of the microstructure of mortars

Mix ID	Ca/Si	Ca/(Si+Al)	(Na+K)/(Ca/(Si+Al))	S/Ca
C1-S4N1-F0	2.34	2.13	0.09	0.021
C2-S4N1-F0	2.35	2.17	0.06	0.030
C1-S4N1-FR	1.92	1.57	0.15	0.039
C2-S4N1-FR	1.60	1.34	0.72	0.043

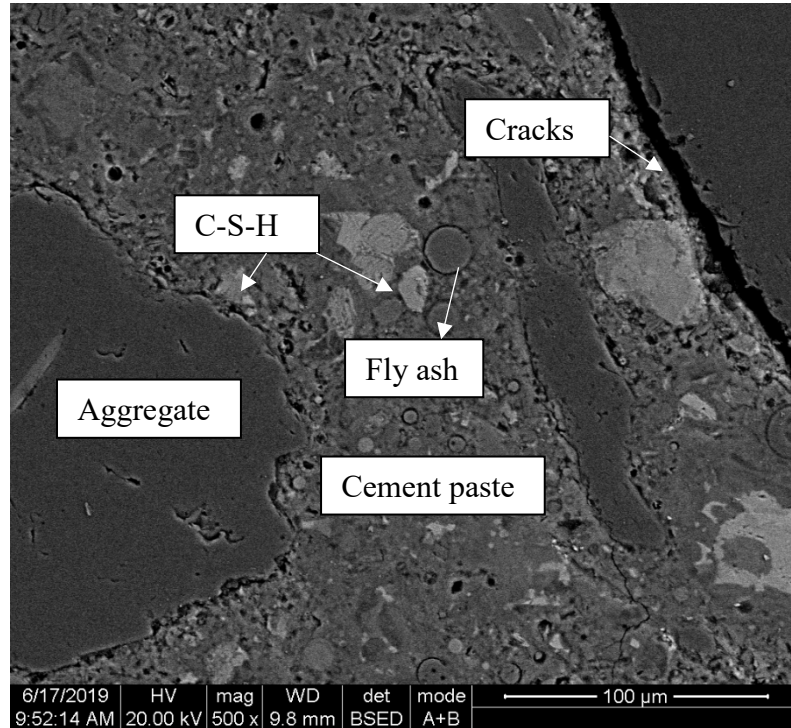


Figure 9.16 Microstructure of C1-S4N1-FR mortar cured at 90°C for 12 hours and subsequently stored in saturated lime water for 500 days

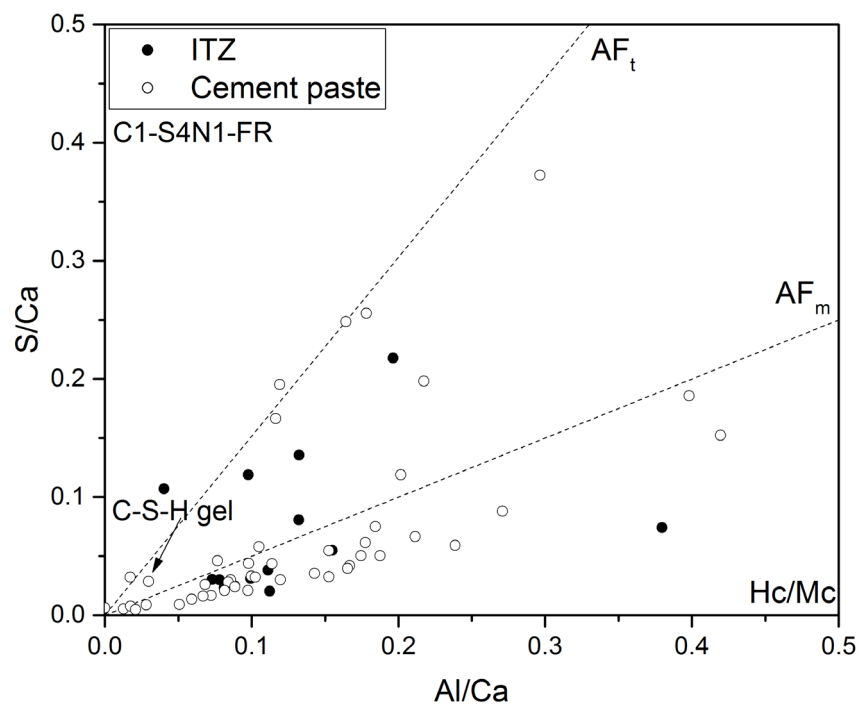


Figure 9.17 Atomic ratio plots of S/Ca vs Al/Ca of C1-S4N1-FR mortar cured at 90°C for 12 hours and subsequently stored in saturated lime water for 500 days

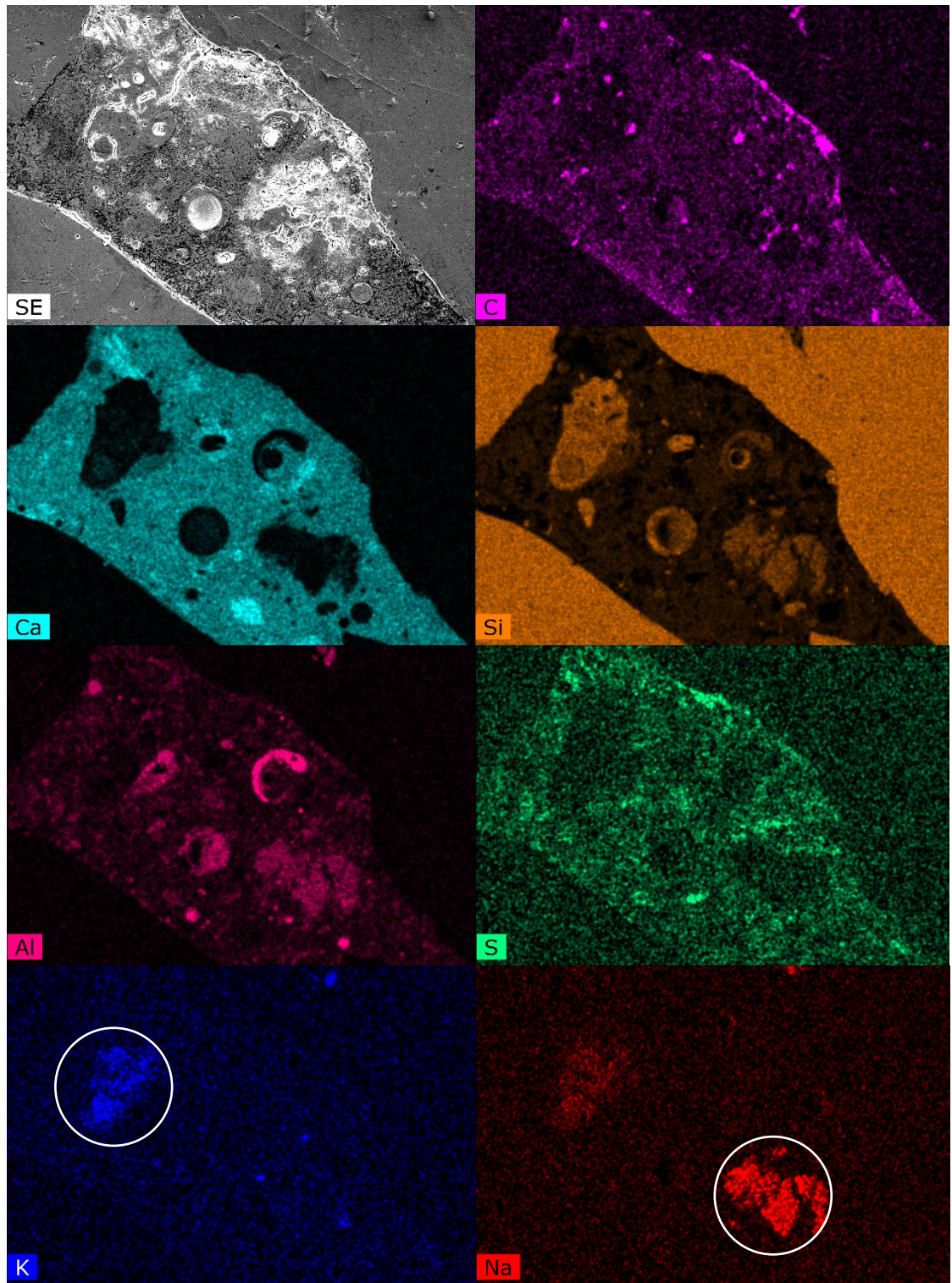


Figure 9.18 Elemental mapping of C, Ca, Si, Al, S, K, Na of C1-S4N1-FR mortar cured at 90°C for 12 hours and subsequently stored in saturated lime water for 500 days

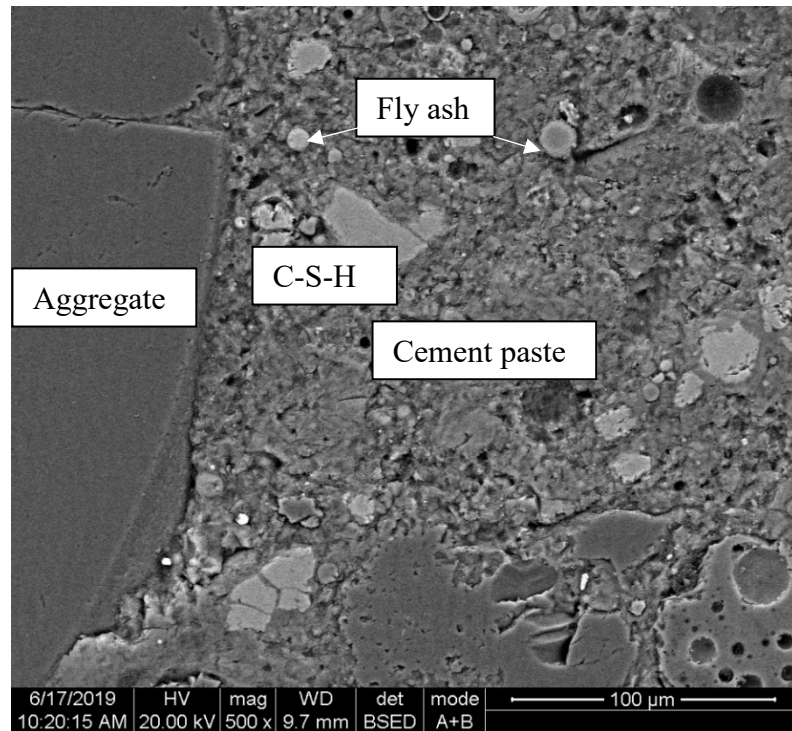


Figure 9.19 Microstructure of C2-S4N1-FR mortar cured at 90°C for 12 hours and subsequently stored in saturated lime water for 500 days

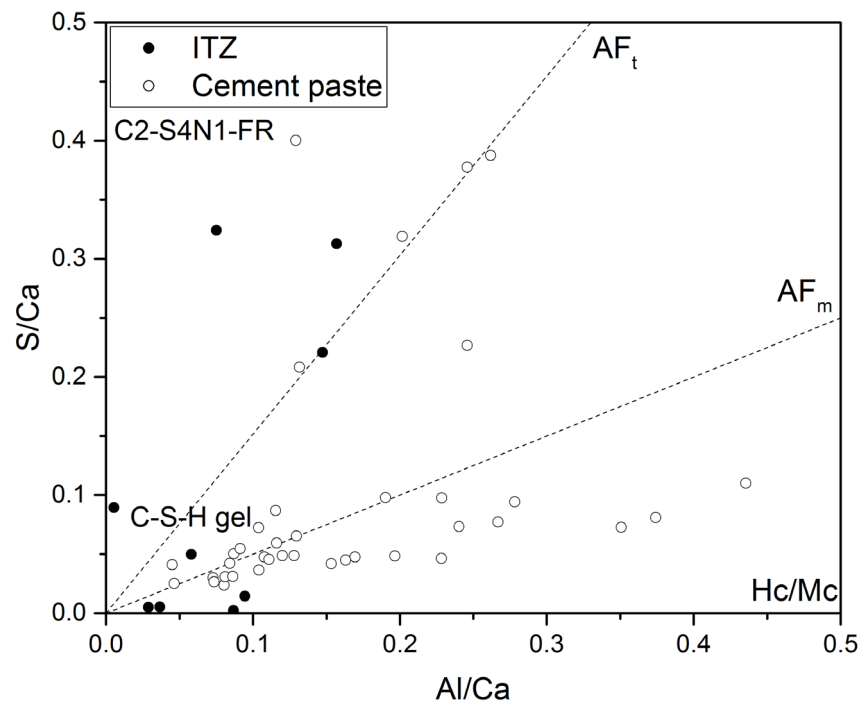


Figure 9.20 Atomic ratio plots of S/Ca vs Al/Ca of C2-S4N1-FR mortar cured at 90°C for 12 hours and subsequently stored in saturated lime water for 500 days

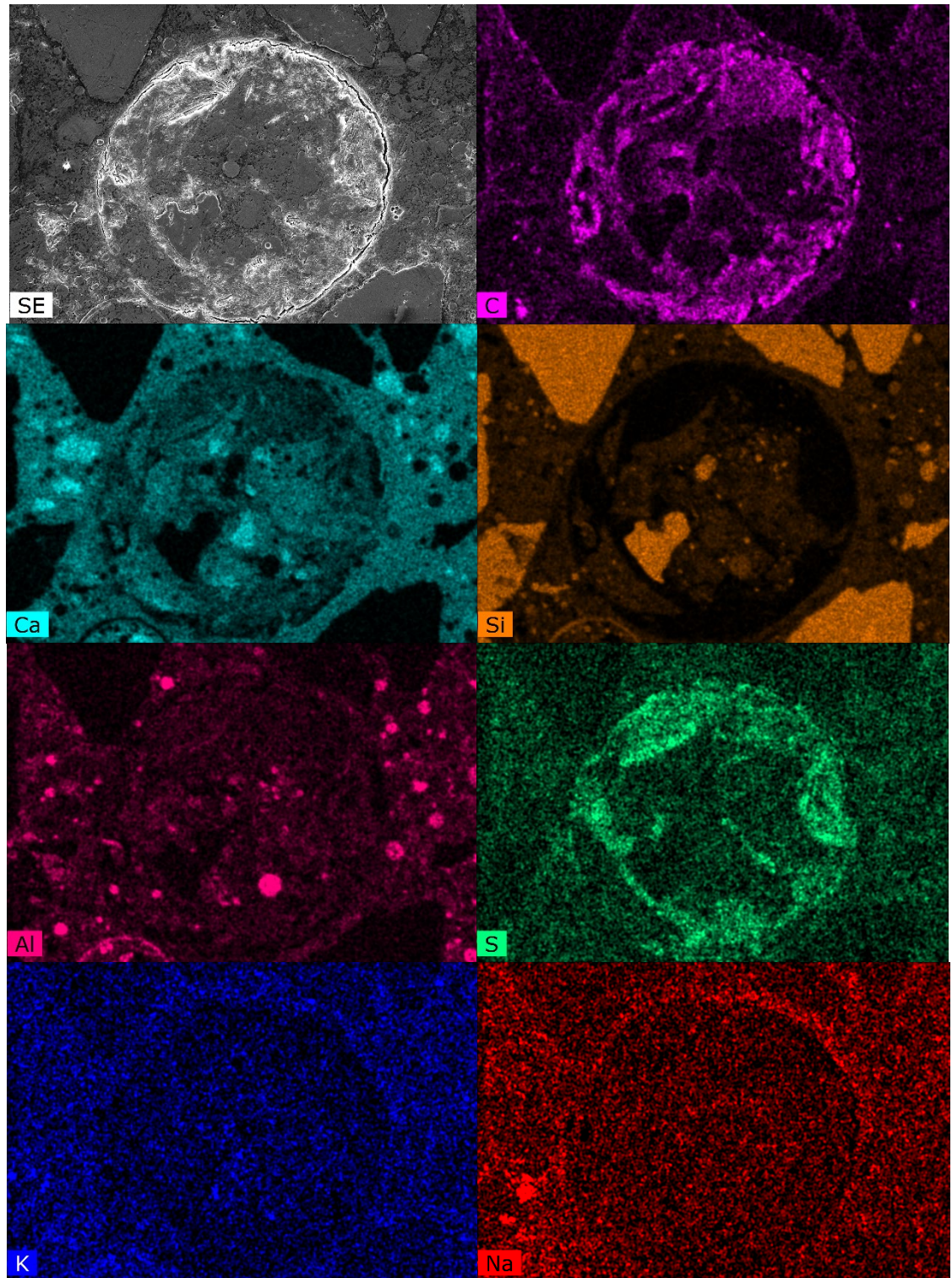


Figure 9.21 Elemental mapping of C, Ca, Si, Al, S, K, Na of C2-S4N1-FR mortar cured at 90°C for 12 hours and subsequently stored in saturated lime water for 500 days

9.4 Electrical resistivity

The Nyquist plots obtained for C1 and C2 mortars by electrochemical impedance spectroscopy (EIS) are provided in Figure 9.22 and Figure 9.23. The non-expansive systems (C1-S4N1-FR, C2-S4N1-FR) with FA showed impedance arcs many folds larger than the highly expansive systems (C1-S4N1-F0, C2-S4N1-F0). The consumption of CH by pozzolanic reactivity to form C-S-H in FA (Section 9.2 Evolution of ionic pore solution characteristics and crystalline phases) resulted in highly impermeable characteristics of FA mortars due to pore refinement (Thomas 2013a). The impermeability likely restricted migration of the pore solution. Similar results of increased electrical impedance in FA added cement systems were obtained by Montemor et al. (1993) and particularly in heat-cured systems by Dhandapani, Scrivener & Santhanam (2017). As the migration of ions within the microstructure was reduced, low ettringite precipitation resulted and occurred DEF was not potent enough to cause expansion. Figure 9.24 shows that as the electrical resistivity increased, the DEF expansion decreased drastically. The mortars that suffered from deleterious DEF had the lowest resistivity values (6.9 to 7.3 ohm.m), whereas the FA-added mortars – despite heat-curing – offered tremendous resistivity (40 to 51 ohm.m). Furthermore, the heat-cured FA-added mortars had much higher resistivity than the reference ambient-cured mortars (in the range 15 to 23 ohm.m) without FA.

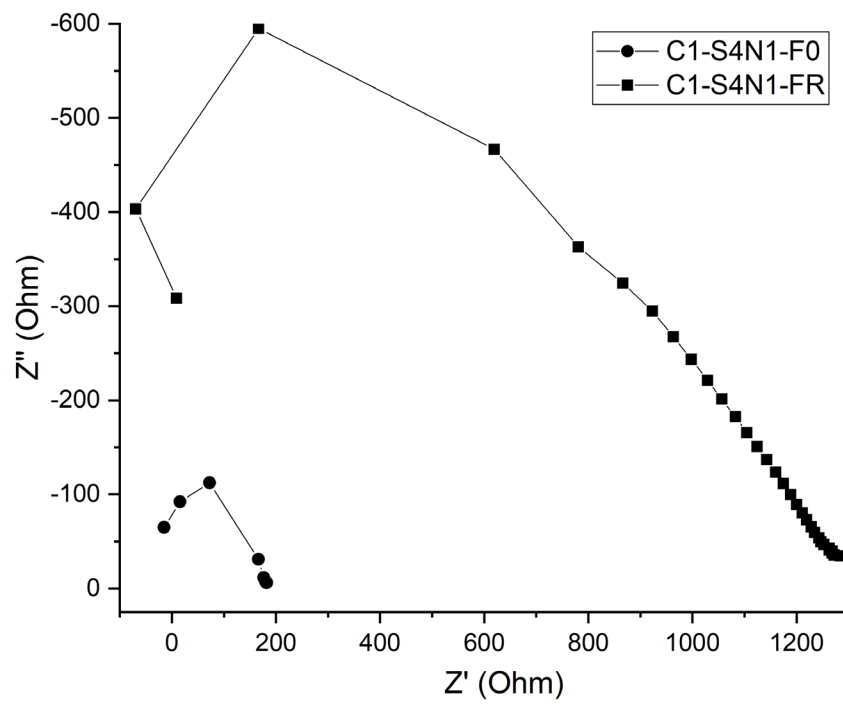


Figure 9.22 Nyquist plots of C1-S4N1 mortars showing the effect of FA– 500 days

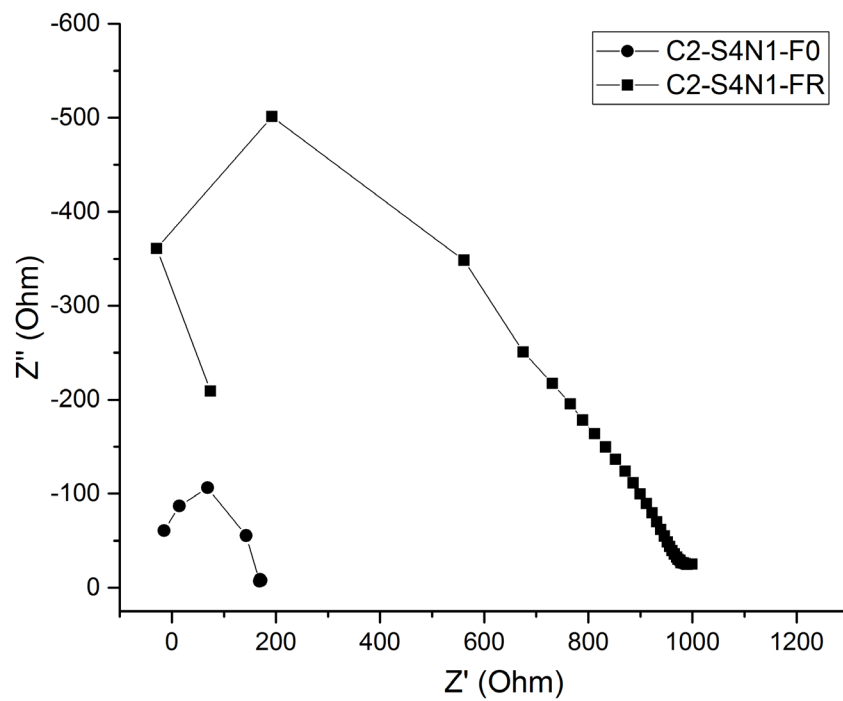


Figure 9.23 Nyquist plots of C2-S4N1 mortars showing the effect of FA– 500 days

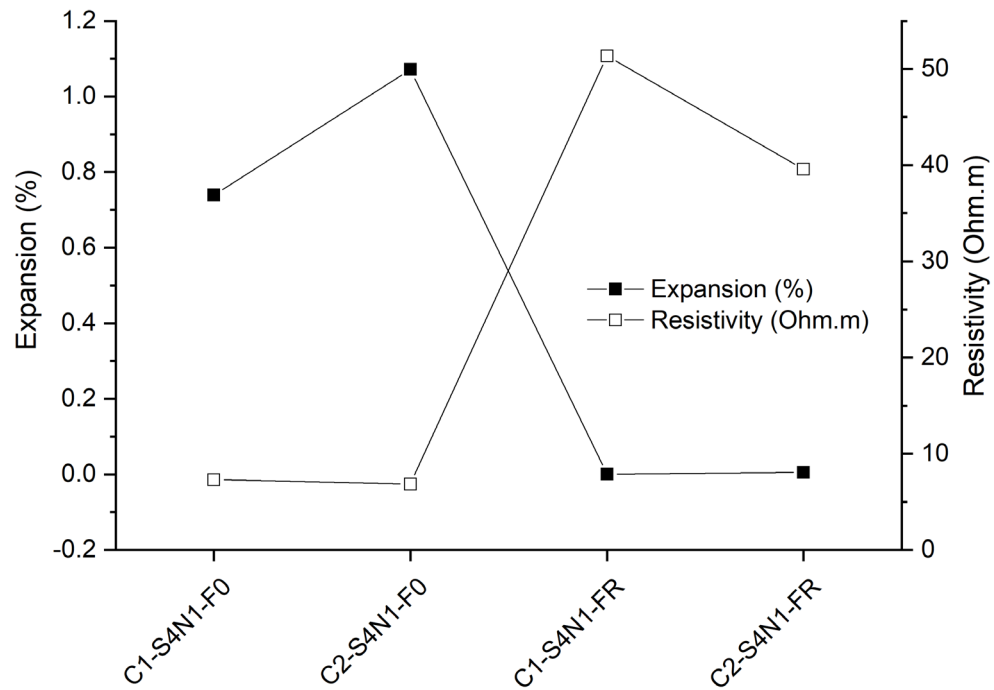


Figure 9.24 Impact of FA in heat-cured C1-S4N1, C2-S4N1 mortars - electrical resistivity and expansion comparison

9.5 Summary

The complete elimination of deleterious expansive DEF was achieved by incorporating FA in the most DEF-vulnerable cement systems, despite exposure to heat-curing at 90°C for 12 hours. The quantity of DEF in the FA-added mortars was much lower than the expansive mortars and can be labelled as non-deleterious. The FA addition partly diluted the cement systems and the sulphate ion availability in the pore solution relatively was less than in the DEF-expansive mortars. In the solid phases, increased sulphate adsorption in the C-S-H reduced the sulphates available for ettringite precipitation. The non-expansive monosulphate formation was favoured over ettringite. The improved electrical resistivity is indicative of pore-structure refinement, which restricted the migration of ions resulted in low local accumulation of the reactants needed to precipitate ettringite. Thus, in many ways adding FA to heat-cured mortars eliminated the detrimental effects of DEF. Although for heat-cured GP cement systems an increase in the SO_3 content or the

combined SO_3 , $\text{Na}_2\text{O}_{\text{eq}}$ content raises the potential of DEF expansion, this is mitigated by the addition of FA. Hence, for standard concretes containing standard GP cements conforming to standard specifications coupled with the addition of FA, the likelihood of DEF is low.

The results obtained in this research work support the recommendation of incorporating FA into heat- or steam-cured precast concrete to eliminate deleterious DEF.

Chapter 10 Conclusions and Recommendations

In this thesis, the influence of different cement composition and various heat-curing regimes on DEF has been investigated and discussed with regard to linear expansion, mass gain, pore solution chemistry, ettringite precipitation – mechanism, quantity & location and other microstructural changes. Further, the role of fly ash in mitigating deleterious DEF also investigated. This chapter summarises the major experimental observations and findings. The last section of this chapter presents recommendations for future works based on the limitations of this research.

10.1 Influence of cement composition

To understand the DEF susceptibility in Australian standard GP cements, two locally sourced cements (of different C_3A content) with unaltered sulphate, alkali were compared with modified sulphate (4-6%), alkali (1-1.5%) and combined sulphate (4%) + alkali (1%).

10.1.1 Standard GP cement systems

- DEF precipitation was observed in heat-cured standard GP cement systems containing low and high C_3A content cements C1 and C2) respectively, without resulting in the significant expansion ($< 0.2\%$), mass gain ($< 2\%$) (refer Section 2.6 for threshold values). The observed expansion and mass gain were similar for both the ambient cured reference mortars and the heat-cured mortars. Deleterious DEF is expected to be observed in the form of ettringite band at ITZ, which was absent in these standard GP cements. Significant reduction in the electrical resistivity was observed in heat-cured standard cement systems compared to ambient cured reference mortars, which is an indication of a change in the porous microstructure due to heat curing rather than DEF.

- Based on these observations, the DEF observed in standard GP cements complying with Australian standard compositions ($\text{SO}_3 < 3.5 \text{ wt\%}$; $\text{Na}_2\text{O}_{\text{eq}} < 0.6 \text{ wt\%}$) may be classified as innocuous or non-deleterious. These results are reflected for curing temperatures 50-90°C, curing duration 8-12 hours and pre-cure time 0-4 hours.

10.1.2 Sulphate modified cement systems

- Despite increasing the sulphate content in the range 4 to 6% for both C1 and C2 cement mortars, heat-curing at 90°C for 8 hours did not result in significant expansion or mass gain. Expansion and mass gain for these mortars was found to be comparable to standard GP cement mortar systems.
- The non-expansive behaviour of higher sulphate cement systems is due to the shift in the molar ratio of ($\text{SO}_3/\text{Al}_2\text{O}_3$) above 1.2% (for 5 to 6% SO_3), suggesting stoichiometrically less alumina available for reaction with sulphates resulting in less ettringite precipitation. This holds good for cements with different alumina content.
- The non-expansive nature of the 4% sulphate mix was limited to 8-hour heat-curing only. At 12-hour heat-curing 4% sulphate systems gave deleterious DEF expansion and mass gain in both cements. The C2 mortars with 4% sulphate expanded more than C1 under 12 hours heat-curing is due to the higher availability of C_3A in C2 cements.
- The obtained results overturn the fallacy that cement with higher sulphate above 4% is always susceptible to deleterious DEF, when heat-cured.

10.1.3 Alkali modified cement systems

- Similar to sulphate modified systems, increasing the alkali content of the cements in the mortar mixes to 1.0, and 1.5% did not result in DEF expansion. The obtained expansion and mass gain were below the threshold value designated as deleterious. Moreover, in some cases the obtained expansion and mass gain were well below the values obtained for reference ambient cured specimens, further stressing that elevated alkali alone is not a cause deleterious DEF.
- Non-expansive nature of alkali increased cements is due to the lower ettringite precipitation as a result of low sulphate content in the cements (~ C1-2.3% to C2-3.0%) and increased solubility of the sulphate which reduces the propensity for ettringite to precipitate.

10.1.4 Sulphate and alkali modified cements

- Significant DEF expansion ($> 0.2\%$) resulted when cements were modified to have sulphate 4% + alkali 1% and were cured in the range 80-90°C for 8 hours. C2 mortars started to show expansion at 80°C, but C1 only showed expansion at 90°C. The difference is due to the lower C_3A in C1 (7.4%) than C2 (11.2%). Also, the induction period to show expansion seems to be impacted by C_3A content as C1 mortars had much longer induction period than C2 mortars.
- The increased alkali content in elevated sulphate content cement binders (4% sulphate + 1% alkali) coupled with elevated temperature heat-curing (80 to 90°C) increases the early age sulphate dissolution. The subsequent reduction in temperature post heat curing results in precipitation of the sulphate and hence an increase in the proportion of DEF leading to deleterious expansion.
- The sulphate 4% + alkali 1% cements systems offered low resistivity with the increase of heat-curing temperature compared to other cement systems, indicating

along with curing temperature, the sulphate and alkali modification plays a role in increasing the porosity of cement systems. This is a result of accelerated hydration at an elevated temperature where higher alkali content plays a vital role in increasing the dissolution of clinker phases.

- The above observations suggest pessimum cement composition required to cause expansive DEF upon heat-curing is sulphate 4% + alkali 1%.

10.2 Influence of heat-curing regimes

To understand DEF susceptibility due to heat-curing, various parameters in the heat-curing process are considered for the study, such as curing temperature 50-90°C, curing duration 8-12 hours and pre-cure time 4-0 hours. Ambient cured (23°C) specimens were used as a reference.

10.2.1 Heat-curing temperature

- Elevated temperature curing accelerates hydration reactions. Overlapping hydration of C₃S and C₃A clinker phases and decomposition of primary ettringite was observed even at 55°C. For ambient cured systems, the formation of stable primary ettringite during the plastic stage of the binder hydration results in non-deleterious ettringite formation.
- Curing temperature 50-90°C did not result in expansive DEF in standard cement systems, as discussed in Section 10.1.1. However, at elevated temperature curing, cavities, cracks and two-tone C-S-H were observed. The increased porosity resulted in heat-cured samples indicated by lower resistivity values.
- Despite the changes in microstructure, at curing temperatures, 50-70°C cementitious systems did not experience expansive DEF, even in the pessimum DEF cement composition 4% sulphate + 1% alkali.

- Although DEF was observed in parallel cured paste specimens for all heat-curing regimes, only samples with the pessimum composition (4% sulphate + 1% alkali) cured at 80 or 90°C showed expansive DEF.

10.2.2 Duration of heat-curing

- Increase in duration of heat-curing from 8 to 12 hours did not cause DEF expansion in standard GP cement systems, as discussed in 10.1.1. However, increasing the curing time has significance in converting non-expansive DEF to expansive DEF in 4% sulphate cement systems. In the pessimum DEF cement composition 4% sulphate + 1% alkali, increasing the heat-curing duration increased the degree of expansion in the range 0.7 to 1.0% and mass gain in the range 2 to 2.5%; both are well above the threshold limit for deleterious DEF as discussed earlier.
- Curing at 90°C for 12 hours, increased the dissolution of alkalis and sulphates in the pore solution in the early age hydration. The cement systems resulted in expansive DEF had much higher sulphate and alkali ion content in the pore solution compared to the non-expansive DEF ones. Similarly, the quantity of ettringite precipitation was significantly higher in the specimens experiencing expansive DEF than the non-expansive specimens.
- Compared to 8 hours curing at 90°C, 12 hours heat-curing reduces the electrical resistivity further, indicating the higher porosity in the microstructure through an increase in the number of conduction pathways. The higher porosity aids the transportation of ions within the microstructure. Concurrently, ettringite is observed in the ITZ in cementitious systems experiencing expansive DEF, suggesting that the increase in porosity is associated with the formation of

microstructural cracks. Since the results link localised precipitation of ettringite with expansion, this research supports the crystal growth theory of expansion.

- In summary, heat-curing at 90°C provides the base heat-curing condition for DEF to occur by decomposing the early ettringite. Increasing the curing duration aggravates the problem by increasing the porosity of the microstructure.

10.2.3 Pre-cure time

- Reducing the pre-cure time from 4 to 0 consistently increased the DEF expansion and mass gain in C2 chemically modified mortars but not in C1 mortars. However, the electrical resistivity found to be reduced further when compared to 4 hour procured samples.
- The role of pre-cure time in expansive DEF was not clear with available results.

10.3 Role of fly ash in mitigating deleterious DEF

Fly ash incorporated in the pessimum DEF cement composition mixes, i.e. mixes made with cements containing 4% sulphate + 1% alkali. 25% fly ash to the weight of cement was added in two ways with and without altering the total cementitious content of the mixes. Complete elimination of deleterious DEF by fly ash was observed, due to the following reasons,

- Alumina content from fly ash diluted the $\text{SO}_3/\text{Al}_2\text{O}_3$ ratio resulted in low precipitation of ettringite and thus eliminating the expansion associated with it.
- The pozzolanic reaction of amorphous silica present in fly ash consumed portlandite to form C-S-H, thereby increasing the impermeability of the microstructure. The increased impermeability was confirmed by a significant increase in the electrical resistivity of the mortars containing FA blended cement.

- The significant increase in impermeability hindered the transportation of ions, especially sulphate ions for the precipitation of ettringite. The precipitation of low sulphate demanding AFm phases resulted instead, thus reducing the potential for the formation of expansive DEF.

10.4 Concluding remarks

From Sections 10.1 and 10.2, it is clear that possible occurrence of expansive DEF is due to the overlapping of cement composition and heat-curing parameters. Heat-curing forms the basis for DEF by decomposing primary ettringite. Then, during storage in lime-saturated water, the alkalinity of pore solution reduced and thus DEF was favoured. However, whether the DEF is expansive or not very much depends on the pessimum cement composition governed by sulphate, alkali and alumina content.

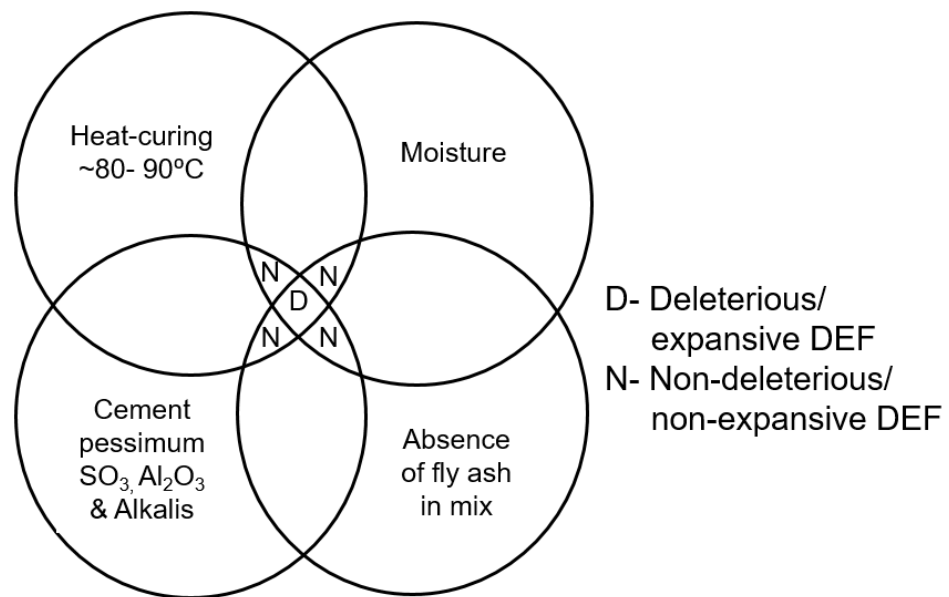


Figure 10.1 Synergistic interaction of factors leading to deleterious DEF

The potential for deleterious DEF occurring is an amalgamation of various factors, as summarised in **Error! Reference source not found..** For deleterious DEF to occur, these pessimum conditions must also occur during heat-curing. Eliminating or controlling any

one of these factors which form these pessimum conditions reduces the potential for the formation of deleterious DEF. Incorporating supplementary cementitious materials (SCMs) such as fly ash in blended cements further minimises the potential for deleterious DEF and hence can be an effective, practical solution to overcome the risk of DEF.

Precast concretes made with mixes containing cements that comply with Australian standards (which have low sulphate and alkali content) along with the addition of FA are more likely to be deleterious DEF free irrespective of heat-curing regimes.

10.5 Recommendations for future studies

1. This study was limited to the investigation of mortars containing elevated alkali and sulphate contents, and it identified a pessimum set of conditions for deleterious DEF. In order to confirm that these conditions are the source of deleterious DEF in concretes, the next step in the investigation is to extend the study to include concrete specimens, focusing on studying cementitious systems and heat-curing regimes impact on physical properties at a macroscale level. Considering the local commercial impact, a detailed study with Australian cements and aggregates would add value to the Australian precast industry, cement manufacturers and the scientific community.
2. The current study found a reduction in alkalinity due to storage in saturated lime water favoured DEF precipitation. However, not all the concrete structures have direct contact with water to create a situation to favour a reduction in alkalinity. Hence future studies should explore the feasibilities of concrete structures encountering alkalinity reduction without direct contact with water as it may increase its susceptibility to deleterious DEF. Reactive aggregates in concrete are one such possibility as it consumes alkalis for alkali-silica reaction (ASR), thereby

may create a lower alkaline environment for DEF precipitation. Hence future studies explore the impact of ASR and DEF occurring together in concrete, by using reactive aggregates and exposing it to heat-curing.

3. In this study, although limestone added cement (C1) upon heat-curing crystallised non-expansive AFm phases such as monocarbonates and hemicarbonates contributing to the lower degree of expansion, the role of limestone is not explicitly clear as C1 has lower C_3A compared to C2. So the future study may systematically study the impact of limestone by varying its percentage in cement.
4. The current study has shown a relationship between reduction in resistivity and microstructural changes contributing to DEF. However, it was limited to one age at 500 days. The future study shall track the resistivity from just after heat-curing to later age hydration, to find a relation between changes in resistivity with respect to ettringite reformation. Further, this should be studied along with pore size changes to find a correlation between ettringite reformation, pore size assemblage and resistivity changes.
5. The current study is limited to DEF occurring in the heat-cured cementitious system. Future works may consider studying the combination of DEF and internal sulphate attack effects in cementitious systems by storing the heat-cured specimens in sulphate solutions instead of lime-saturated water.
6. In the current study, fly ash was used to mitigate deleterious DEF. As globally coal power plants may reduce production or shutdown in future, exploring other SCMs for deterioration mitigations will be useful. So the future studies may consider calcined clay as an alternative SCMs for DEF mitigation.

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