Microstructure and Thermal Stability of Ettringite under Microwave Heating

by

Shuqiong Luo

A thesis submitted for the degree of

Doctor of Philosophy

of

University College London

Department of Civil, Environmental and Geomatic Engineering
University College London

November 2019
I, Shuqiong Luo, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.
Abstract

Microwave heating is being increasingly recognised as a potential, alternative low-carbon curing technique for precast concrete industry. However, when microwave heating is applied to curing concrete, in addition to its thermal effect which can effectively heat up concrete, its non-thermal effect may result in the modification to the microstructure of hydrated products, leading to the potential concerns over the microstructure and thermal stability of ettringite. As a result, the maximum temperature to be adopted in microwave curing of concrete is uncertain as this is normally determined by the thermal stability of ettringite in order to avoid delayed ettringite formation (DEF).

This thesis, thus, investigates the microstructure and thermal stability of different ettringites, including pure ettringite, Fe-ettringite, Cr-ettringite, Mn-ettringite as well as the ettringites formed in both Portland cement and calcium sulfoaluminate cement, under both microwave and conventional heating at 60, 70 and 80°C using XRD, TEM, SEM, TG, XPS and NMR.

The results show that the microwave curing does change the microstructure of ettringite slightly due to the loss of reversibly exchangeable water molecules held in its structure compared to the conventional heating which is possibly caused by the non-thermal effects of microwaves, leading to a reduction in thermal stability. However, the differences in both the microstructure and thermal stability are subtle. The ettringites heated by microwaves begin to decompose at 70°C to form monosulfate and gypsum or even bassanite in some cases, which is similar to those heated by conventional heating. Therefore, it is considered by the author
that the maximum temperature as recommended in the current standards for accelerated curing could be used in microwave curing, although caution should be taken when additional sulfate source is potentially available internally due to the slightly reduced thermal stability of ettringite under microwave curing.
Impact statement

Precast concrete has become widely used in the construction industry but is energy intensive and time-consuming. Microwave heating, due to its volumetric heating nature, which can reduce both the curing duration and energy consumption, is being increasingly recognised as a potential, alternative low-carbon curing technique for precast concrete industry. However, similar to steam curing, the maximum curing temperature has to be determined by the thermal stability of ettringite in order to avoid delayed ettringite formation (DEF) as this can cause cracking and durability issues of concrete products. When microwave heating is applied to curing precast concrete, in addition to its thermal effect which can effectively heat up concrete, its non-thermal effect may lead to the modification to the microstructure of hydrated products. As a result, there are some concerns as to whether the microstructure and, thus, the thermal stability of ettringite could be affected by microwaves. Consequently, whether the currently adopted limit on the maximum curing temperature in the existing standards could still be applied in microwave curing is questionable. To address this issue, this study has investigated in detail the microstructure and thermal stability of different ettringites, including pure ettringite, Fe-ettringite, Cr-ettringite, Mn-ettringite as well as the ettringite formed in cements pastes under both microwave and conventional heating at 60, 70 and 80°C. The results show that the microwave curing does change the microstructure of ettringite slightly due to the loss of reversibly exchangeable water molecules held in its structure compared to conventional heating which is possibly caused by the non-thermal effects of microwave, leading to a reduction in its thermal stability.
The study has both academic and societal impacts. Firstly, it provides data that are crucial to the fundamental understanding of how microwaves interact with ettringite crystals. Secondly, it will lay a good foundation on the development of a novel microwave curing technique for precast concrete industry in the future. It is found that microwave curing does change the microstructure of ettringite slightly due to the non-thermal effects. However, the differences in both the microstructure and thermal stability are subtle. The ettringites heated by microwaves begin to decompose at 70°C to form monosulfate and gypsum or even bassanite in some cases, which is similar to those heated by conventional heating. Therefore, the maximum temperature as recommended in the current standards for accelerated curing could be used in microwave curing. Overall, the outcome from this research project will not only benefit the UK and other countries by making effective contributions to the ultimate development of a rapid, low-carbon curing technique for precast concrete industry, but will also benefit human society to build a sustainable world in the future. Furthermore, this project will also make contribution to the UK Government’s ambition to have buildings to be constructed 50% faster, 33% cheaper and with half the lifetime carbon emissions by 2025 through the ultimate development of a more efficient and low-carbon microwave-based concrete curing technique.
Acknowledgement

First of all, I would like to express my deepest gratitude to my supervisors, Prof Yun Bai, Dr Judith Zhou and Prof Neil Milestone, for their support, invaluable advice and guidance through this research. In particular, I want to thank Prof Bai for offering me the opportunity to do a PhD at UCL, during which I have learned how to do independent research work. Thanks to Dr Judith Zhou who is like a sweet sister, for encouraging me whenever I was in trouble and helping me a lot. Many thanks to Prof Milestone for his prompt feedback on my research questions and patience on revising the thesis.

I am grateful to Dr Sam Ghazizadeh, Dr Shi Shi, Dr Min Liu, Dr Yongliang Liu and Mr Lunqiao Xiong for their valuable comments on my writing.

I would like to extend my huge gratitude to Prof Xuemao Guan from Henan Polytechnic University (HPU), Jiaozuo, China, for his great financial support at the hardest but critical time as well as allowing me to use all the analytical equipments in the School of Materials and Science engineering. Many thanks to my colleagues in HPU, Dr Guangxin Fan, Dr Haibo Zhang and Dr Wenpeng Yang, and my student Jindan Chang, for their tremendous help on XRD, SEM and TEM characterisation.

Many thanks go to Dr Colum McCague for help obtaining Portland cement clinker with high content of $\text{C}_3\text{A}$. Many thanks go to Dr Hongbo Tan and Dr Xiao Chen in Wuhan University of Technology for their great support on XPS and NMR characterisation. Great thanks are also given to Dr Suguo Huo from London
Centre for Nanotechnology at UCL for help on SEM characterisation, Mr Jian Guo from the Chemistry Department at UCL for the valuable advice on XPS.

Secondly, I would like to acknowledge all the support from the Department of Civil, Environmental and Geomatic Engineering (CEGE) at UCL. A big ‘Thank you’ goes to Mr Warren Gaynor, Mr Raman Mangabhai and Mr Ian Seaton for their support in the laboratory. I would like to give sincere gratification to Sarah Davies for her strong support on every aspect during my study in CEGE. Many thanks to all the members of Advanced & Innovative Materials (AIM) Group in CEGE at UCL for their support and encouragement.

Many thanks go to Dr Matthias Fabian for his support and assistant to the application of optical fibre sensor.

Thirdly, I also want to thank all my dearest friends who always cheer me up and help me fight through obstacles. Special thanks are given to Ms Limin Lu, Prof Shuhua Liu, Prof Zuquan Jin, Dr Tongsheng Zhang, Dr Guowen Sun, Dr Shi Shi, Dr Jun Ren, Dr Min Liu, Mr Shaoyong Yu, Mr Biao Song, Miss Fan Huang and Miss Like Xu for sharing ups and downs in the past five years, Ms Na Xu and Ms Dongxia Xu for financial support and help.

Last but not least, my deepest love goes to my beloved family. I am greatly indebted to my husband who always gave strong support whenever whatever happened during those hard years, my lovely daughter, Luolan Yang, who gave me a driving force whenever I felt frustrated and hopeless. Huge gratitude goes to my parents-in-law who took good care of my daughter and the family, allowing
me to concentrate on my research work. I am also indebted to my parents for their unconditional love, my two younger sisters who looked after my parents well in China. My aunt, Ms Xuanmin Ma gave me so much support, but sadly she is suffering from Alzheimer’s disease. Without these, I cannot imagine how I can keep going on the research journey.

This project is sponsored by the China Scholarship Council (CSC) and UCL.
# Table of Contents

Abstract ............................................................................................................................................. I
Impact statement ........................................................................................................................... III
Acknowledgement .......................................................................................................................... V
Table of Contents ........................................................................................................................... VIII
List of Tables .................................................................................................................................... XV
List of Figures ................................................................................................................................... XVI
List of Abbreviations ....................................................................................................................... XXIV
Chapter 1 Introduction .................................................................................................................... 1
  1.1 Research background .............................................................................................................. 1
  1.2 Aims and objectives ............................................................................................................... 4
  1.3 Outline of the thesis .............................................................................................................. 5
Chapter 2 Literature Review .......................................................................................................... 7
  2.1 Steam curing in precast concrete .......................................................................................... 7
    2.1.1 Introduction .................................................................................................................... 7
    2.1.2 Steam curing process ..................................................................................................... 8
    2.1.3 Hydration of cement under steam curing ........................................................................ 9
    2.1.4 Maximum curing temperature limits ............................................................................. 12
    2.1.5 Issues arising from steam curing .................................................................................. 14
  2.2 Ettringite ............................................................................................................................... 15
    2.2.1 Introduction .................................................................................................................... 15
    2.2.2 Structure ........................................................................................................................ 16
    2.2.3 Morphology .................................................................................................................... 19
    2.2.4 Thermal stability ............................................................................................................ 21
      2.2.4.1 Effect of temperature ............................................................................................... 22
3.3.1 Synthesis of ettringite ................................................................. 69
3.3.2 Calcium sulfoaluminate cement ................................................. 71
3.3.3 Portland cement clinker ........................................................... 72
3.4 Heating treatment ...................................................................... 73
  3.4.1 Microwave heating ................................................................. 73
  3.4.2 Conventional heating ............................................................. 77
3.5 Sample preparation ................................................................... 78
  3.5.1 Pure ettringite synthesised under heat treatment .................... 78
  3.5.2 Synthetic pure ettringite and metal ion doped ettringite exposed to
       heat treatment ........................................................................... 79
  3.5.3 Cement system subjected to heat treatment ......................... 80
  3.5.4 Measurement of pH value ...................................................... 81
  3.5.5 Measurement of dielectric properties .................................... 82
3.6 Characterisation methods ........................................................... 83
  3.6.1 X-ray diffraction ................................................................. 84
  3.6.2 Transmission electron microscopy ........................................ 84
  3.6.3 Scanning electron microscopy ............................................... 86
  3.6.4 Thermogravimetric analysis ................................................ 86
  3.6.5 X-ray photoelectron spectroscopy ....................................... 88
  3.6.6 Solid-state nuclear magnetic resonance spectroscopy ............ 89
Chapter 4 Microstructure and Thermal Stability of Ettringite Synthesised under
  Microwave Heating .................................................................... 91
  4.1 Introduction ............................................................................. 91
  4.2 Sample preparation ............................................................... 92
  4.3 Results ................................................................................... 94
    4.3.1 Effect of microwave heating on the crystalline structure of ettringite . 94
4.3.2 Effect of microwave heating on the morphology of ettringite .......... 104
4.3.3 Effect of microwave heating on the thermal stability of ettringite ..... 106
4.3.4 Effect of microwave heating on the binding energy of elements in ettringite.................................................................................. 109
4.3.5 Effect of microwave heating on $^{27}$Al nucleus in ettringite .......... 112
4.4 Discussion .................................................................................. 113
4.5 Conclusions .............................................................................. 117
Chapter 5 Microstructure and Thermal Stability of Synthetic Ettringite and Metal Ion-doped Ettringite Exposed to Microwave Heating .................. 119
5.1 Introduction .................................................................................. 119
5.2 Microstructure and thermal stability of synthetic ettringite exposed to microwave heating................................................................. 121
  5.2.1 Sample preparation .................................................................. 121
  5.2.2 Effect of microwave heating on the crystalline structure of synthetic ettringite........................................................................ 122
  5.2.3 Effect of microwave heating on the crystalline morphology of synthetic ettringite........................................................................ 129
  5.2.4 Effect of microwave heating on the thermal stability of synthetic ettringite............................................................................. 130
  5.2.5 Effect of microwave heating on the binding energy of elements in synthetic ettringite................................................................. 133
  5.2.6 Effect of microwave heating on the $^{27}$Al NMR nucleus in synthetic ettringite............................................................................. 135
  5.2.7 Discussion .................................................................................. 137
5.3 Microstructure and thermal stability of metal ion-doped ettringite exposed to microwave heating....................................................... 141
5.3.1 Sample preparation ................................................................. 141
5.3.2 Effect of microwave heating on the crystal structure of synthetic Fe-
ettringite, Cr-ettringite and Mn-ettringite ........................................ 143
5.3.3 Effect of microwave heating on the morphology synthetic Fe-
ettringite, Cr-ettringite and Mn-ettringite ........................................ 154
5.3.4 Effect of microwave heating on the thermal stability of synthetic Fe-
ettringite, Cr-ettringite and Mn-ettringite ........................................ 158
5.3.5 Effect of microwave heating on the binding energy of elements in
synthetic Fe-ettringite, Cr-ettringite and Mn-ettringite ....................... 166
5.3.6 Effect of microwave heating on the $^{27}$Al nucleus in synthetic Fe-
ettringite, Cr-ettringite and Mn-ettringite ........................................ 171
5.3.7 Discussion ............................................................................... 174
5.4 Conclusions ............................................................................... 177

Chapter 6 Microstructure and Thermal Stability of Ettringite in Cement Systems
Subjected to Microwave Curing ............................................................ 179

6.1 Introduction ............................................................................... 179
6.2 Microstructure and thermal stability of ettringite in CSA paste subjected to
microwave curing ............................................................................. 180
6.2.1 Sample preparation ................................................................. 180
6.2.2 Effect of microwave curing on the crystalline structure of ettringite
formed in CSA paste ........................................................................ 181
6.2.3 Effect of microwave curing on the morphology of ettringite formed in
CSA paste ....................................................................................... 186
6.2.4 Effect of microwave curing on the thermal stability of ettringite formed
in CSA paste ................................................................................... 188
6.2.5 Discussion ............................................................................... 190
6.3 Microstructure and thermal stability of ettringite in PC paste subjected to microwave curing

6.3.1 Sample preparation

6.3.2 Effect of microwave curing on the crystalline structure of ettringite formed in PC paste

6.3.3 Effect of microwave curing on the morphology of ettringite formed in PC paste

6.3.4 Effect of microwave curing on the thermal stability of ettringite formed in PC paste

6.3.5 Discussion

6.4 Conclusions

Chapter 7 Conclusions and Recommendations for Future Work

7.1 Introduction

7.2 Conclusions

7.2.1 Microstructure and thermal stability of the ettringite synthesised under microwave heating

7.2.2 Microstructure and thermal stability of the synthetic ettringite and metal ion-doped ettringite exposed to microwave heating

7.2.3 Microstructure and thermal stability of ettringite formed in cement systems subjected to microwave curing

7.3 Recommendations for future work

7.3.1 Modelling the kinetic process of the decomposition of ettringite under microwave heating

7.3.2 Influence of pressure and humidity on the thermal stability of ettringite under microwave heating
7.3.3 Influence of different pH values on the thermal stability of ettringite under microwave heating .........................................................212

7.3.4 Thermal stability of ettringite in concretes containing various additions under microwave heating .........................................................212

References .................................................................213
List of Tables

Table 2.1 Hydration characteristics of PC constituents (Taylor, 1997, Hewlett and Liska, 2019) .................................................................................................................. 10

Table 2.2 Threshold curing temperatures for precast concrete (Hwang et al., 2012).......................................................................................................................... 13

Table 2.3 Summary of decomposition temperature of ettringite under different conditions ........................................................................................................... 32

Table 2.4 Dielectric constant of concrete components (Khoylou et al., 2014) ... 61

Table 3.1 Mineral compositions of CSA clinker (wt%) ........................................ 71

Table 3.2 Mix proportion of CSA paste ..................................................................... 72

Table 3.3 Mineral phases of the clinker of PC with high C₃A ................................ 72

Table 3.4 Mix proportion of PC paste ......................................................................... 73

Table 3.5 pH values of samples .................................................................................. 82

Table 3.6 Dielectric properties of relevant materials ............................................... 83

Table 4.1 Details of ettringite synthesised under different conditions ........... 93

Table 5.1 Details of synthetic ettringite exposed to microwave heating .......... 121

Table 5.2 Details of synthetic Fe-ettringite exposed to microwave heating ....... 141

Table 5.3 Details of Cr-ettringite exposed to microwave heating ..................... 142

Table 5.4 Details of Mn-ettringite exposed to microwave heating ................. 142

Table 6.1 Details of CSA pastes subjected to microwave and conventional curing at 60, 70 and 80°C .......................................................... 181

Table 6.2 Details of PC pastes subjected to microwave and conventional curing at 60, 70 and 80°C .......................................................... 194
List of Figures

Figure 2.1 Typical low-pressure steam-curing cycle (Smith, 2013)..........................9

Figure 2.2 Diagram of ettringite structure (Taylor, 1997). (I) Part of a single column in (1120 projection; A=Al, C=Ca, H=O of an OH group, W=O of an H2O molecule. Hydrogen atoms are omitted, as are the H2O molecules attached to those calcium atoms lying in the central vertical line of the figure. (II) Projection on the ab-plane, showing columns (large circles) and channels (small circles); the unit cell, with a=b =1.123 nm, is outlined. .................................................................17

Figure 2.3 SEM micrograph of synthetic ettringite (Shimada and Young, 2004) .................................................................................................................................19

Figure 2.4 Six-sided needle-like morphology of ettringite grown in solution without additives (Cody et al., 2001).................................................................20

Figure 2.5 Micrograph of colloidal ettringite in the presence of lime, 72 hours, 6000× (Mehta, 1973).................................................................................................20

Figure 2.6 Massive ettringite on aggregate surface and ball ettringite in pores (Tosun and Baradan, 2010).................................................................................21

Figure 2.7 XRD patterns of ettringite samples conditioned at 50°C under different R. H. (Baquerizo et al., 2016).................................................................25

Figure 2.8 Data for decomposition of ettringite showing convergence of weight loss on a product containing 10-13 H2O (Zhou and Glasser, 2001)..............26

Figure 2.9 Data for the decomposition of ettringite (Zhou and Glasser, 2001)..27

Figure 2.10 Schematic illustration of the formation of reaction products and the reduction of the volume of pore space with time in a Portland cement paste (Locher, Richartz, and Sprung, 1976).................................................................37
Figure 2.11 Characteristic crystal morphologies of (a) Ettringite (AFt) and (b) monosulfate (AFm) (Bothe Jr and Brown, 1998) .................................................. 38

Figure 2.12 Deteriorated precast concrete channel section (Ozol and Strand, 2000) .................................................................................................................. 41

Figure 2.13 Fine aggregate particle rimmed with fibrous ettringite, and ettringite-filled cracks in the paste (Ozol and Strand, 2000) .................................................. 41

Figure 2.14 Electromagnetic wave: A ‘vertically polarized’ electromagnetic wave with wavelength \( \lambda \) has its electric field vector \( \mathbf{E} \) (red) oscillating in the vertical direction. The magnetic field \( \mathbf{B} \) is always at right angles to it (blue), and both are perpendicular to the direction of propagation (z) (Metaxas and Meredith, 1983) ........................................................................................................ 51

Figure 2.15 Mechanism of microwave curing (Makul et al., 2009) .......................... 53

Figure 3.1 Flow chart of overall research programme .............................................. 68

Figure 3.2 The diagram of the custom-made microwave oven ............................... 74

Figure 3.3 Custom-made MHTO350 microwave oven with mixing apparatus ..75

Figure 3.4 Custom-made SS500 microwave oven .................................................. 76

Figure 3.5 Optical fibres used for a 25cm×25cm×25cm (a) and a 50cm×50cm×50cm (b) custom-made mould respectively ........................................... 77

Figure 3.6 Water bath for synthesising ettringite ................................................... 78

Figure 3.7 Isothermal conduction calorimeter ........................................................ 78

Figure 3.8 25cm×25cm×25cm mould .................................................................. 80

Figure 3.9 50cm×50cm×50cm mould .................................................................. 80

Figure 4.1 XRD patterns of ettringite synthesised with microwave and conventional heating at 60 (a), 70 (c) and 80°C (e), whereas (b), (d) and (f) show the changes of the (0001) d-spacings of the corresponding samples by enlarged main peak of ettringite (~9.0° 2\( \Theta \) ) ........................................................................ 95
Figure 4.2 Calculated lattice parameters of a (a) and c axes (b) of ettringite synthesised under microwave and conventional heating at 60, 70 and 80°C...

Figure 4.3 Electron diffraction patterns of ettringite synthesised at room temperature (a), at 70°C under microwave (b) and conventional heating (c)...

Figure 4.4 Schematic diagram of corresponding reflection crystal faces with the electron beam paralleled to [2201] zone axis...

Figure 4.5 Crystal structure of ettringite, viewed along a axis (Moore and Taylor, 1970)

Figure 4.6 TEM micrograph of ettringite at room temperature (a) or at 70°C under microwave (b) and conventional heating (c)

Figure 4.7 SEM micrographs of ettringite synthesised at room temperature (a), under microwave (b,d,f) and conventional heating (c,e,g) at 60, 70 and 80°C, respectively...

Figure 4.8 TG and DTG patterns of ettringite synthesised at room temperature, 60 (a), 70 (b) and 80°C (c)

Figure 4.9 Summary of peak temperatures of the decomposition of ettringite synthesised under microwave and conventional heating at 60, 70 and 80°C.

Figure 4.10 Water molecules contained in the ettringite synthesised at room temperature, and under microwave and conventional heating at 60, 70 and 80°C.

Figure 4.11 Binding energy and FWHM of Al 2p (a), Ca 2p (b) and S 2p (c) spectra of ettringite synthesised at room temperature, under microwave and conventional heating at 70°C

Figure 4.12 $^{27}$Al NMR spectra of ettringite synthesised under microwave and conventional heating at 70°C. Figure (a) shows the the patterns over 200-(-250) ppm range, whereas (b) shows enlarged range 25-0 ppm for clarity
Figure 5.1 XRD patterns of synthetic ettringite exposed to microwave and conventional heating at 60 (a), 70 (c) and 80°C (e), whereas (b), (d) and (f) show the changes of the (0001) d-spacings of the corresponding samples with an enlarged main peak of synthetic ettringite (~9.0° 2Θ) ..................................................123

Figure 5.2 Calculated lattice parameters of a (a) and c axes (b) of synthetic ettringite exposed to microwave and conventional heating at 60, 70 and 80°C .................................................................125

Figure 5.3 Electron diffraction patterns of ettringite synthesised at room temperature (a), synthetic ettringite exposed to microwave (b) and conventional (c) heating at 70°C .............................................................................................................127

Figure 5.4 TEM micrograph of ettringite synthesised at room temperature (a), synthetic ettringite exposed to microwave (b) and conventional heating (c) at 70°C .........................................................................................................................128

Figure 5.5 SEM micrographs of ettringite synthesised at room temperature (a), synthetic ettringite exposed to microwave (b,d,f) and conventional heating (c,e,g) at 60, 70 or 80°C ..................................................................................................................129

Figure 5.6 TG and DTG patterns of ettringite synthesised at room temperature, synthetic ettringite exposed to microwave and conventional heating at 60 (a), 70 (b) and 80°C (c) ..................................................................................................................131

Figure 5.7 Summary of the peak temperatures of the decomposition of synthetic ettringite samples exposed to microwave and conventional heating at 60, 70 and 80°C .............................................................................................................132

Figure 5.8 Water molecules incorporated in the ettringite synthesised at room temperature, and synthetic ettringite exposed to microwave and conventional heating at 60, 70 and 80°C .............................................................................................................133
Figure 5.9 Binding energy and FWHM of Al 2p (a), Ca 2p (b) and S 2p (c) spectra of ettringite synthesised at room temperature, synthetic ettringite exposed to microwave and conventional heating at 70°C

Figure 5.10 $^{27}$Al NMR spectra of ettringite synthesised at room temperature, synthetic ettringite exposed to microwave and conventional heating at 70°C. Figure (a) shows the patterns over 200-(-250) ppm range, whereas (b) shows 25-0 ppm for the sake of clarity

Figure 5.11 XRD patterns of synthetic Fe-ettringite exposed to microwave and conventional heating at 60 (a), 70 (c) and 80°C (e), with (b), (d) and (f) showing the changes of (0001) d-spacings of the corresponding samples in the enlarged main peak of synthetic Fe-ettringite (~9.0° 2$\Theta$)

Figure 5.12 XRD patterns of synthetic Cr-ettringite exposed to microwave and conventional heating at 60 (a), 70 (c) and 80°C (e), with (b), (d) and (f) showing the changes of (0001) d-spacings of the corresponding samples by enlarged main peak of synthetic Cr-ettringite (~9.0° 2$\Theta$)

Figure 5.13 XRD patterns of synthetic Mn-ettringite exposed to microwave and conventional heating at 60 (a), 70 (c) and 80°C (e), with (b), (d) and (f) showing the changes of (0001) d-spacings of the corresponding samples from the enlarged main peak of synthetic Mn-ettringite (~9.0° 2$\Theta$)

Figure 5.14 Calculated lattice parameters of a (a) and c axes (b) of Fe-ettringite exposed to microwave and conventional heating at 60, 70 or 80°C

Figure 5.15 Calculated lattice parameters of a (a) and c axes (b) of Cr-ettringite exposed to microwave and conventional heating at 60, 70 or 80°C

Figure 5.16 Calculated lattice parameters of a (a) and c axes (b) of Mn-ettringite exposed to microwave and conventional heating conditions at 60, 70 or 80°C
Figure 5.17 Electron diffraction patterns of Cr-ettringite synthesised at room-temperature (a), synthetic Cr-ettringite exposed to microwave and conventional heating .............................................................. 151

Figure 5.18 Electron diffraction patterns of Mn-ettringite synthesised at room-temperature (a), synthetic Mn-ettringite exposed to microwave and conventional heating .............................................................................. 152

Figure 5.19 TEM micrograph of Cr-ettringite synthesised at room temperature (a), synthetic Cr-ettringite exposed to microwave and conventional heating at 70°C ...................................................................................... 153

Figure 5.20 TEM micrograph of Mn-ettringite synthesised at room temperature (a), synthetic Mn-ettringite exposed to microwave and conventional heating at 70°C ...................................................................................... 153

Figure 5.21 SEM micrographs of Fe-ettringite synthesised at room temperature (a), synthetic Fe-ettringite exposed to microwave heating (b,d,f) and conventional heating (c,e,g) at 60, 70 and 80°C, respectively .......... 155

Figure 5.22 SEM micrographs of Cr-ettringite synthesised at room temperature (a), synthetic Cr-ettringite exposed to microwave heating (b,d,f) and conventional heating (c,e,g) at 60, 70 and 80°C, respectively .......... 156

Figure 5.23 SEM micrographs of Mn-ettringite synthesised at room temperature (a), synthetic Mn-ettringite exposed to microwave heating (b,d,f) and conventional heating (c,e,g) at 60, 70 and 80°C, respectively .......... 157

Figure 5.24 TG and DTG patterns of Fe-ettringite synthesised at room temperature, synthetic Fe-ettringite exposed to microwave and conventional heating at 60 (a), 70 (b) and 80°C (c) ................................................................. 159
Figure 5.25 TG and DTG patterns of Cr-ettringite synthesised at room temperature, synthetic Cr-ettringite exposed to microwave and conventional heating at 60 (a), 70 (b) and 80°C (c) .................................................................160

Figure 5.26 TG and DTG patterns of Mn-ettringite synthesised at room temperature, synthetic Mn-ettringite exposed to microwave and conventional heating at 60 (a), 70 (b) and 80°C (c) .................................................................161

Figure 5.27 Summary of peak temperatures of the decomposition of synthetic Fe-ettringite (a), Cr-ettringite (b) and Mn-ettringite exposed to microwave and conventional heating at 60, 70 and 80°C .................................................................163

Figure 5.28 Water molecules contained in the synthetic Fe-ettringite (a), Cr-ettringite (b) and Mn-ettringite exposed to microwave and conventional heating at 60, 70 and 80°C .........................................................................................165

Figure 5.29 Binding energy and FWHM of Al 2p (a), Ca 2p (b) and S 2p (c) spectra of Fe-ettringite synthesised at room temperature, synthetic Fe-ettringite exposed to microwave and conventional heating at 70°C .................................................................167

Figure 5.30 Binding energy and FWHM of Al 2p (a), Ca 2p (b) and S 2p (c) spectra of Cr-ettringite synthesised at room temperature and synthetic Cr-ettringite exposed to microwave and conventional heating at 70°C .....................168

Figure 5.31 The binding energy and FWHM of Al 2p (a), Ca 2p (b) and S 2p (c) spectra of Mn-ettringite synthesised at room temperature, synthetic Mn-ettringite exposed to microwave and conventional heating conditions at 70°C ...........................................................................................................169

Figure 5.32 $^{27}$Al NMR spectra of synthetic Fe-ettringite exposed to microwave and conventional heating at 70°C. Figure (a) shows the patterns over 200-(−250) ppm range, whereas (b) shows 25-0 ppm for clarity .............................................171
Figure 5.33 $^{27}$Al NMR spectra of synthetic Cr-ettringite exposed to microwave and conventional heating at 70°C. Figure (a) shows the the patterns over 200-(-250) ppm range, whereas (b) shows 25-0 ppm for clarity ..................................172

Figure 5.34 $^{27}$Al NMR spectra of synthetic Mn-ettringite exposed to microwave and conventional heating at 70°C. Figure (a) shows the the patterns over 200-(-250) ppm range, whereas (b) shows 25-0 ppm for clarity ..................................172

Figure 6.1 XRD pattern of CSA clinker ..........................................................182

Figure 6.2 XRD patterns of CSA pastes subjected to microwave and conventional curing at 60 (a), 70 (b) and 80°C (c) ...........................................183

Figure 6.3 Changes of the maxima of ettringite (a), ye’elimite (b) and gypsum (c) at d=9.70, 3.76 and 7.60 Å respectively in XRD diagrams .......................184

Figure 6.4 SEM micrographs of CSA pastes cured at room temperature (a), under microwave (b,d,f) and conventional curing (c,e,g) at 60, 70 and 80°C ..187

Figure 6.5 TG and DTG patterns of CSA paste samples subjected to microwave and conventional curing at 60 (a), 70 (b) and 80°C (c) ..................................189

Figure 6.6 XRD patterns of PC pastes subjected to microwave and conventional curing at 60 (a), 70 (b) and 80°C (c) .........................................................195

Figure 6.7 SEM micrographs PC pastes cured at room temperature (a), under microwave (b,d,f) and conventional curing (c,e,g) at either 60, 70 or 80°C ....198

Figure 6.8 TG and DTG patterns PC paste samples subjected to microwave and conventional curing at 60 (a), 70 (b) and 80°C (c) ..................................200
## List of Abbreviations

<table>
<thead>
<tr>
<th>Term</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>Portland cement</td>
</tr>
<tr>
<td>CŘA</td>
<td>Calcium sulfoaluminate cement</td>
</tr>
<tr>
<td>C₃S</td>
<td>Tricalcium silicate (3CaO·SiO₂)</td>
</tr>
<tr>
<td>C₂S</td>
<td>2CaO·SiO₂</td>
</tr>
<tr>
<td>C₃A</td>
<td>3CaO·Al₂O₃</td>
</tr>
<tr>
<td>C₄AF</td>
<td>4CaO·Al₂O₃·Fe₃O₄</td>
</tr>
<tr>
<td>H</td>
<td>H₂O</td>
</tr>
<tr>
<td>CH</td>
<td>Ca(OH)₂</td>
</tr>
<tr>
<td>Ettringite or Af</td>
<td>Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O</td>
</tr>
<tr>
<td>Fe-ettringite or Fe-Af</td>
<td>Ca₆·(Al, Fe)₂(SO₄)₃(OH)₁₂·26H₂O</td>
</tr>
<tr>
<td>Cr-ettringite or Cr-Af</td>
<td>Ca₆·(Al, Cr)₂(SO₄)₃(OH)₁₂·26H₂O</td>
</tr>
<tr>
<td>Mn-ettringite or Mn-Af</td>
<td>Ca₆·(Al, Mn)₂(SO₄)₃(OH)₁₂·26H₂O</td>
</tr>
<tr>
<td>Monosulfate or Af</td>
<td>Calcium monosulfoaluminate</td>
</tr>
<tr>
<td>Fe-monosulfate or Fe-Af</td>
<td>Ca₄·(Al, Fe)₂SO₄(OH)₁₂·6H₂O</td>
</tr>
<tr>
<td>Cr-monosulfate or Cr-Af</td>
<td>Ca₄·(Al, Cr)₂SO₄(OH)₁₂·6H₂O</td>
</tr>
<tr>
<td>Mn-monosulfate or Mn-Af</td>
<td>Ca₄·(Al, Mn)₂SO₄(OH)₁₂·6H₂O</td>
</tr>
<tr>
<td>R.H.</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>DEF</td>
<td>Delayed ettringite formation</td>
</tr>
<tr>
<td>FBG</td>
<td>Fibre Bragg grating</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TG</td>
<td>Termogravimetric analysis</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance spectroscopy</td>
</tr>
<tr>
<td>GGBS</td>
<td>Ground granulated blast furnace slag</td>
</tr>
</tbody>
</table>
Chapter 1 Introduction

1.1 Research background

Over the last few decades, precast concrete has been widely used in the construction industry due to the advantages it offers compared to cast-in-place concrete. Using precast concrete allows increased construction speed, enhanced quality of concrete products, reduction in the level of dust pollution and makes construction financially more viable. Therefore, precast concrete is considered as an environmentally friendly construction component, which includes items such as masonry blocks, pipes, slabs (Yee and Eng, 2001, Kuch et al., 2013).

In the manufacturing process for precast concrete, fresh concrete is first mixed and then cast into a reusable mould. Subsequently, the reusable mould is transferred into a controlled environment for curing, usually accelerated. Once hardened, the mould is stripped and the component is transported to a construction site. The accelerated curing procedure is very important in the process, because it ensures that concrete samples develop sufficient strength quickly, allowing early demoulding. Steam curing is usually utilised, during which the precast concrete in its mould is placed into a chamber filled with steam at a temperature of less than 70°C and cured for more than 10 hours (Ong and Akbarnezhad, 2014, Kosmatka and Wilson, 2011).

In spite of its wide application, the steam curing of precast concrete suffers from a number of drawbacks. Firstly, the process is energy intensive as the whole
steam curing process takes more than 10 hours, consuming a huge amount of energy.

At the same time, a large number of reusable moulds are required. Secondly, in reports from the literature (Liu et al., 2005, Yazıcı et al., 2005, Ramezanianpour et al., 2013, Alunno-Rossetti et al., 1974), the long-term strength of concrete cured by steam curing is lower than that cured at room temperature, which is due to tensile stress caused by the non-homogeneous heating of steam curing. Thirdly, many documented reports show that concrete subjected to a steam curing process can undergo long-term expansion if it is exposed to moist, or stored in, wet conditions during its service life (Tosun and Baradan, 2010, Bouzabata et al., 2012). This expansion would damage concrete, and it has been generally ascribed to the delayed formation of ettringite (abbreviated as DEF), widely known as a severe durability issue with precast concrete.

At temperatures above 70°C, ettringite becomes unstable; i.e. it easily decomposes to calcium monosulfoaluminate (denoted as monosulfate) and gypsum or bassanite in some cases (Scrivener and Taylor, 1993, Scrivener and Young, 2014). When exposed to a moist or wet environment, the monosulfate phase reversibly transforms back into ettringite if gypsum is present. This reformation of ettringite results in damaging expansion in precast concrete. As a result, the precast concrete manufacturers have set a limit for the maximum curing temperature allowed during the manufacturing process of precast concrete (Hwang et al., 2012, Hime, 1996).
To address the above challenges, microwave curing could provide an effective alternative to steam curing to reduce energy consumption and to shorten curing hours. All the components in concrete including water, cement and aggregate, are dielectric materials (Khoylou et al., 2014, Ong and Akbarnezhad, 2014). As a result, concrete itself can be considered as a dielectric material. When exposed to the electromagnetic field of microwaves, the dipolar molecules of dielectric materials vibrate, which generates friction between the molecules, converting the microwave energy into heat energy, instantly and volumetrically (Pozar, 2009). Microwave curing can potentially reduce the energy consumption associated with the manufacture of precast concrete due to its high efficiency of volumetric heating (Makul et al., 2009, Bukhari et al., 2015). It can also shorten the turnover time of reusable moulds and reduce the time needed to cure precast concrete. Therefore, it is highly likely that the cost of producing precast concrete can be reduced significantly.

Up to now, there have been a number of studies associated with the effects of microwaves on the properties of cementitious materials, especially the development of strength at 1, 3 and 7 days (Makul and Agrawal, 2011, Makul and Agrawal, 2012, Wu et al., 1987, Leung and Pheeraphan, 1995, Hutchison et al., 1991, Griffin and Coveney, 1999, Sohn and Johnson, 1999, Rattanadecho et al., 2016, Shi et al., 2016). These results show that microwave curing can significantly enhance the strength development at early ages and does not reduce the 28-day strength, compared to conventional thermal curing. However, in those studies, the output of microwave power was just adjusted, rather than employing a precise temperature control system. Importantly, there is very limited
research available on the microstructure and thermal stability of ettringite under microwave curing.

In this project, a customised microwave oven with an accurate temperature and humidity control system using an FBG optical sensor has been employed to investigate the microstructure and thermal stability of ettringite under microwave heating. As discussed in the literature (Huheey et al., 2006, Robb, 2005, Rybakov et al., 2008, Horikoshi and Serpone, 2014), the microwave effect includes both thermal and non-thermal effects. The question arises, is ettringite stable under microwave heating? What is the microstructure and decomposition temperature of ettringite under microwave heating? To answer these questions, it is necessary to conduct a detailed study on the microstructure and thermal stability of ettringite under microwave heating. From this information, it should be possible to provide some reference for using microwave curing to manufacture precast concrete.

1.2 Aims and objectives

This study aims to understand the mechanism of microstructural formation and thermal stability of ettringite under microwave irradiation to lay the foundation for the potential use of microwaves to cure precast concrete. As such, this study investigates how microwave irradiation affects the microstructure and thermal stability of ettringite. In particular, a precise temperature control system is used, thus providing reliable fundamental information for establishing the maximum curing temperature for the industrial manufacture of microwaves cured precast concrete. To achieve this goal, the main objectives are as follows:

- To investigate changes in the microstructure and crystal morphology of synthesised pure ettringite, Fe-ettringite, Cr-ettringite, Mn-ettringite as well
as the ettringite formed in cement pastes under different microwave treatments.

- To explore the relationship between the thermal stability of ettringite and its microstructure and morphology when microwaved and to explain how the mechanism of microwaves can affect the microstructure and thermal stability of ettringite;

- To provide a reference for setting the curing temperature for microwaves cured precast concrete based on the thermal stability of ettringite. The findings of this project will provide the fundamental information to allow an industry-scale microwaves cured production of precast concrete.

### 1.3 Outline of the thesis

Chapter 2 reviews (i) the steam curing adopted in precast concrete, (ii) the fundamental properties of ettringite and the formation and damage mechanisms of delayed ettringite formation, and (iii) the principle of microwave heating as well as its potential influence on thermal stability of ettringite. This is followed by two proposed research questions (i) “Is ettringite stable under microwave irradiation?” and (ii) “What is the microstructure and decomposition temperature of ettringite subjected to microwave irradiation?”

Chapter 3 describes the methodology and experimental programme established for this project.

Chapter 4 investigates the microstructure and thermal stability of pure ettringite synthesised under microwave irradiation.
Chapter 5 investigates the microstructure and thermal stability of room temperature pre-synthesised pure ettringite and metal ion-doped (Fe$^{3+}$, Cr$^{3+}$ and Mn$^{2+}$) ettringite exposed to microwave irradiation.

Chapter 6 studies the microstructure and thermal stability of ettringite formed in calcium sulfoaluminate cement and Portland cement pastes.

Chapter 7 draws the main conclusions and makes some recommendations for future work.
Chapter 2 Literature Review

This chapter reviews (i) the steam curing adopted in precast concrete industry, (ii) the fundamental properties of ettringite, the formation and damage mechanisms of delayed ettringite formation, (iii) the principle of microwave heating as well as its potential influence on thermal stability of ettringite. The purpose of this chapter is to gain an understanding of the existing research and debates relevant to the thesis topic, and to provide foundation of knowledge in analysing and discussing the experimental results.

2.1 Steam curing in precast concrete

2.1.1 Introduction

Concrete is the world’s most widely used building material, but the construction industry is facing increasing challenges, including its high carbon footprint and high energy consumption. To address these issues, precast construction is widely recognised as a more sustainable, durable and environmentally friendly alternative to conventional (on-site) construction (Yee and Eng, 2001, Kuch et al., 2013). Precast concrete has been used in high-rise buildings, modern factories, spacious shopping warehouses and large-scale infrastructures, partly because it is less expensive and less time consuming than its conventional counterparts. Along with this, efforts have also been devoted to developing precast methods where the efficiency of the curing process could be increased whilst the energy consumption could be reduced (Ong and Akbarnezhad, 2014, Ramezanianpour et al., 2013, Won et al., 2013).
The main curing technique used in precast concrete industry is steam curing. This method accelerates cement hydration and therefore shortens the curing duration. The following sections explain the mechanism underlying steam curing of precast concrete.

### 2.1.2 Steam curing process

Accelerated curing is a must for precast industry where the efficient use of workshop spaces is essential to the economy of precast technology. This approach, normally, refers to thermal treatments via four methods: convection and conduction heating, electrical heating, low-pressure steam (referred to as steam curing) and high-pressure steam (referred to as autoclave curing) (Kuch et al., 2013).

Steam curing is the most commonly used curing technique for manufacturing of precast concrete products. The purpose of using steam curing is to accelerate the process of cement hydration by raising temperature without losing the sufficient moisture required for hydration reactions. This is achieved by injecting steam into a closed environment to minimise the loss of heat and moisture. Overall, the steam curing process increases the diffusion rate of water molecules within the concrete and helps the formation of hydration products. As a result, the precast concrete can reach a high early-age strength which enables de-moulding within 24 hours, thus reducing the curing cycle time, energy consumption and total cost (Erdem et al., 2003).
A typical operation cycle of steam curing is shown in Figure 2.1 (Smith, 2013). The steam curing process includes four stages: initial delay, temperature increase, constant temperature and temperature decrease. First, the curing process starts with an initial delay period of about 3 to 5 hours at ambient temperature to allow the concrete to set and gain initial strength so that it can resist the internal expansion tension caused during the process of steam curing. Then the temperature increase period begins at a rate of 10 to 20 °C per hour until the target temperature is reached, usually within the range of 60 to 70 °C, followed by a period of constant temperature where the concrete products are cured at the maximum temperature for 6 to 12 hours. Finally a temperature decrease period with a rate of less than 40°C per hour is applied to finish the curing cycle (Smith, 2013).

![Figure 2.1 Typical low-pressure steam-curing cycle (Smith, 2013)](image)

### 2.1.3 Hydration of cement under steam curing

The strength development of concrete over time is mainly controlled by the reaction of cement with water (via a process called hydration) which involves a
series of chemical reactions. Portland cement (hereafter PC), which is the most widely used type of cement, is composed of four major minerals: 3CaO·SiO$_2$ (C$_3$S), 2CaO·SiO$_2$ (C$_2$S), 3CaO·Al$_2$O$_3$ (C$_3$A) and 4CaO·Al$_2$O$_3$·Fe$_3$O$_4$ (C$_4$AF). The proportions of these four phases vary in different types of PC, which determine the rate of cement hydration. When mixed with water, cement phases undergo a sequence of hydration reactions that lead to the setting and hardening of the mixture. The hydration characteristics of PC, namely the reaction rate, heat of reaction and contribution to the ultimate strength development, are summarized in Table 2.1 (Taylor, 1997, Hewlett and Liska, 2019).

Table 2.1 Hydration characteristics of PC constituents (Taylor, 1997, Hewlett and Liska, 2019)

<table>
<thead>
<tr>
<th>Cement constituent</th>
<th>Reaction rate</th>
<th>Reaction heat liberation</th>
<th>Contribution to cement strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3$S</td>
<td>Moderate</td>
<td>Moderate</td>
<td>High</td>
</tr>
<tr>
<td>C$_2$S</td>
<td>Slow</td>
<td>Low</td>
<td>Initially low but high later</td>
</tr>
<tr>
<td>C$_3$A+ C$_5$H$_2$</td>
<td>Fast</td>
<td>Very high</td>
<td>Low</td>
</tr>
<tr>
<td>C$_4$AF+ C$_5$H$_2$</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
</tr>
</tbody>
</table>

*Note: C$_5$H$_2$: CaSO$_4$·2H$_2$O (gypsum)*

As shown in Table 2.1, C$_3$A and C$_3$S are the most reactive constituents, while C$_2$S has considerably slower hydration rate. However, the rate of hydration does not necessarily have a direct influence on the rate of strength development. For example, C$_3$A hydrates very rapidly (known as “flash-set”) and generates much heat, but it contributes little to the strength gain. In order to avoid flash setting of cement due to the rapid hydration of C$_3$A, normally a certain amount of gypsum (less than 5%) is added into PC. When mixed with water, gypsum reacts with C$_3$A in a through-solution reaction to generate calcium sulfoaluminate hydrate (called ettringite) which precipitates around the cement particles to retard diffusion of the
dissolving ions and hinder the formation of the hexagonal hydrates, thus avoiding
the flash setting of cement (Black et al., 2006). It is the calcium silicates (C₃S and
C₂S) that are the main constituents contributing to strength development of PC.
C₃S is responsible for the development of most of the early strength in the first 4
weeks, with both C₃S and C₂S contributing almost equally to the long-term
strength of concrete. The hydration reactions of C₃S, C₂S, C₃A, and C₄AF are
shown in Equations (2.1), (2.2), (2.3) and (2.4) respectively (Fukuhara et al., 1981,
Hewlett and Liska, 2019).

\[
\begin{align*}
2C₃S + 11H & \rightarrow C₃S₂H₈ + 3CH \quad (2.1) \\
2C₂S + 9H & \rightarrow C₃S₂H₈ + CH \quad (2.2) \\
C₃A + 3C₅H₂ + 26H & \rightarrow C₆A₃H₃₂ \quad (2.3) \\
C₄AF + 4C₅H₂ + 35 \frac{1}{3} H & \rightarrow \frac{4}{3} [C₃(A₀.₇₅,F₀.₂₅) \cdot 3C₅ \cdot H₃₁] + \frac{2}{3} FH₃ \quad (2.4)
\end{align*}
\]

The hydration products of C₃S and C₂S are similar, except the amount of calcium
hydroxide (CH) produced is different. Calcium silicate hydrate (C₃S₂H₈, usually
referred to as C-S-H) is the main hydration product of C₃S and C₂S. It is a very
poorly crystallised material formed at very small particle sizes less than 1 µm in
all three dimensions and is often referred to as gel with variable water content.

The steam curing enhances the early-age hydration rate of PC and thus results
in an increased rate of the hardening process as well as an increase in the early
strength development rate, which allows the large-scale production of cast
components in a relatively short time. When compared with the concrete products
cured in an ambient environment, the same chemical reactions occur during the
steam curing, but the induction period becomes shorter and the early hydration
of cement takes place more rapidly, especially for C₃S. Meanwhile, at early ages,
as the temperature rises, the rate of hydration increases, but after 1 day of curing,
the percentage of hydration is independent of temperature (Alunno-Rossetti et al., 1974). As a result, faster hardening of the cement occurs, and the rate of strength gain also increases (Yang and Sharp, 2001, Liu et al., 2005, Ramezanianpour et al., 2013, Lee et al., 2016). Other reported benefits of steam curing include reduced drying shrinkage and creep compared to moist-cured concrete (Boukendakdji et al., 1996). However, the steam curing method often leads to slight reductions in the ultimate strength of concrete (Alunno-Rossetti et al., 1974, Lee et al., 2016).

### 2.1.4 Maximum curing temperature limits

Although a higher temperature can improve the efficiency of manufacturing precast concrete products and therefore decrease total cost, it can lead to a loss in later age strength. This was confirmed by the investigation showing that the optimum temperature for steam curing of PC concrete was between 65 and 70°C, beyond which there were considerable losses in the later age strength (Türkel and Alabas, 2005). Also, some cement pastes or mortars subjected to early heat curing were reported to undergo long-term expansion during moist or wet storage (Lawrence, 1995, Glasser, 1996, Barbarulo et al., 2005, Escadeillas et al., 2007, Adamopoulou et al., 2011). The expansion is associated with the delayed ettringite formation (DEF) in the matured mortar, which may take a long time to manifest itself. DEF was first identified by Ludwig (1980). It was observed that the mortar and concrete made with a German high early-strength PC revealed expansions during subsequent water storage when the curing temperature was beyond 70°C. Therefore, curing temperatures above 70°C should be avoided for two reasons. One reason is that higher temperatures can result in an undue
reduction in the long-term strength, as well as requiring more energy. The other reason is that a higher temperature can lead to the decomposition of ettringite into monosulfate during the accelerated curing process, which can reform ettringite in moist conditions at later stage. This reformation is a volumetric increase process, thus, causing DEF (Ramezanianpour et al., 2013). Due to these reasons, a number of different standards are put in place to limit the maximum curing temperature of precast concrete products, as shown in Table 2.2 (Hwang et al., 2012).

<table>
<thead>
<tr>
<th>Resource</th>
<th>Set period (h)</th>
<th>Maximum rate of heating (°C/h)</th>
<th>Maximum temperature (°C)</th>
<th>Maximum rate of cooling (°C/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACI Committee 517</td>
<td>2</td>
<td>22-23</td>
<td>74</td>
<td>22-23</td>
</tr>
<tr>
<td>UK Highway Standard SERIES 1700</td>
<td>4</td>
<td>20</td>
<td>70</td>
<td>20</td>
</tr>
<tr>
<td>Macrete, UK</td>
<td>4</td>
<td>20</td>
<td>60</td>
<td>20</td>
</tr>
<tr>
<td>China Railway Standard TB/T 2190-2013</td>
<td>3</td>
<td>15</td>
<td>60</td>
<td>15</td>
</tr>
<tr>
<td>CSA A23.4</td>
<td>initial set, at least 3 h after final placement</td>
<td>20</td>
<td>70 for dry conditions 60 for damp conditions</td>
<td>15</td>
</tr>
<tr>
<td>Korea Concrete Institute</td>
<td>2 to 3</td>
<td>20</td>
<td>65</td>
<td>Not specified</td>
</tr>
<tr>
<td>PCI Bridge Design Manual, MNL-133-97</td>
<td>3 to 5 after initial set</td>
<td>11 to 44</td>
<td>70 to prevent DEF</td>
<td>Not specified</td>
</tr>
<tr>
<td>AASHTO LRFD Bridge Design Specifications, 2004</td>
<td>initial set</td>
<td>22</td>
<td>71</td>
<td>22</td>
</tr>
</tbody>
</table>
It can be seen from Table 2.2 that in the different standards, the maximum curing temperature is generally fixed at around 70°C. Furthermore, in PCI Bridge Design Manual (MNL-133-97), it is specified that the purpose of the maximum temperature limits is to prevent DEF, which is in good agreement with the detailed description of DEF as stated in Section 1.1 of Chapter 1. In addition to this aspect, the undue reduction in the ultimate strength and extra energy consumption should be taken into account as well. Based on the above evidence, it is vital to set limits on the maximum curing temperatures for precast concrete manufacture.

2.1.5 Issues arising from steam curing

As stated above, steam curing does play an important role in manufacturing precast concrete, because it accelerates cement hydration, thus resulting in sufficient early strength of precast concrete that allows for demoulding in a short time. However, based on the previous literature review, three main issues arising from steam curing of precast concrete can be identified as follows.

(1) High energy consumption

The duration of steam curing for precast concrete requires more than 10 hours, during which a huge amount of energy is consumed and a number of reusable moulds are required. The average energy consumption in the UK for manufacturing one tonne precast concrete product is around 50-90 kWh over the period of 2007 to 2011 (Smith, 2013).

(2) Reduction in the long-term strength of precast concrete

As the heating mechanism of steam curing is dependent on the thermal conductivity of specimens from the external to the internal, it results in a non-
uniform hydration of cement, as a consequent of tensile stress, thus leading to the appearance of cracking and hereby a slight reduction in the long-term strength of precast concrete.

(3) Possibility of decomposition of ettringite

Due to the stability of ettringite dependent on temperature, the curing temperature has to be limited below 70°C to avoid DEF. Therefore, as DEF is closely related to the thermal stability of ettringite, so before the formation and damage mechanisms of DEF are reviewed, it is necessary to first represent the fundamental information about ettringite in the following section.

2.2 Ettringite

2.2.1 Introduction

Ettringite is an important hydration product of PC, formed from the reaction of C₃A with gypsum and water. It plays a crucial role in controlling the setting time of fresh PC paste or mortar but can also be responsible for the premature deterioration of hardened concrete if it forms at later stages (Cody et al., 2004). Ettringite is also the main hydration product of calcium sulfoaluminate cement (C₅S₆A), which is a low-CO₂ potential alternative to PC, containing about 30-70 wt% ye’elimite (C₄A₃S) in the clinker (Zhang, 2000, Gartner, 2004). It forms from the reaction of ye’elimite (C₄A₃S) with gypsum or anhydrite and water during the period between initial and final set.
To better understand ettringite stability under thermal curing, this section reviews the chemical composition, crystal structure, morphology and thermal stability of ettringite as well as the factors influencing the thermal stability of ettringite. It also highlights how the thermal stability changes with increasing temperature and how this could change the structure of ettringite.

### 2.2.2 Structure

The structure of ettringite has been widely investigated in the past with its crystal structure first being reported by Moore and Taylor using diffractometer and film techniques in 1970 (Moore and Taylor, 1970). Since then, various techniques such as neutron diffraction and time-of-flight neutron diffraction of the atoms have been used to precisely determine the location of the atoms within the structure, especially the hydrogen atoms (Goetz-Neunhoeffer and Neubauer, 2006, Hartman and Berliner, 2006). These findings help understand the hydrogen bonding network within the ettringite structure, thus assisting in analysing the ettringite structure and how it thermally decomposes.

It is generally believed that the structure of ettringite is based on columns and channels. The columns, with the empirical formula \( \text{Ca}_6[\text{Al(OH)}_6]_2\cdot24\text{H}_2\text{O}\)\(^6^+\), run parallel to the \(c\) axis or needle direction and consist of \([\text{Al(OH)}_6]_3\)\(^3^-\) octahedral alternating with triangular groups of edge-sharing \(\text{CaO}_8\) polyhedral, with which they share \(\text{OH}^-\) (Taylor, 1973, Moore and Taylor, 1970). Each Ca atom is also coordinated by four \(\text{H}_2\text{O}\) molecules, forming the cylindrical surface of the column. Between the columns lie the sulfate ions \((\text{SO}_4^{2^-})\) and remaining water molecules \((\text{H}_2\text{O})\) (zeolitic water) (Figure 2.2). The columns are linked to the species in the channels by hydrogen bonds. Ettringite has the empirical formula
Ca₆[Al(OH)₆]₂(SO₄)₃·26H₂O and can readily be synthesised. It forms prismatic crystals, which are hexagonal in cross-section. It is trigonal, with a=1.12 ± 0.002 nm, c=2.145 ± 0.005 nm (Peacock and Berry, 1949).

The ettringite structure is capable of extensive substitution by both anions like CO₃²⁻, CrO₄²⁻, Cl⁻, IO₃⁻, and even para-nitrobenzoate and cations such as Fe³⁺, Cr³⁺, Mn³⁺, Ti³⁺, Ga³⁺, and Sr³⁺ (Taylor, 1973, Moore and Taylor, 1970, Hall et al., 1996b, Carmona-Quiroga and Blanco-Varela, 2013). In addition, marked changes in the morphology of ettringite occur when it forms in the presence of organic additives (i.e. plasticizers such as sorbitol, citrate, and tartrate, lignosulfonate air-entraining admixtures) (Cody et al., 2004, Afridi et al., 1994).
When ettringite is formed in PC, Fe\(^{3+}\) commonly occupies some Al\(^{3+}\) sites in the structure to form Fe- ettringite. The replacement of Al\(^{3+}\) by Fe\(^{3+}\) is a slow process, which takes half a year to reach the equilibrium (Fukuhara et al., 1981, Möschner et al., 2007). Fe- ettringite was found to be stable in the pH range of 11.0-13.0 and its solubility is very close to the solubility of Al- ettringite (K\(_{so}=-44.9\)) (Möschner et al., 2007, Möschner et al., 2008). The interatomic distances of Fe- ettringite are somewhat larger than those of Al- ettringite, as the size of Fe\(^{3+}\) is larger than that of Al\(^{3+}\) (Huheey et al., 2006). However, the morphology of both Al- and Fe- ettringite is the same, typically needle-like shapes (Möschner et al., 2009).

As Cr\(^{3+}\) has comparable ionic radii as Al\(^{3+}\), Cr\(^{3+}\) can also replace Al\(^{3+}\) in the structure of ettringite (Seryotkin et al., 2018, Wieczorek-Ciurowa et al., 2001, You et al., 2007a). At [M(OH)\(_6\)] octahedral sites, all Al\(^{3+}\) can be substituted by Cr\(^{3+}\) to form Cr- ettringite. As Cr\(^{3+}\) is a common pollutant in the waste, the immobilisation of Cr\(^{3+}\) in ettringite shows great potential application of ettringite in waste treatment. It was found that the formation of sole Cr- ettringite requires both suitable reagent concentration and a suitable pH value. Nonetheless, Cr- ettringite and Al- ettringite have similar crystal lattices (Wieczorek-Ciurowa et al., 2001).

When Mn\(^{2+}\) is doped in the ettringite that forms during the hydration of PC, Mn\(^{2+}\) can partly substitute Al\(^{3+}\) to form Mn- ettringite, as seen in the formula of sturmanite
\[
Ca_6(Fe^{3+}\cdot1.5Al_{0.3}Mn^{2+}0.2)\cdot2.0(SO_4)\cdot2.3(B(OH)\cdot1.2(OH)\cdot12.0\cdot25.7H_2O.
\]

Therefore, likewise, it is possible for ettringite to immobilise Mn\(^{2+}\) in wastes.
Therefore, the structure of ettringite is very complicated over various systems and its stability is influenced by many factors which is further elaborated below.

2.2.3 Morphology

The morphology and size of the ettringite crystals changes in different conditions. The observation obtained from most scanning electron microscope (SEM) studies showed that ettringite morphology is normally slender needle-like crystals with a prismatic hexagonal cross section, as shown in Figure 2.3 and Figure 2.4 (Mehta, 1973, Famy et al., 2001, Scrivener and Skalny, Shimada and Young, 2004, Ogawa and Roy, 1981, Association, 2001). The crystal size depends on the water to cement ratio, which determines the availability of sufficient space for ettringite to grow. It was found that ettringite crystals formed in air voids and cracks were typically 20 to 30 µm in length and 2 to 4 µm in diameter (Association, 2001). Another report showed that the morphology of ettringite prepared in PC pastes with low water-cement ratios differed from that prepared in dilute solutions (Mehta, 1969). In PC pastes, ettringite formed as short prisms with a hexagonal cross section and had a thickness to length ratio of 1 to 3, while in dilute solutions it appeared as long and slender needles.

Figure 2.3 SEM micrograph of synthetic ettringite (Shimada and Young, 2004)
Mehta (1973) reported that the colloidal ettringite formed rather long lath-like crystals in the presence of lime, as shown in Figure 2.5 (Mehta, 1973).

Tosun and Baradan (2010) claimed that in aged concrete, ettringite typically formed in air and water voids, cracks and aggregate-paste interfaces, indicating that its morphology heavily depends on the microstructure of paste. In their study, two types of ettringite were identified: ball type ettringite (non-expansive) and massive ettringite (expansive) as shown in Figure 2.6. Their description indicated
that ettringite formed in narrow spaces such as in the matrix, small pores and interfaces between aggregate and paste, seemed to be massive, whereas the ettringite formed in larger air voids was ball-shaped (Tosun, 2006, Tosun and Baradan, 2010). It should be noted that although different sizes and morphology of ettringite have been reported, its chemical composition in all forms is always the same.

![Figure 2.6 Massive ettringite on aggregate surface and ball ettringite in pores (Tosun and Baradan, 2010)](image)

### 2.2.4 Thermal stability

Thermal stability in chemistry is defined as the stability of a molecule when it is exposed to a very high temperature. The thermal stability of ettringite has been the subject of numerous studies (Lou et al., 2019, Ndiaye et al., 2017, Wang et al., 2016, Kaufmann et al., 2016, Guimarães et al., 2016, Fridrichová et al., 2016, Baquerizo et al., 2016, Jiménez and Prieto, 2015, Carmona-Quíroga and Blanco-Varela, 2013), but some of the aspects relevant to the definite description on thermal stability, such as the accurate determination of the decomposition temperature, mechanisms and reaction kinetics of ettringite decomposition and reconstitution, have not yet been clarified. Skoblinskaya et al. (1975) described the process of decomposition of ettringite under the combination of vacuum and
heating as the following three stages: 1) water loss from the additional apices of trigonal prisms \((n=30-18)\), the symbol \(n\) represents the number of water molecules in the formula of ettringite) allowed the structure of the crystal to be maintained; 2) water loss from the main apices \((n=18-6)\) caused the crystals to become X-ray amorphous; 3) water loss from the main apices \((n=6-0)\) led to the ruptures on the longitude and transverse, and disintegration of crystals. The second stage shows that after loss of 12 to 24 water molecules, ettringite is transferred to amorphous phase, which is monosulfate. This stage can be used to assess whether the specific ettringite is stable or not. Once monosulfate begins to form, it indicates that ettringite is not stable.

The thermal stability of ettringite can be affected by many factors, including temperature, pressure, humidity, pH value, the grain size of ettringite phase as well as the concentration of its components (Ghorab and Kishar, 1985). The decomposition temperature, mechanism and reaction kinetics of ettringite decomposition and reconstitution have been shown to vary depending on the conditions. Reviewing the studies on the thermal stability of ettringite conducted in the past will help understand and establish the thermal stability and decomposition mechanism under microwave treatment. Therefore, the factors affecting the thermal stability of ettringite are reviewed in detail in the sections below.

\section*{2.2.4.1 Effect of temperature}

It is generally believed that ettringite is thermally unstable at elevated temperatures. However, specific decomposition temperature varies depending on individual situations.
Damidot and Glasser (1992) found that ettringite was unstable above 45°C in the CaO-Al₂O₃-CaSO₄-H₂O system, instead, monosulfate became increasingly stable. Taylor et al. (2001) claimed that ettringite in concrete was thermally unstable at temperatures greater than 70°C, which would result in the formation of DEF when the concrete was exposed to wet or moist environment, intermittently or permanently. Zhou et al. (2004) discovered that a new phase, meta-ettringite, one of the decomposition products of ettringite, typically formed in the temperature range between 50 and 100°C. At temperatures of 110-114°C, ettringite decomposed into calcium sulfate hemihydrate, water, and an amorphous compound that was probably a monosulfate phase. In addition, the results of a study on the thermal decomposition of an ettringite-group crystal showed that the onset of dehydration and decomposition happened at about 55°C and the dehydration was completed by 175°C (Deb et al., 2003).

Ettringite is generally considered to contain 32 H₂O molecules, where 30 H₂O are fixed in the columns and 2 H₂O are present as zeolitic (reversibly exchangeable) water that are more loosely bound in the channels (Skoblinskaya and Krasilnikov, 1975, Taylor, 1973, Renaudin et al., 2010) (see Figure 2.2). A number of studies have been carried out on the thermal stability of ettringite. Although there is no agreement over the exact order of the hydroxyl and free water leaving the crystal, there is a general agreement that a large water loss occurred at ~110°C, followed by amorphization of the sample after the loss of 20 units of water with the dehydration completed by 175°C. This led to the loss of its crystallization water and an amorphous state (monosulfate) appearing (Skoblinskaya and Krasilnikov, 1975, Skoblinskaya et al., 1975, Hartman et al., 2006, Hall et al., 1996a).
2.2.4.2 Effect of humidity

Relative humidity (abbreviated as R.H.) is also an important parameter that influences the thermal stability of ettringite (Baquerizo et al., 2014, Baquerizo et al., 2016, Mehta, 1972). Mehta (1972) claimed that a high R.H. can enhance the thermal stability of ettringite. In his study, when ettringite was exposed to a dry environment, it began to decompose at 93°C. While in moist hot environments, even if the ettringite was heated at 93°C for 1 hour, there is no sign of the decomposition of ettringite. Similar results were also reported by Baquerizo et al. (2016). This study showed the thermal stability of ettringite conditioned for 20 months was quite different under different R.H.. When the R.H. was below 31%, the formation of AFm even started at 50°C, which means the ettringite has become unstable and begun to decompose. When R.H. was 74% and 96%, no AFm formed, which confirmed that at that R.H. level, ettringite was stable and did not decompose to AFm. These can be clearly seen from Figure 2.7, which shows the XRD patterns of an ettringite conditioned at 50°C under different humidity.
2.2.4.3 Effect of pressure

There have been a number of studies focusing on the decomposition mechanism of ettringite under different pressure. For example, some of them were carried out under vacuum while others under hydrothermal conditions, but many of them were characterized by exposing ettringite to isothermal decomposition at uncontrolled partial water vapour pressures ($P_{H2O}$). When ettringite was exposed to very low values of $P_{H2O}$ (6 mmHg) at 65°C, meta-ettringite was the primary product of decomposition (Zhou and Glasser, 2001).

Hall et al. (1996a) studied the decomposition of dry ettringite in a sealed cell so that ettringite-water paste can be observed under well-defined conditions of both temperature and pressure. Decomposition occurred rapidly at 114°C at an estimated saturated water vapour pressure of 1.63 bar. The decomposition reaction is presented below:
\[
\text{Ca}_6[\text{Al(OH)}_6]_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O} \rightarrow \text{Ca}_4[\text{Al(OH)}_6]_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O} + 2\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O} + 17\text{H}_2\text{O}
\] (2.5)

As shown in Equation (2.5), the phases formed from the decomposition of ettringite were AFm-14H and bassanite. The reaction is reversible with ettringite reforming at low temperatures with hysteresis.

The thermal stability of ettringite in conditions of controlled P_{H2O} and temperature was investigated by Zhou and Glasser (2001). Ettringite could be thermally stable when temperature was lower than 120°C, depending on the P_{H2O} (Figure 2.8). At P_{H2O} of 6, 35, 75 and 400 mmHg, the corresponding decomposition temperature of ettringite was about 65, 85, 95 and 105°C, respectively. This means the decomposition temperature of ettringite is closely related to the value of P_{H2O}.

During the dehydration process, the hydroxyl and water molecules were lost from the structure Figure 2.9, which is in good agreement with the results obtained by Hartman et al. (2006). Zhou et al. (2004) reported that when ettringite decomposed to a product containing 10-13 H_2O molecules per formula unit, the product was amorphous and is termed meta-ettringite.

![Figure 2.8 Data for decomposition of ettringite showing convergence of weight loss on a product containing 10-13 H_2O (Zhou and Glasser, 2001)](image_url)
Figure 2.9 Data for the decomposition of ettringite (Zhou and Glasser, 2001)

Clark et al. (2008) showed that by using infrared and diffraction data, a transformation in ettringite was identified which occurred at 3 GPa, where channel water and some hydroxyl molecules were lost as the pressure was increased.

2.2.4.4 Effect of pH value

In addition to temperature, pressure and humidity, the pH value of the surrounding solution may also affect the thermal stability of ettringite. Ettringite was generally stable between the pH of 10.5 to 13.0 (Damidot and Glasser, 1993). However, in a low-lime environment, even the pH was only decreased to 11.5-12.0, gypsum was identified from the decomposition reaction of ettringite, indicating ettringite was unstable under this particular condition (Biczok and Szilvássy, 1967).

Ghorab and Kishar (1985) found that ettringite was stable up to 60°C in a solution of a pH value around 11, but gypsum appeared when pH value was below 9. Similar result was reported by Jiménez and Prieto, showing that ettringite was the
most stable phase in a solution with a pH value of 11.5 (Jiménez and Prieto, 2015).

Generally, ettringite is stable in the range of pH value 10.5-13.0, but the actual value changes with the change of surrounding environment of ettringite.

2.2.4.5 Effect of foreign ions

Foreign ions incorporated into ettringite from the aqueous phase can affect the thermal stability of ettringite, as shown by the following investigations.

The study performed by Ogawa and Roy (1981) showed that in deionized water, ettringite decomposed to AFm as the main product, along with a small amount of calcium sulphate hemi-hydrate (CaSO$_4$·0.5H$_2$O) and anhydrite (CaSO$_4$) at 130-150°C in the pressure range of 100 to 600 psi. In a 20% NaCl solution, ettringite decomposed to gypsum and chloroaluminate hydrate (C$_3$A·CaCl$_2$·H$_{10}$) as the main products between 95°C and 105°C over a similar pressure range.

Shimada and Young (2004) studied the thermal stability of ettringite in NaOH solutions at 0.25 M and above, showing that when C$_3$S was absent, ettringite converted to the U phase (a sodium-substituted AFm phase) at 80°C. However, in NaOH solutions above 0.5 M at the same temperature (80°C), the presence of C$_3$S prevented the U Phase formation and caused a complete conversion of ettringite to AFm.
Damidot and Glasser (1993) studied the thermodynamics of the CaO-Al₂O₃-CaSO₄-H₂O system at 25°C and the influence of Na₂O. Results showed that ettringite was stable over a wide range of composition and pH in water.

### 2.2.4.6 Effect of other factors

In addition to the factors described above, including temperature, humidity, pressure, pH value and incorporated ions, other factors such as autoclave, combination of temperature and pressure, different drying regimes, SO₃:Al₂O₃ ratio, and so on also have effects on the stability of ettringite. Relevant investigations are as follows.

Mehta (1972) investigated the stability of ettringite under dry, moist and autoclave conditions, and the results are as follows: a part of ettringite decomposed at 93°C under drying conditions but there was almost no decomposition observed at 100% R.H.; in an autoclave, at 149°C, ettringite decomposed to AFm; while at 232°C C₃AH₆ was the main component, but a small amount of ettringite still remained. Lieber (1963) discovered that in water, ettringite can exist even at 90°C. Satava and Veprek (1975) prepared ettringite by mixing C₁₂A₇ with Ca(OH)₂ and gypsum in stoichiometric ratios with water to investigate the thermal decomposition of ettringite under hydrothermal conditions. The results of differential thermal analysis (DTA) and X-ray diffraction showed that when pure ettringite was heated in saturated steam for 8 hours at 110°C, no decomposition took place. However, at 112°C, ettringite decomposed completely in 5 hours. Based on these results, the decomposition temperature of ettringite lay at 111 ± 1°C.
From thermodynamic studies and calculations of the free energy of formation of AFm and ettringite, Babuskin et al. (1985) claimed that above 70°C, AFm was more stable than ettringite. Water activities influenced by some dissolved components have a great impact on the stability of ettringite as well. Table 2.3 lists some typical decomposition temperatures of ettringite reported under certain conditions. It can be seen in this table, TG was employed as the common characterisation technique for measuring the decomposition temperature of ettringite. As the heating conditions employed for the TG measurement are different, the decomposition temperature obtained varies significantly. Therefore, no consistent information about the decomposition temperature has been obtained as yet.

The sulfur/aluminium (SO\textsubscript{3}:Al\textsubscript{2}O\textsubscript{3}) ratio also has an effect on the stability of ettringite. When the sulfur/aluminium(SO\textsubscript{3}:Al\textsubscript{2}O\textsubscript{3}) ratio is below 3:2, ettringite is unstable and converts to monosulfate, liberating sulfate ions which can react with unhydrated C\textsubscript{3}A to produce more monosulfate until all the C\textsubscript{3}A or sulfate is consumed (Black et al., 2006, Taylor, 1997). The SO\textsubscript{3}:Al\textsubscript{2}O\textsubscript{3} ratio in cements ranges from 1:2 to 9:10, with an average of about 3:5, which is much less than the 3:2 required to prevent the conversion of ettringite into monosulfate (Bensted and Barnes, 2002).

As temperature rises, the water molecules at the interlayers are removed and the OH\textsuperscript{-} groups of C-S-H gel condense, leading to a more polymerised and disordered structure with a smaller basal-spacing. This results in more adsorption of SO\textsubscript{4}\textsuperscript{2-} ions, thus accelerating the transformation of ettringite into monosulfate. The increase of temperature alters the sulfate equilibrium between the sulfate
hydrates and the hydrated C-S-H, favouring the physical adsorption of sulfates by C-S-H (Divet and Randriambololona, 1998).

Limestone incorporation can also stabilise ettringite formed in cementitious materials at the early age (Matschei et al., 2007, Zajac et al., 2014, Ma et al., 2020). This is because in the presence of limestone, the unreacted C₃A can react with calcium carbonate instead of ettringite, inhibiting the transformation of ettringite to monosulfate.
Table 2.3 Summary of decomposition temperature of ettringite under different conditions

<table>
<thead>
<tr>
<th>Source of ettringite</th>
<th>Existing condition</th>
<th>Heating temperature (° C)</th>
<th>Products heating</th>
<th>Characterization</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ettringite in cement pastes</td>
<td>Dry environment</td>
<td>66</td>
<td>Ettringite</td>
<td>XRD</td>
<td>(Mehta 1972)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>93</td>
<td>Ettringite, monosulfate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moist hot environments</td>
<td>1 h heating at 93</td>
<td></td>
<td>Little reduction of ettringite peak</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Saturated steam with autoclave</td>
<td>At 149 for 1 h</td>
<td></td>
<td>Ettringite, monosulfate</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>At 232</td>
<td></td>
<td>Ettringite, monosulfate and a large amount of hydrogarnet (3H₂O·Al₂O₃·6 H₂O)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure ettringite prepared by mixing C₁₂A₇ with Ca(OH)₂ and gypsum</td>
<td>Saturated steam for 8 hours (autoclave)</td>
<td>At 110</td>
<td>Ettringite</td>
<td>DHA with a heating rate of 10k/min, XRD</td>
<td>(ŠATAVA and VEPŘEK, 1975)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>111</td>
<td>Monosulfate, C₅SH₀.₅</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt;190</td>
<td>C₃AH₆, CI₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt;280</td>
<td>C₄A₃H₃₅, CH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure ettringite prepared by stirring anhydrous tricalcium aluminate with gypsum at mole ratio of 1 to 3 in excess redistilled water for 10 days at room temperature</td>
<td>Pure water one hour boiling in water with the splitting of 2.25 moles sulfate</td>
<td>100</td>
<td>Monosulfate</td>
<td>XRD</td>
<td>(Ghorab and Kishar 1985)</td>
</tr>
</tbody>
</table>
### Table 2.3 (continued)

<table>
<thead>
<tr>
<th>Source of ettringite</th>
<th>Existing Condition</th>
<th>Heating temperature (°C)</th>
<th>Products heating</th>
<th>Characterization</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ettringite from the hydration of $C_4A_3S$ with $CaSO_4$ and $Ca(OH)_2$</td>
<td>In the range of 100 psi to 600 psi in deionized water (autoclave)</td>
<td>130-150</td>
<td>Monosulfate, a small amount of hemihydrate ($C\overline{S}H_{0.5}$) and anhydrite ($C\overline{S}$)</td>
<td>XRD, SEM</td>
<td>(Ogawa and Roy 1981)</td>
</tr>
<tr>
<td></td>
<td>In a 20% NaCl solution, a range of 100 psi to 600 psi (autoclave)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Between 95 and 105 in</td>
<td></td>
<td>Gypsum, Friedel's salt ($C_3A \cdot CaCl \cdot H_{10}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Synthetic ettringite</td>
<td>At ordinary humidity</td>
<td>110-150</td>
<td>Monosulfate, $C\overline{S}H_{0.5}$</td>
<td>TG with a heating rate of 10 k/min, XRD</td>
<td>(Taylor 1997)</td>
</tr>
<tr>
<td>Cr(III)-ettringite from synthesis of $Cr_2(SO_4)_{3} \cdot 18H_2O, CaCO_3$</td>
<td>At ambient environment</td>
<td>100</td>
<td>Began to decompose</td>
<td>TG with a heating rate of 12K/min, XRD</td>
<td>(Wieczorek-Ciurowa, Fela et al. 2001)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>$CaSO_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>$CaSO_4, CaCrO_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>800</td>
<td>$CaSO_4, CaO, Cr_2O_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Synthetic ettringite from stirring mixture solution of $Ca(OH)_2$ and $Al_2(SO_4)_3$ for 24 h</td>
<td>In NaOH solutions at above 0.5 M with Ca$_3$S</td>
<td>80</td>
<td>Monosulfate, Alite, calcium hydroxide, calcium carbonate</td>
<td>TG with a heating rate of 5k/min, XRD, SEM, NMR</td>
<td>(Shimada and Young 2004)</td>
</tr>
<tr>
<td>Source of ettringite</td>
<td>existing Condition</td>
<td>Heating temperature (°C)</td>
<td>Products heating</td>
<td>Characterization</td>
<td>References</td>
</tr>
<tr>
<td>---------------------------------------------------------</td>
<td>-----------------------------------------</td>
<td>--------------------------</td>
<td>-----------------------------------------------------</td>
<td>-------------------------------------------------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>Natural Ettringite specimen ettringite</td>
<td>Exposed to atmosphere</td>
<td>138</td>
<td>Amorphous phase because no crystalline substance is detected by XRD</td>
<td>TG with a heating rate of 10 K/min, DSC, XRD</td>
<td>(Jiménez and Prieto, 2015)</td>
</tr>
<tr>
<td>Synthetic ettringite</td>
<td>Exposed to atmosphere</td>
<td>130</td>
<td>Gypsum, calcite</td>
<td>TG with a heating rate of 10 K/min, DSC, XRD</td>
<td>(Jiménez and Prieto, 2015)</td>
</tr>
<tr>
<td>Synthetic synthesized in distilled water from calcium nitrate, sodium aluminate and sodium sulphate</td>
<td>The sample was filtered and dried at 50 until characterization</td>
<td>93</td>
<td>Monosulfate</td>
<td>TG with a heating rate of 25 K/min, DSC</td>
<td></td>
</tr>
<tr>
<td>Ettringite synthesized by the method of Struble et al (Struble, 1986)</td>
<td>In the presence of ammonium sulfate solution</td>
<td>120</td>
<td>Monosulfate</td>
<td>TG-DSC with a heating rate of 10 K</td>
<td>(Wang et al., Guimarães et al., 2016)</td>
</tr>
</tbody>
</table>
2.2.5 Summary

As stated above, the decomposition mechanism of ettringite is very complex, and considerably influenced by temperature, pressure, humidity, solution pH, \( \text{SO}_3: \text{Al}_2\text{O}_3 \) ratio and components in different systems as well as some components dissolved in water. In general, ettringite stability decreases with the increase of temperature and pressure as well as the decrease of humidity. The pH value where ettringite remains stable is between 10.5 to 13.0, but this changes as the surrounding environment of ettringite changes. Foreign ions incorporated into ettringite also affect the thermal stability of ettringite. Moreover, when TG is used to determine the decomposition temperature of ettringite, the preparation method of ettringite and the heating condition of ettringite are always different, so that the decomposition temperature measured varies significantly. This can explain why there is very little consistent information about the stability of ettringite and its decomposition temperature obtained until now.

2.3 Delayed ettringite formation and its influence on the properties of concrete

DEF can be defined as the re-formation of ettringite from AFm in a hardened cement-based matrix, in which the sulfate comes from inside the cement paste and is recognised as one of the potential destructive reactions affecting the durability of concrete (Ozol and Strand, 2000, Sahu and Thaulow, 2004). It is
heavily affected by its early-age temperatures caused by heat treatment, or internal heat released during hydration. Hence, for precast concrete the maximum curing temperature is crucial to limit the DEF. To understand the mechanism of DEF, detailed relevant information is given below.

2.3.1 Fundamentals

The natural occurrence of ettringite was first found in 1874 (Dana, 1997). It is a rare, naturally occurring mineral, but it is prevalent in the chemistry of PC, as an important hydration product. This is because $C_3A$, one of the four main phases in a typical PC clinker, hydrates very rapidly with water when mixed with water, and causes flash set without the presence of gypsum. To adjust the setting time and the hardening speed of cement paste, gypsum is added to react with $C_3A$ rapidly to form an ettringite membrane around the $C_3A$ grains and therefore slows down the hydration rate, as shown in Equation (2.6) (Taylor, 1997):

$$3CaO \cdot Al_2O_3 + 3(CaSO_4 \cdot 2H_2O) + 26H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$$

This formation of ettringite takes place in the plastic stage of the cement mixture, so it does not produce any destructive expansion. At 24-48 hours, once all gypsum is consumed, ettringite reacts further with $C_3A$ to form the monosulfate phase, as shown in Equation (2.7) (Taylor, 1997):

$$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + 3C_3A + 27H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 2CaSO_4 \cdot 42H_2O$$
\[2(3\text{CaO} \cdot \text{Al}_2\text{O}_3) + 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O} + 4\text{H}_2\text{O} \rightarrow 3(3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O})\]

(2.7)

From the above two equations, the content of ettringite in a PC paste should be relatively high in the initial 24 hours, then decrease gradually with time, as shown in Figure 2.10.

![Figure 2.10 Schematic illustration of the formation of reaction products and the reduction of the volume of pore space with time in a Portland cement paste (Locher, Richartz, and Sprung, 1976)](image)

In a hydrated PC paste, both ettringite and monosulfate phases coexist, the ratio of which is dependent on the initial content of both C₃A and gypsum. The morphology of monosulfate is quite different from that of ettringite, as compared in Figure 2.11. The morphology of monosulfate is recognized as thin hexagonal plates (Figure 2.11 (b)), while the morphology of ettringite is hexagonal prisms or needles (Figure 2.11 (a)).
Figure 2.11 Characteristic crystal morphologies of (a) Ettringite (AFt) and (b) monosulfate (AFm) (Bothe Jr and Brown, 1998)

If the PC hydration products are exposed to a wet environment with additional sulfate, a further reaction (shown in Equation (2.8)) will happen, which results in the reformation of ettringite which leads to cracking and spalling of hardened concrete caused by expansion (Fu and Beaudoin, 1996).

\[
3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O} + 2(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}) + 16\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}
\]  

(2.8)

There are several arguments for the mechanism of the expansion associated with DEF as follows: 1) The simplest explanation for expansion is that the precipitation of ettringite results in an increase in the solid volume (Polivka, 1973). However, no evidence has shown that there is a direct link between the expansion and the amount of ettringite formed (Taylor et al., 2001). Moreover, there are also other hydrated products like C-S-H which could result in solid volume increase but do not necessarily cause expansion. 2) Mehta (1973) found that colloidal ettringite with high specific surface could lead to expansion by absorbing a great number of water molecules from environment. However, there is not enough theoretical
evidence to support this hypothesis. Furthermore, he claimed that colloidal ettringite only formed in the presence of lime or calcium hydroxide, whereas expansion also occurred when lime was absent. 3) Another opinion claims that expansion arose from the solid formation of ettringite surrounding the cement grains, but the totally different crystal structure of ettringite from any of its precursors made such theories invalid (Ogawa and Roy, 1981). However, the most plausible one is the theory of crystallization pressure (Bizzozero et al., 2014). This theory was developed and experimentally validated more than a century ago (Taber, 1916). Namely, when monosulfate reforms into ettringite in confined pores from a supersaturated solution, a crystallization pressure is generated and exerted on the pore walls in the matrix of concrete. Once this pressure exceeds the elastic limit of the system, expansion will happen, thus leading to cracking (Skalny et al., 2002).

However, an alternative hypothesis for the breakdown of primary ettringite in cement paste at elevated temperature has also been presented. Above 65°C, calcium silicate hydrate (C-S-H) adsorbs sulfate ions quickly from gypsum, reducing the amount available for ettringite formation. Consequently, the ettringite formed in the first few hours of hydration reacted with C₃A to form a certain amount of monosulfate. Later on, when the temperature of the C-S-H is returned to normal, the monosulfate reacts with sulfate that is slowly released into
the pore solution to reform DEF (Fu et al., 1995, Divet and Randriambololona, 1998).

2.3.2 Damage caused by DEF

Over the past few decades, most damage in precast concrete products cured at elevated temperatures has been largely attributed to DEF in precast concrete products cured at elevated temperatures (Sahu and Thaulow, 2004, Ozol and Strand, 2000). A number of case studies have demonstrated that DEF can lead to cracking in heat cured precast concrete components. A typical example is that in Finland concrete ties were subjected to high temperature steam cured at 75-80°C during precast manufacture. After service of 15 years, large amounts of ettringite was observed in the pores and cracks of concretes (Tepponen and Eriksson, 1987). Another example is the DEF occurred in the bleacher seats in the Brewer Stadium, Appalachian State University, Boone, NC. The bleacher seats were made of steam-cured, precast lightweight concrete channel sections in 1962, but within a few years, spalling was observed. By 1995, approximate 350 of 860 precast channel sections were deteriorated as shown in Figure 2.12 and Figure 2.13 (Ozol and Strand, 2000).
In Sweden, a number of steam cured railroad ties showed premature deterioration caused by DEF (Sahu and Thaulow, 2004). These ties were manufactured from 1992 to 1996, but by the winter of 1999, it was observed that there was obviously visible map cracking in a few ties.

In addition to the concrete products cured with accelerated curing at elevated temperature, there are also concerns that cracking may occur in large, in-situ concrete structures resulting from the build-up of heat from hydration in the early stage. For instance, in the southern U.S.A, bridge columns were cast in the late...
1980s, but after service of 10 years, they showed premature deterioration caused by DEF in some columns (Thomas et al., 2008).

In summary, DEF has indeed caused deterioration of precast concrete cured at temperatures of higher than 70°C, leading to serious durability issues of precast concrete. To avoid DEF, it is essential to understand the factors resulting in DEF.

### 2.3.3 Factors affecting the formation of DEF

Recognising the factors that contribute to the formation of DEF can provide a better understanding of the complex expansion mechanism of DEF, thus helping to find suitable preventive measures to avoid DEF-induced expansion. From the wide range of research carried out, three main factors have been shown to contribute to the formation of DEF, namely, late sulfate release (from cement clinker, aggregate or thermal decomposition of ettringite), any pre-existing micro-cracks, and intermittent or continuous exposure to a moist environment (Lawrence, 1995, Taylor et al., 2001, Fu and Beaudoin, 1996, Divet and Randriambololona, 1998, Zhang et al., 2002, Collepardi, 2003a, Sahu and Thaulow, 2004, Barbarulo et al., 2005, Tosun, 2006, Escadeillas et al., 2007, Adamopoulou et al., 2011, Pavoine et al., 2012, Nguyen et al., 2013). The details of each factor will be given as follows.

**(1) Presence of monosulfate and sulphate**

The presence of monosulfate and sulphate are essential elements for the
formation of DEF. In the case of precast industry, when the concrete products subjected to steam curing, the monosulfate and sulfate could come from the thermal decomposition of the primary ettringite formed during the first 24 hours. It is commonly agreed that high curing temperatures (>70°C) can potentially cause DEF (Kosmatka and Wilson, 2011, Odler and Chen, 1995, Ghorab et al., 1980). In 1995, Lawrence (1995) studied the expansion behaviour of 55 Portland cements cured over the temperature range of 65 to 100°C and found that the critical curing temperature for DEF lies between 65 and 70°C.

(2) Presence of micro-cracks

Pre-existing micro-cracks are considered as another essential element for delayed ettringite formation as the formation of ettringite requires sufficient space. In precast concrete, pre-existing micro-cracks can be caused by high-temperature curing, a too high rate of temperature rise or decrease, and a too short pre-curing period at room temperature (Fu and Beaudoin, 1996, Fu et al., 1994, Wong et al., 2009).

Fu et al.(1994) studied the significance of pre-existing cracks on nucleation of DEF in steam cured cement paste. Microcracks were induced during the specimen preparation process, and a study on expansion was carried out under different curing conditions that included moist curing at 23°C, steam curing at 65°C followed by moist curing at 23°C and steam curing at 90°C followed by moist
curing 23°C. The results showed that: 1) under the supersaturation condition of the solution in cement pastes, ettringite prefers to form in crack zones rather than on solid plane surfaces; 2) high temperature curing and drying of the cement paste with pre-existing cracks provide critical conditions for the formation of DEF; and 3) larger pre-existing cracks can give rise to high expansion due to DEF. Therefore, pre-existing micro-cracks were considered as a prerequisite to DEF. Diamond (Diamond, 1996) also found that prior cracking induced by ASR, freezing, or even shrinkage provides space for DEF.

(3) Exposure to moisture

The third element necessary for DEF is intermittent or continuous exposure to water or a wet environment. The presence of water in the concrete pores is essential for the migration of reactant ions including $\text{SO}_4^{2-}$, $\text{Al(OH)}_4^-$ and $\text{Ca}^{2+}$ to the microcracks where ettringite precipitation can take place (Fu et al., 1994, Escadeillas et al., 2007). Field experience indicates that concrete ties subjected to alternative rainy and sunny actions undergo more destruction than those subjected to rain but in permanent shadow. This difference in behaviour could be ascribed to the crucial role played by the degree of supersaturation which favours DEF precipitation (Sahu and Thaulow, 2004, Yang et al., 1999).

As for precast concrete, the most effective way to mitigate DEF-induced deterioration is to limit the maximum curing temperature to avoid ettringite decomposition and reduce microcracks (Famy, 1999, Collepardi, 2003b).
However, the decomposition temperature of ettringite depends on its thermal stability under different conditions (Wang et al., 2016, Ndiaye et al., 2017, Kaufmann et al., 2016). Therefore, this is why various limits have been given on the maximum curing temperature for manufacturing precast concrete as shown in Section 2.1.4.

2.3.4 Summary

Based on the details related to DEF illustrated above, one of essential factors resulting in DEF is the presence of monosulfate, which often comes from the decomposition of ettringite caused by an elevated environmental temperature or by depletion of sulfate ions due to the adsorption by C-S-H gel generated during the hydration of cement. This is exacerbated by an elevated environmental temperature which facilitates the adsorption of sulfate ions by C-S-H gel, accelerating the transformation of ettringite to monosulfate. When the precast concrete is exposed to wet environment during its service period, monosulfate can react with sulfate ions desorbed from the C-S-H gel, reforming into ettringite (DEF) in confined pores from a supersaturated solution. This DEF leads to the generation of a crystallization pressure, exerted on the pore walls in the matrix of concrete. Once this pressure exceeds the elastic limit of the system, expansion occurs and leads to cracking. Therefore, to avoid DEF in precast concrete, it is particularly important to limit the highest curing temperature for manufacturing precast concrete.
2.4 Potential of microwave curing for precast concrete

2.4.1 Introduction

It is well known that steam curing increases the early strength of concrete, but it can cause a decrease in the long-term strength of concrete compared to normal curing (Ba et al., 2011, Ramezanianpour et al., 2013, Kosmatka and Wilson, 2011). One reason is that steam curing uses conventional thermal heating relying on heat conduction. Generally, concrete is not a good thermal conductor because of its comparatively low thermal conductivity which is in the range of 1.4-3.6 W/(m·K) (Kim et al., 2003). As steam curing proceeds, heat is transferred from the external surface to the interior by thermal conduction which leads to a thermal gradient. In addition, since the components in concrete have different thermal expansion coefficients, thermal stresses easily form inside the concrete, causing microcracks which are harmful to the long-term strength of concrete, as well as potentially lead to DEF (Boukendakdji et al., 1996). Therefore, in a manner of speaking, it is the non-uniform heating limiting the steam curing (Kosmatka and Wilson, 2011).

In addition to the non-uniform heating, steam curing is an energy-intensive process, as it usually takes more than 10 hours to perform a curing cycle prior to the concrete specimens being demoulded. This energy consumption results from the following aspects. Firstly, water, with its high heat of vaporisation leading to
considerable energy consumption as the transformation rate of water to steam is slow. Secondly, the specimen heating is a thermal conduction process from the exterior to the interior of the concrete pieces and takes a long time, in which large amounts of energy are required. Thirdly, large amounts of energy are absorbed by the moulds as well as by curing tunnels and racks, resulting in a further increase in energy consumption (Kuch et al., 2013).

Microwave heating, as a high-frequency electromagnetic heating, are capable of reducing the non-uniform heating caused by steam curing due to a phenomenon known as volumetric heating of microwave. Water is a good microwave absorber due to its polar molecules with a high dielectric constant of 80.3 at the frequency of 2.45 GHz at room temperature and can be readily heated up in microwave (Franks, 2012). In microwave heating/curing of concrete, the electromagnetic energy can be easily converted into thermal energy through absorption by the components of concrete. Based on this, it is possible to replace steam curing with microwave curing to accelerate cement hydration (Ong and Akbarnezhad, 2014, Wu et al., 1987, Makul et al., 2010, Rattanadecho et al., 2016). Compared to steam curing, microwave curing has the following advantages. Firstly, microwaves can heat a specimen instantly and volumetrically, reducing the non-uniform heating, so the performance of the cement-based materials might be improved (Christo, 1989). Secondly, the heating rate and the energy absorption can be better controlled, which allows concrete to reach the desired curing
temperature in a shorter period, thus saving a great amount of energy (Rattanadecho et al., 2016, Makul et al., 2014b). At the same time, a shorter duration results in a shorter turnover time, allowing a higher production rate and less mould is required (Mak et al., 2003).

As microwave curing can bring potential benefits including increased productivity, capital saving and reduction of storage area, it provides a great opportunity to transform the precast concrete industry in order to reduce the CO₂ emission of construction sector. If microwave curing is applied to precast concrete, one of the factors needed to be considered is the thermal stability of ettringite as this will eventually determine the limit of the temperature which could be applied in the future microwave curing regime. However, up to date, there is no existing research on the influence of microwave curing on the thermal stability of ettringite.

2.4.2 Mechanisms of conventional heating

In order to demonstrate the advantages of microwave curing over steam curing, it is rational to start from conventional heating and to compare it with microwave curing. The process of the conventional heating is actually a process of heat transfer resulting from a temperature difference that can be considered as a driving force leading to heat flow (Goldstein et al., 2005). As mentioned above, steam curing is one of the conventional heating methods. In general, there are
three types of heat transfer mechanisms involved in conventional heating, namely, conduction, convection, and radiation (Janna, 1999).

Conduction is a dominant mode of heat transfer through solids, liquids and gases in conventional heating. As for solids, conduction is the only mode of heat transfer. For fluids, conduction is the primary mode of heat transfer only when the bulk velocity of fluid is zero. Gases are the poorest conductor because their molecules are relatively far apart and so interact less frequently than those in solids and liquids (Incropera et al., 2007).

There are two types of heat transfer with convection which is due to the bulk movement of liquid or gas. One termed ‘forced convection’, is caused by an external device such as a fan which provides fluid movement, enhancing the heat transfer. The other is termed ‘natural or free convection’, which results from the density differences of the fluid or gas due to the process of energy transfer (Eckert et al., 1997).

Radiation, on the other hand, is a mode of energy transfer by electromagnetic radiation. In fact, all substances emit radiant heat causing heat to flow from high to low temperature regions. Therefore, a cooler substance absorbs more radiant energy than it emits (Thomas, 1980).
In the case of the steam curing employed in precast concrete industry, the heating process is mainly dependent on the heat transfer caused by conduction and, to a very much lesser extent, convection. Steam curing takes considerable time for the centre of concrete to reach the target temperature. This can be very well exemplified by curing a huge concrete slab as concrete is a poor heat conductor.

### 2.4.3 Mechanisms of microwave heating

#### 2.4.3.1 Introduction

Microwaves are a form of electromagnetic wave with a frequency in the range of 300 MHz to 300 GHz with corresponding wavelengths ranging from 1.0 meter to 1.0 millimetre (Mehdizadeh, 2015). A microwave is composed of a coupled oscillating electric field and a magnetic field, which are always perpendicular both to each other and to the direction of wave propagation. The propagation of the electromagnetic wave is shown in Figure 2.14 (Metaxas and Meredith, 1983). The primary frequencies used for industrial heating are 2.45 GHz and 896 MHz.
Electromagnetic wave: A ‘vertically polarized’ electromagnetic wave with wavelength $\lambda$ has its electric field vector $E$ (red) oscillating in the vertical direction. The magnetic field $B$ is always at right angles to it (blue), and both are perpendicular to the direction of propagation ($z$) (Metaxas and Meredith, 1983)

2.4.3.2 Microwave heating system

A typical microwave-heating system consists of four basic components: a microwave generator (i.e. magnetron), a waveguide (an applicator to deliver the power to the material), a control system, and a microwave cavity. The microwave generator is connected to a power supply unit, which converts the 50 Hz alternating current (a.c.) to the desired fixed frequency for microwave radiation. Waveguides are important components that are usually made of sheet metal which guide the microwaves to a target (i.e. sample) placed in a microwave cavity (Cronin, 1995). A control system is used to monitor and regulate the power to the target. The microwave cavity is a chamber in which specimens are processed, where the microwave energy is absorbed and reflected.

2.4.3.3 Thermal effect of microwave

The mechanism by which microwaves interact with substances depends on the physical state, the dielectric properties and the temperature of the material.
Generally, there are two ways in which microwaves can interact with the material, described as thermal processes and non-thermal interactions.

The thermal process induced by microwave radiation has been widely accepted by researchers, which refers to the interaction based on the volumetric or specific nature of microwave heating. There are two forms of heating processes associated with the thermal process which applies to the majority of solid and liquid substances (Robb, 2005). One is dielectric heating, the process occurs when the dipolar molecules in a material re-orientate themselves to the applied electric field. The second is conduction heating which takes place when a poor electrical conductor is placed in the microwave field and it is often heated by the surrounding dielectric substances. It should be noted that similar mechanisms can operate where a magnetic field interacts with and causes heating in magnetic materials.

(1) **Dielectric heating**

For materials to be dielectrically heated, they must contain permanent or induced dipoles (either electric or magnetic). When these are placed in an electric field induced by microwaves, the dipolar molecules within the materials will orientate in order to follow the alternating high frequency electric field, as shown in Figure 2.15 (Makul et al., 2009). As the charged particles are displaced from their equilibrium positions, they lag behind the alternation of the electric field and are
unable to align themselves with the electric field, resulting in vibration and friction between the particles. In this way, the microwave energy is converted into thermal heat energy, thereby heating materials instantly and volumetrically (Makul et al., 2014b).

Figure 2.15 Mechanism of microwave curing (Makul et al., 2009)

The characteristics of microwaves propagating in a material can be described by its complex permittivity, \( \varepsilon \) (F/m), which consists of a real part \( \varepsilon' \) and an imaginary part \( \varepsilon'' \) (de la Hoz and Loupy, 2013). Equation (2.9) shows the relation between them.

\[
\varepsilon = \varepsilon' - j\varepsilon''
\]  

(2.9)

where \( \varepsilon \) is the complex permittivity; \( \varepsilon' \) is the dielectric constant, which is the real part of the complex dielectric permittivity, measuring the ability of a material to be polarised by an electric field; \( j = \sqrt{-1} \); \( \varepsilon'' \) refers to the dielectric loss, which is the imaginary part of the complex dielectric permittivity, indicating the ability of a material to convert dielectric energy into heat. The ratio of the energy lost (the dielectric loss) to the energy stored (the dielectric constant) in a material is expressed as the dielectric loss tangent \( \tan \delta \), as given in Equation (2.10).

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'}
\]  

(2.10)
\( \tan \delta \) determines the heating efficiency of a material in a dielectric field. It defines the ability of a material to convert electric energy into heat energy at a given frequency and temperature. The value \( \tan \delta \) is affected by several factors including electromagnetic waves, the temperature, the physical state and composition of the mixture (Fini and Breccia, 1999, Mehdizadeh, 2015).

Moreover, the dielectric constant \( \varepsilon' \) and the dielectric loss \( \varepsilon'' \) are governed by Debye Equations (2.11) an (2.12) (Meredith, 1998).

\[
\begin{align*}
\varepsilon' &= \varepsilon'_\infty + \frac{\varepsilon'_0 - \varepsilon'_\infty}{1 + \omega^2 \tau^2} \\
\varepsilon'' &= \frac{\varepsilon'_0 - \varepsilon'_\infty \omega \tau}{1 + \omega^2 \tau^2}
\end{align*}
\]

where \( \varepsilon'_\infty \) and \( \varepsilon'_0 \) are defined as the high frequency and static dielectric constants, respectively; \( \omega \) represents the rotation frequency of polarisation build-up; \( \tau \) is indicative of the corresponding relaxation time characteristic of the material.

(2) Conduction heating

Conduction heating occurs when a material behaves as a poor electrical conductor in the microwave field and can act alone or in combination with dielectric heating. The resistivity of a material is finite and consequently generates heat if a current flows (Gupta and Leong, 2008). A good example is an ionic salt solution where the presence of dissolved salt in pure water greatly increases the conductivity. If the concentration of salt is sufficient, the conduction heating that
arises may dominate the dielectric effects. If the conduction losses are considered, the complex permittivity can be expressed in Equation (2.13).

\[
\varepsilon = \varepsilon'_\infty + \frac{(\varepsilon'_0 - \varepsilon''_\infty)}{(1 + i\omega \tau)} - \frac{i\sigma}{\omega \varepsilon'_0}
\]  

(2.13)

where \( \sigma \) is the conductivity of the material. For solid materials processed at high temperatures, conduction losses dominate (Desiraju, 2001). As the electrical field frequency (GHz) is slow on the time scale of ionic and electronic motion (THz), the charged particles will move in phase with the electric field (Meredith, 1998).

The magnitude of the conduction effect is proportional to the number of charge carriers (ions and electrons) that are free to couple with the electric field, and that depends on temperature. Generally, at higher temperatures, the bonds between ions in ionic crystals are considerably weakened so most salts become more soluble and the ions can move, while in covalent materials the electrons can be promoted to the conduction band (Huang et al., 2009). As a result, microwave absorption and heating rate increase rapidly with temperature, e.g. the conductivity of alumina, a very low microwave-absorbing material at room temperature, increases with a rise of temperature, as electrons are promoted into the conduction band from the O(2p) valence band (Mingos and Whittaker, 1997).

Many researchers use increasing temperature as a common method to couple microwaves with poor microwave-absorbing (low dielectric constant) materials.

For some low dielectric constant materials, once they are heated to their critical temperatures, microwave absorption becomes sufficient to cause self-heating.
This can account for why some hybrid heating techniques e.g. a gas or electric furnace in conjunction with microwaves, were used in some studies (Wroe and Rowley, 1996).

### 2.4.3.4 Non-thermal effect

Non-thermal effects of microwave were claimed to occur initially in the study on hydrolysis and esterification reactions under microwave heating (Galema, 1997). These results derive from increases in reaction rate that could not be explained by the heating characteristics of microwaves. These non-thermal interactions of microwaves with materials may include changes in activation energy and the Arrenhius pre-exponential factor, and mass transport enhancement.

1. Change of activation energy and the Arrenhius pre-exponential factor

A number of studies have shown that exposure to microwave radiation can increase the chemical reaction rate significantly, which has been attributed to a non-thermal effect generated by microwaving (Stuerga and Gaillard, 1996, Wroe and Rowley, 1996, Robb, 2005, Galema, 1997). This non-thermal effect has been attributed to the changes in the activation energy and the Arrenhius pre-exponential factor. In the Arrhenius’ equation shown in Equation (2.14), the pre-exponential Arrhenius factor, A, depends on the frequency of vibration of atoms at the reaction interface (Menezes et al., 2012). In a microwave field, the dipoles vibrate at the frequency of microwave radiation, so microwaves could change the value of the pre-exponential factor A, which is a constant for each chemical
reaction and varies depending on the order of the reaction (Binner et al., 1995).

For activating a component in the reaction pathway, changes could occur as well as the activation energy $E_a$ (Fini and Breccia, 1999, Gupta and Leong, 2008). Either of these could result in an increase of the chemical reaction rate $K$.

$$K = Ae^{-Ea/RT}$$  \hspace{1cm} (2.14)

where $T$ is the temperature in °K and $R$ is the universal gas constant.

For example, Brosnan et al. (2003) performed a study involving microwave and conventional heating. They showed that microwave-sintered samples reached 95% density at 1350°C versus 1600°C for conventionally heated samples. One possible reason is that the activation energy has been lowered to $85 \pm 10$ kJ mol$^{-1}$ under microwave compared to $520 \pm 14$ kJ mol$^{-1}$ under conventional heating. A suggested mechanism may be that the alignment of molecules in microwave electric field generates heat. The heat simultaneously increases the probability of contact between molecules and atoms (entropy effect), enhancing the reaction rate and reducing activation energy (Fini and Breccia, 1999), thus leading to the reduction of the minimum energy required to start a chemical reaction.

Moreover, Binner et al. (1995) reported that synthesis of titanium carbide powder via the carbothermal reduction of the oxide with microwave are more than three times faster than those observed during conventional processing at the same temperature. In their study, they attributed this to the increase in the Arrhenius
pre-exponential factor, $A$, without changing the activation energy. Nevertheless, the pre-exponential factor, $A$, of reaction in a microwave field is different from that in a conventional heating field, which can be expressed in equation (2.15).

$$A = \gamma \lambda^2 \Gamma$$

(2.15)

where $\gamma$ is a geometric factor including the number of nearest-neighbour jump sites; $\lambda$ is the distance between the adjacent lattice planes, i.e. jump distance; and $\Gamma$ is the jump frequency. The jump frequency ($\Gamma$) can be expressed by equation (2.16).

$$\Gamma = \nu \exp\left(\frac{-\Delta G^+}{kT}\right)$$

(2.16)

where $\nu$ is the natural vibration frequency of the atoms, $\Delta G^+$ is the activation energy, $k$ is the diffusion rate constant and $T$ is the absolute temperature. Since $\Delta G^+$ seems not to be affected in many cases, it would appear that the microwave field is somehow affecting $\nu$, especially for phenomena relying on diffusion along grain boundaries or across surfaces where frequency factors are less well defined (Binner et al., 1995).

(2) Mass transport enhancement

High temperatures are necessary to activate the mass transport phenomena. It has been demonstrated that microwave heating can not only increase heating efficiency, but also can enhance the reaction rate as a result of the increase in the mass transport rate (Ostoréro et al., 1997, Vaidhyanathan et al., 1998).
Mass transport in a solution or solid phase implies diffusion of some species through the solution or the structure. An important mechanism in crystalline solids is the diffusion of vacancies. Vacancy formation requires energy, $U$, to deform the lattice, but this results in an increase in the entropy, $S$. The vacancy concentration established from the minimum Helmholtz energy at equilibrium depends on the temperature and the stresses acting on the crystal body (Stuerga and Gaillard, 1996). The Helmholtz energy $F$ is given by:

$$F = U - TS$$  \hspace{1cm} (2.17)

where $T$ is a given temperature. The vacancy diffusion coefficient, $D$, is proportional to the probability of atom transferring into a neighbouring vacant lattice site as follows (Booske et al., 1992):

$$D \propto a^2 v_0 \exp \left(-\frac{\Delta A}{kT}\right)$$  \hspace{1cm} (2.18)

where $a$ is the lattice parameter, $v_0$ is the vibration frequency of the atom and $k$ is Boltzmann’s constant. Equation (2.18) is similar to the Arrhenius equation, which means that diffusion is a thermally activated process when the temperature exceeds some critical value. This equation has been used to describe the mechanism of sintering ceramic (Agrawal, 1998, Whittaker, 2005, Menezes et al., 2012). Diffusion can occur in several ways including at the surface, at the grain boundary, and through the bulk. It was demonstrated that microwave field can provide a nonlinear driving force for mass transport of ions (Rybakov et al., 1997, Whittaker, 2005, Li et al., 2010, Wroe and Rowley, 1996).
There are two leading theories which can account for the enhanced ion diffusion. They are termed as ‘non-equilibrium excitations’ and ‘ponderomotive effects’ (Booske et al., 1992). As for the theory of non-equilibrium excitations, it is reported that under these non-equilibrium conditions, some lattice vibrations will have more energy than usual for a given temperature, resulting in increased probability for atoms to diffuse into adjacent vacancies.

A ponderomotive force is a nonlinear force that a charged particle experiences in an inhomogeneous, oscillating electromagnetic field such as microwaves, causing the particle to move forwards the region of weaker field strength. According to the theory of ponderomotive effects, transport effects are the result of gradients in charge mobility, e.g. near surfaces and boundaries. This is because the electric field from microwave radiation is concentrated at the interparticle boundaries or lattice defects and results in an enhancement of ion mobility. This theory was first clearly demonstrated in the study of diffusion in microwave-heated ceramics (Whittaker, 2005). In crystalline solids, the microwave field acts on electrically charged vacancies.

2.4.4 Microwave curing concrete

Concrete is a dielectric material, so its intrinsic properties will affect the way it interacts with the electric and magnetic fields of microwaves (Abdelghani-Idrissi, 2001, Makul et al., 2014b). The dielectric properties of concrete are a function of
a number of factors, such as the constituent materials, mix proportions, water content, microwave frequency, and temperature (Ong and Akbarnezhad, 2014).

In concrete, the main components are cement, water, sand and coarse aggregate. All these components can absorb microwave energy to some degree. Their dielectric constants are listed in Table 2.4 with water being the highest by far.

<table>
<thead>
<tr>
<th>Components</th>
<th>Cement</th>
<th>Water</th>
<th>Silica sand</th>
<th>Coarse aggregate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric constant</td>
<td>2.2</td>
<td>80.3</td>
<td>2</td>
<td>7~9</td>
</tr>
</tbody>
</table>

As highlighted before, under the electromagnetic field, dipolar molecules can vibrate, generating friction between the molecules. This effectively converts microwave energy into heat energy instantly (Metaxas and Meredith, 1983). Hence, microwave curing is particularly efficient for heating dielectric materials with high dielectric constants. From the data in Table 2.4, water with its high dielectric constant of 80.3 will be heated by microwaves rapidly and volumetrically. Hence, precast concrete can be readily heated by microwaves through the heat dissipation caused by the water molecules vibrating because of its high dielectric constant. It is reported that microwave curing is at least double the efficiency of conventional methods in terms of heating dielectric materials (Rattanadecho et al., 2016). This is because when microwave propagates into a dielectric material, the microwave energy is absorbed by the dielectric material and then converted to heat instantly and volumetrically within the region that microwave reaches,
leading to the so called efficient ‘volumetric heating’ (Metaxas and Meredith, 1983, Ong and Akbarnezhad, 2014).

This unique capability of microwave curing has attracted the attention of civil engineers, and concrete specialists. Since the 1980s, microwave curing has been used to make cement-based past/mortar/concrete in lab-scale research due to its merits of fast heating and volumetric heating. It enables the curing period to be shortened with the matrix more uniformly heated compared with traditional thermal curing, which has been demonstrated in the following research.

In 1987, microwave was initially used to speed up the hydration of PC mortars (Wu et al., 1987). The mortar specimens made with type I cement were cured by microwaving for 15 to 30 minutes and then subjected to water curing at 20°C for 3, 7 and 28 days. The results showed that for mortar bars cured by microwaves, the increase in strength at early ages was greater than that at later ages. The 28-day compressive strength of the samples subjected to the 30-minute microwave curing was higher than those subjected to traditional thermal curing. This indicated that microwave curing did increase the long-term strength of mortar. The authors considered that the enhanced early-age strength was attributed to an increase of hydration rate. This was also confirmed by their permeability measurements, which showed the microwave cured specimens had a lower permeability.
Other studies associated with microwave treatment on cement mortar or concrete have also been performed. Hutchison et al. (1991) used microwaves to accelerate the hydration of cementitious materials. Their results showed that although microwave curing shortened the induction period and enhanced the rate of hydration in the first 24 hours, but it did not alter significantly the 28-day compressive strength of the specimens compared to the specimens cured at 20°C.

Leung and Pheeraphan (1995) also showed that with only 45-minute microwave curing, the 7 day-strength of concrete was superior to that of water bath cured concrete. Moreover, the overall performance of microwave cured concrete (4.5 hours and 7 days) was comparable to that of concrete containing accelerators as well as commercial rapid hardening concrete (Leung and Pheeraphan, 1995). In addition, Oriol and Pera (1995) claimed that microwave curing increased the pozzolanic activity of metakaolin and reduced the curing period (Oriol and Pera, 1995).

The study of microwave curing effects on the 28-day strength of cement-based materials consisting of Type I PC with some pozzolanic materials such as slag, silica fume, or class F fly ash indicated that microwave curing with feedback temperature control greatly reduced the final setting times of cement-based mortars and the 28-day strength was not degraded. At the same time, both
temperature and curing time were important parameters for the improvement of 28-day strength of cement-based mortars cured by microwaving (Sohn and Johnson, 1999).

Kong et al., (2016) revealed that microwave curing improved the compressive strength of mortar before the age of 28 days, reduced the pores in the range of >100 nm greatly, and increased the adsorption of K, S and Mg by C-S-H.

The study by (Rattanadecho et al., 2016) further demonstrated that the early compressive strength of concrete subjected to microwave curing was greater than obtained under air curing or water wet-curing conditions.

Based on the above review on microwave curing cement-based paste/mortar/concrete, it has been demonstrated that microwave curing can be successfully to accelerate the curing process. The work reviewed was generally conducted at laboratory scale. It has also shown that microwave curing can enhance the early-strength of cement-based paste/mortar/concrete compared with conventional curing.

2.5 Research question

To date, a number of studies have reported the effect of microwave on cement hydration (Rattanadecho et al., 2008). However, it is still unclear how microwave
irradiation alters the physicochemical properties of hydration products, including ettringite which is the focus of this thesis. Ettringite is particularly important as its crystal structure and hydration state are sensitive to heating. Based on the non-thermal effects of microwave discussed in Section 2.4.3.4, the process underlying the formation or decomposition of ettringite could potentially be affected by a microwave field due to the unique vibration of the photons at the frequency of microwave irradiation (Binner et al., 1995, Ostoréro et al., 1997, Fini and Breccia, 1999). However, the exact effects on ettringite are not documented in the literature.

Therefore, it is of scientific interest and practical importance to investigate the influence of microwave curing on ettringite. This study will not only help expand the application of microwave heating in precast industry, but it will also provide data that are crucial to the fundamental understanding of microwave interaction with ettringite crystals.

On the basis of the above, the primary research question in this thesis is to investigate the extent to which microwave affects the microstructure and thermal stability of ettringite, in the form of both synthetic material as well as precipitates forming in cement pastes.
Chapter 3 Experimental and Research Methods

3.1 Introduction

This chapter provides detailed information on the materials, heating treatment, sample preparation and characterisation methods used for the experiments carried out in Chapters 4-6.

3.2 Overall experimental programme

Figure 3.1 shows the overall experimental programme. The programme consists of three stages as follows:

Stage 1 (Chapter 4) investigates the microstructure and thermal stability of ettringite synthesised under microwave heating to simulate ettringite formation/decomposition during initial hydration.

Stage 2 (Chapter 5) focuses on the microstructure and thermal stability of pure ettringite and metal ion-doped ettringite. Typically, ettringite formed during the hydration of cements could be doped by various metal ions, the most common of which are Fe$^{3+}$, Cr$^{3+}$ and Mn$^{2+}$. In this study, the ettringite and ettringite analogues of these typical metal ions were synthesised at room temperature, before being subjected to microwave heating.
Stage 3 (Chapter 6) examines the influence of microwave curing on the microstructure and thermal stability of ettringite formed in C₃A and PC pastes. As ettringite is the main hydration product of C₃A cement, much more ettringite is formed in C₃A cement so that it is easy to observe any possible changes that occurred in ettringite. Then, the investigation is extended to PC pastes, the main binding material in precast concrete, to provide the reference and basic information for microwave curing precast concrete.
Chapter 3

Microstructure and thermal stability of ettringite under microwave heating

Is ettringite thermally stable under microwave heating?

Chapter 4

Microstructure and thermal stability of ettringite synthesised under microwave heating

Chapter 5

Microstructure and thermal stability of synthetic pure ettringite and metal ions-doped ettringite exposed to microwave heating

Pure ettringite
Metal ions-doped ettringite

Crystal Structure
Morphology
Ettringite decomposition
Binding energy of elements
Resonance of $^{27}$Al-NMR

XRD, TEM
SEM
TG
XPS
NMR

Chapter 6

Microstructure and thermal stability of ettringite formed in cement system subjected to microwave curing

Crystal Structure
Morphology
Ettringite decomposition

XRD
SEM
TG

Figure 3.1 Flow chart of overall research programme
3.3 Materials

3.3.1 Synthesis of ettringite

Two types of ettringite were studied throughout this thesis: pure and metal ion-doped. This section explains how they were synthesised.

(1) Pure ettringite

The raw materials used for synthesising pure ettringite were analytical grade calcium hydroxide $\text{Ca(OH)}_2$ and aluminium sulphate $\text{Al}_2(\text{SO}_4)_3\cdot 18\text{H}_2\text{O}$. The pure ettringite sample was synthesised according to Strube’s method, employing a solution of $\text{Ca(OH)}_2$ and aluminate sulphate ($\text{Al}_2(\text{SO}_4)_3\cdot 18\text{H}_2\text{O}$) as raw materials (Struble and Brown, 1984). The chemical reaction equation is below:

$$\text{Al}_2(\text{SO}_4)_3\cdot 18\text{H}_2\text{O}+6\text{Ca(OH)}_2+8\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O} \ (3.1)$$

The synthesis procedure can be described as follows:

1) 22.2 g of $\text{Ca(OH)}_2$ was dissolved in 800 ml deionized water;
2) 33.3 g of $\text{Al}_2(\text{SO}_4)_3\cdot 18\text{H}_2\text{O}$ was dissolved in 100 ml deionized water;
3) These two solutions were mixed and then put in a plastic container, which was then filled with nitrogen gas to minimise carbonation. After the container was tightly sealed, the mixed solution was kept stirring by a stirrer or rotating on a rotator for the required period before the ettringite was separated by vacuum filtration (Whatman No.40 paper) and dried under vacuum in a desiccator.
(2) Synthesis of metal ions-doped ettringite

Besides the raw materials employed to synthesise pure ettringite, analytical grade ferric sulfate Fe₂(SO₄)₃, chromic sulfate Cr₂(SO₄)₃·15H₂O and manganous sulfate MnSO₄·H₂O, were used to synthesise doped Fe-ettringite, Cr-ettringite and Mn-ettringite. In theory, Fe³⁺, Cr³⁺ and Mn²⁺ would partly replace Al³⁺ to form Ca₆·(Al, Fe)₂(SO₄)₃(OH)₁₂·26H₂O, Ca₆·(Al, Cr)₂(SO₄)₃(OH)₁₂·26H₂O and Ca₆·(Al, Mn)₂(SO₄)₃(OH)₁₂·26H₂O, respectively, i.e. Fe-ettringite, Cr-ettringite and Mn-ettringite. The synthesis procedures for these ettringites are as follows.

- For synthesis of Fe-ettringite, 50% molar ratio of Al₂(SO₄)₃·18H₂O was replaced by Fe₂(SO₄)₃, so 9.997 g Fe₂(SO₄)₃ and 16.65 g Al₂(SO₄)₃·18H₂O were dissolved in 100 ml deionized water.

- For synthesis of Cr-ettringite, 5% molar ratio of Al₂(SO₄)₃·18H₂O was replaced by Al₂(SO₄)₃·18H₂O, hence 3.31 g Cr₂(SO₄)₂·15H₂O and 29.97 g Al₂(SO₄)₃·18H₂O were dissolved in 100 ml deionized water.

- For synthesis of Mn-ettringite, 10% MnSO₄·H₂O by molar ratio of Al₂(SO₄)₃·18H₂O was incorporated, namely, 0.845 g MnSO₄·H₂O and 33.3 g Al₂(SO₄)₃·18H₂O were dissolved in 100 ml deionized water.

Following this, the three prepared solutions were mixed with the Ca(OH)₂, respectively, and then put in a plastic container, which was filled with nitrogen gas to minimise carbonation. After the container was tightly sealed, the containers containing the mixed solutions for synthesising Fe-ettringite, Cr-ettringite and Mn-ettringite were kept rotating for 14 days.
Chapter 3

3.3.2 Calcium sulfoaluminate cement

In the $\text{CS}_3\text{A}$ cement system, $\text{CS}_3\text{A}$ clinker and gypsum are the main raw materials. The $\text{CS}_3\text{A}$ clinker with a ye’elimite content >70% was supplied by Hanson UK (Scunthorpe). The $\text{CS}_3\text{A}$ clinker used in this thesis is Type III grade with fineness of 421 m$^2$/kg, the mineral compositions of which are given in Table 3.1.

<table>
<thead>
<tr>
<th>Ye’elimite</th>
<th>Lamite</th>
<th>Perovskite</th>
<th>Mayenite</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_4\text{A}_3\text{S}_5$</td>
<td>$\text{C}_2\text{S}$</td>
<td>$\text{CT}$</td>
<td>$\text{C}_{12}\text{A}_7$</td>
<td></td>
</tr>
<tr>
<td>77.2</td>
<td>14.3</td>
<td>5.7</td>
<td>1.6</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Table 3.1 Mineral compositions of $\text{CS}_3\text{A}$ clinker (wt%)  

High purity gypsum (>99% purity) was supplied by Hanson UK (grade FG200). The decomposition temperature of this gypsum is around 113.0°C, which was determined by DTG (see TG test in Section 3.6.4).

The gypsum content is typically in the range of 15-25%, chosen for optimum setting time, strength development and volume stability (Glasser and Zhang, 2001). To assure ettringite formation from the reaction of Ye’elimite with gypsum at most, 25% gypsum by weight of $\text{CS}_3\text{A}$ clinker was used. Considering the available space for ettringite to form well-formed crystals, combined with the requirement for the water to solid (W/S) ratio in the practical application of $\text{CS}_3\text{A}$ cement, the appropriate W/S was determined to be 0.65 with the mix proportions of $\text{CS}_3\text{A}$ paste shown in Table 3.2.
Table 3.2 Mix proportion of $C_3A$ paste

<table>
<thead>
<tr>
<th>Components</th>
<th>$C_3A$ clinker (g)</th>
<th>Gypsum (g)</th>
<th>Water (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight</td>
<td>1000</td>
<td>250</td>
<td>812.5</td>
</tr>
</tbody>
</table>

3.3.3 Portland cement clinker

Portland cement clinker with a high content of $C_3A$ (Hanson Cement Ltd, UK), complying with BS EN 197-1:2011 (BSI, 2011), was purposely used throughout the experiment in order to promote the maximum formation of ettringite. Its fineness is 400 $m^2/kg$ and the mineral phases are displayed in Table 3.3. Gypsum employed for PC paste is the same as mentioned in Section 3.3.2.

Table 3.3 Mineral phases of the clinker of PC with high $C_3A$

<table>
<thead>
<tr>
<th>$C_3S$</th>
<th>$C_2S$</th>
<th>$C_3A$</th>
<th>$C_4AF$</th>
</tr>
</thead>
<tbody>
<tr>
<td>57.2</td>
<td>18.1</td>
<td>10.5</td>
<td>8.3</td>
</tr>
</tbody>
</table>

In order to ensure the sufficient reaction of $C_3A$ in the PC clinker, 10% gypsum by weight of PC clinker was adopted. It should be highlighted that the gypsum level used in this study is relatively high compared to the normal practice. This is because the main objective of this study is to investigate the stability of ettringite. Additionally, with the higher level of $C_3A$ existing in the cement clinker, more gypsum is also needed to react with $C_3A$. Meanwhile, as available space is important for ettringite formation, the W/S ratio at 0.45 was used for PC paste. The mix proportions used for the PC paste are presented in Table 3.4.
Table 3.4 Mix proportion of PC paste

<table>
<thead>
<tr>
<th>Components</th>
<th>PC clinker (g)</th>
<th>Gypsum (g)</th>
<th>Water (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight</td>
<td>1000</td>
<td>100</td>
<td>495</td>
</tr>
</tbody>
</table>

3.4 Heating treatment

3.4.1 Microwave heating

Microwave heating was supplied by two custom-made microwave ovens (MHTO350 and SS500) developed in Advanced Materials Group (AIM) at University College London (UCL) under a TSB project (Project No: 20217-13825). The target temperature of sample can be precisely controlled through an optical fibre Bragg grating (FBG) that is inserted into the sample (Shi, 2017).

Figure 3.2 shows setup of the custom-made microwave oven that includes a microwave oven, a temperature FBG optical sensor and a control system. The sensing interrogator provides the light source for the FBG sensor. The control unit (interface box) allows communication between the computer software and the microwave oven to accomplish automatic temperature control.
Two microwave systems were employed in this research: MHTO350 was used for heating treatment when pure ettringite was synthesised; and SS500 was used for microwave heat treatment of all the other samples including synthetic pure ettringite and metal ions-doped ettringite after being synthesised at room temperature as well as C₃S₆A and PC pastes. Details of these two microwave systems are described below.

Figure 3.3 displays a photo of the custom-made MHTO350 microwave oven manufactured by Industrial Microwave System Ltd, UK, which was used for heating treatment when pure ettringite was synthesised.
Chapter 3

The microwave power can be continuously variable in the range of 0-1000 W. The turntable is made of polypropylene (PP), on which there is a mica sheet that can reflect microwaves. A microwave safe plastic container containing the sample is placed in the centre of the turntable. The turntable rotates clockwise and anticlockwise to avoid the optical fibre being twisted during the microwave heating process. A mixing apparatus consisting of a stirring control and a mixing paddle was designed by myself and fitted in house to homogenise the reactors and products throughout the whole process.

Figure 3.3 Custom-made MHTO350 microwave oven with mixing apparatus

Figure 3.4 presents a photo of the custom-made SS500 microwave oven that was also manufactured by Industrial Microwave System Ltd, UK.
This microwave oven can supply microwave with two frequencies, 2.45 GHz and 896 MHz. For each frequency, the power can be changed continuously in the range of 0-250 W. The turntable for this microwave oven is very similar to that of the MHTO350 microwave oven. In order to allow an increase in the output power of microwave, which may enhance the intensity of microwave working on samples, 6 plastic containers filled with 1300 ml tap water to provide a heat load were placed around the central sample. As there was no synthesis procedure involved, there was no need of a stirring system.

To control temperature, FBG sensors were inserted into the centre of the samples to measure the temperature of the sample. The photos of the two optical fibres are shown in Figure 3.5, the shorter used for a 25cm×25cm×25cm mould and the longer for a 50cm×50cm×50cm custom-made mould.
3.4.2 Conventional heating

Conventional heating treatment was used to compare with microwave heating. In this investigation, both water bath and an Isothermal Conduction Calorimeter (ICC) were used as conventional heating treatments to simulate steam curing. In both water bath and ICC, the temperature can be precisely controlled. In addition, the humidity in the sealed ampoules can be regarded as above 90% as the ampoules were tightly sealed. The water bath and ICC are shown separately in Figure 3.6 and Figure 3.7.
The plastic container containing the mixed solution was fixed in the centre of water bath with a custom-made steel shelf immersed in water. The temperature of the water bath and the ICC machine were always maintained at a target temperature (60, 70 or 80°C).

3.5 Sample preparation

3.5.1 Pure ettringite synthesised under heat treatment

For ettringite synthesised during microwave heating, the solution containing the
materials was continuously stirred while being heated in the MHTO350 microwave oven or with conventional heating in the water bath at 60, 70 and 80°C for 24 hours. Once filtered by vacuum filtration, the samples were dried under vacuum in a desiccator at a pressure of 0.45 bar for 7 days.

### 3.5.2 Synthetic pure ettringite and metal ion doped ettringite exposed to heat treatment

For ettringite synthesised at room temperature and then exposed to heating treatment, the container containing the materials solution was kept rotating on a rotator for 10 days at 30 rpm to obtain pure ettringite, followed by vacuum filtration. The filtrated paste of synthetic ettringite was transferred into a 50cm×50cm×50cm custom-made mould (Figure 3.8) made from polyether ether ketone (PEEK), a microwave transparent material, for microwave curing and 4 plastic ampoules for ICC curing. All specimens were heated at 60, 70 and 80°C for 8 hours. At last, the resulting samples were dried under vacuum in a desiccator for 7 days for further characterisation.

The three metal ion doped ettringite, Fe-ettringite, Cr-ettringite and Mn-ettringite, were synthesised at room temperature by rotating containers containing the corresponding materials solution (referred to Section 3.3.1) on a rotator for 14 days that aimed to obtain as much possible pure ions doped ettringite, followed by suction filtration. The filtrated pastes of synthetic Fe-ettringite, Cr-ettringite and Mn-ettringite were then transferred into 50cm×50cm×50cm custom-made moulds
(Figure 3.9), and into 4 plastic ampoules subjected to microwave and ICC curing as described in Section 3.5.1.

![Figure 3.9 50cm×50cm×50cm mould](image1)

![Figure 3.8 25cm×25cm×25cm mould](image2)

### 3.5.3 Cement system subjected to heat treatment

The cements include C Ş A and PC. For the C Ş A cement, 25% of gypsum was mixed with 75% of clinker at a W/S ratio of 0.65. The mixing procedures complied with the standard BS EN 196-3:2005+A1 2008. C Ş A clinker and gypsum were weighed and then dry mixed manually in a plastic container for three minutes. Subsequently the required water was added into the mixing bowl, followed by the pre-mixed solid powder materials. After mixing for 90 seconds at a slow speed, the mixer was stopped for 30 seconds, and the material from the blade, bottom and wall of the bowl were scraped down and put back into the middle of the bowl again. The mixer was then switched on for another 90-second mixing at a fast speed. After mixing, C Ş A cement paste was cast into a 25cm×25cm×25cm custom-made mould (Figure 3.8) and into 4 plastic ampoules. Subsequently, the
FBG optical sensor was inserted into the mould with paste and then subjected to 1-hour delay in a standard curing room to develop some early strength, in a similar way to steam curing. The mould was then wrapped with three layers of cling film and put into the custom-made SS500 microwave oven for microwave heating, while the 4 ampoules were placed into an ICC machine for conventional heating. Finally, the resulting hardened C̅S̅A cement paste samples were crushed into relatively large pieces and put into a glass bottle filled with 200 mL isopropanol, and soaked for 3 days to stop hydration. The samples were then removed from the isopropanol bottle and dried in a vacuum desiccator for 7 days.

For the PC system, 10% of gypsum by weight was incorporated with the PC clinker and a W/S ratio of 0.45 was employed to prepare pastes. The procedures for preparing PC paste samples were the same as those for preparing the C̅S̅A paste samples.

### 3.5.4 Measurement of pH value

As mentioned in the literature review in Chapter 2, pH value is an important parameter as it can affect the thermal stability of ettringite. The pH value of all the samples prepared was measured at room temperature before they were subjected to microwave heating using a ROSS 8165BNWP Sureflow pH electrode. The results are shown in Table 3.5.
When these samples were subjected to high-temperature treatments, the pH value of each sample was affected by different temperatures. Therefore, for each sample subjected to the same temperature under either microwave or conventional heating, the effect of pH value change on the thermal stability of ettringite was ignored.

### 3.5.5 Measurement of dielectric properties

The dielectric properties of water, and all the prepared samples as well as some experimental materials were measured by the coaxial probe method (Note, 2006) at 20°C under a microwave frequency of 2.45 GHz. The measured data are listed in Table 3.6.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ettringite</th>
<th>Fe-ettringite</th>
<th>Cr-ettringite</th>
<th>Mn-ettringite</th>
<th>CSA paste</th>
<th>PC paste</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>10.5</td>
<td>11.7</td>
<td>10.6</td>
<td>11.0</td>
<td>10.8</td>
<td>13.0</td>
</tr>
</tbody>
</table>
Table 3.6 Dielectric properties of relevant materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Dielectric constant ($\varepsilon'$)</th>
<th>Dielectric loss ($\varepsilon''$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>77.29</td>
<td>9.18</td>
</tr>
<tr>
<td>calcium hydroxide</td>
<td>0.96</td>
<td>0.01</td>
</tr>
<tr>
<td>Al$_2$(SO$_4$)$_3$·18H$_2$O</td>
<td>1.80</td>
<td>0.05</td>
</tr>
<tr>
<td>Pure ettringite</td>
<td>2.00</td>
<td>0.14</td>
</tr>
<tr>
<td>Fe-ettringite</td>
<td>1.90</td>
<td>0.22</td>
</tr>
<tr>
<td>Cr-ettringite</td>
<td>1.72</td>
<td>0.13</td>
</tr>
<tr>
<td>Mn-ettringite</td>
<td>1.56</td>
<td>0.10</td>
</tr>
<tr>
<td>1-hour hydrated C$_5$A</td>
<td>2.52</td>
<td>0.21</td>
</tr>
<tr>
<td>1-hour hydrated PC</td>
<td>2.83</td>
<td>0.22</td>
</tr>
</tbody>
</table>

3.6 Characterisation methods

All ettringite samples were characterised by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), thermogravimetric analysis (TG), X-ray electron spectroscopy (XPS) and solid-state nuclear magnetic resonance spectroscopy (NMR). The cement paste samples were characterised by XRD, SEM and TG. Prior to being characterised by TG, XRD, TEM, XPS and NMR, a small amount of sample was hand ground using an agate mortar to pass through a 63 µm sieve. The rest of the unground samples were stored in sealed plastic valve bags for SEM measurement.
3.6.1 X-ray diffraction

XRD technique allows identification of the existence of a well crystallised material in a compound and can provide information on unit cell dimensions. The interaction of X-rays with electrons and the resultant scattering of the X-rays provides to a diffraction pattern (Lee, 2017).

In XRD patterns, ettringite is readily recognised by its strong, low-angle peaks at 0.973 nm and 0.561 nm. In all experiments, the XRD patterns were recorded over $\theta$ ranging from 5 to 45° with a scanning rate of 1°·min$^{-1}$ using Cu Kα radiation with $\lambda=1.5406$ Å. The X-ray tube was operated with a voltage and current of 40 kV and 150 mA, respectively. An X-ray diffractometer (Smartlab, Rigaku Corporation Japan) was used for this research. XRD data was analysed using MDI Jade 6.0 software.

3.6.2 Transmission electron microscopy

TEM uses electromagnetic lenses to focus electrons and produce images or diffraction patterns of a thin sample. The merit of TEM is its resolution is high. Therefore, the sample required is very thin so that the most important signal loses little energy when colliding with atoms (Luo, 2015). Samples were prepared by dispersing ettringite powder in isopropanol with ultrasonic agitation and then drying a drop of the resulting suspension on a copper mesh grid that has a carbon support film. The samples were observed in a JEM-2010 Temscan microscope operated at 200 kV. With good care, ettringite samples can be handled in the high
vacuum (1.5×10⁻⁵ Pa) of the electron microscope without significant decomposition provided that the exposure time is brief (50 ms) and the beam intensities are kept low to minimise heating.

Lattice parameters of ettringite samples can be calculated based on the electron diffraction patterns. The details of calculation procedures are as follows: (i) the interplanar spacings of low-index planes are calculated using the measured values of reciprocal vectors, i.e., the diffraction spots close to direct beam spot; (ii) following this, in combination with the PDF data of ettringite, the interplanar indices are proposed; (iii) angle values of proposed interplanar indices are calculated according to Formula (3.2), and the indices of the two interplanars are determined if the calculated value matches with the measured value (the angle of reciprocal vectors of corresponding interplanars ϕ); (iv) the experimental values of lattice parameters (a and c) are calculated based on the interplanar index (hkl) and the measured value of the corresponding interplanar spacing (d_hkl) as shown in Formula (3.3).

\[
\begin{align*}
\cos \phi &= \frac{h_1h_2+k_1k_2+\frac{3}{2}(h_1k_2+h_2k_1)+\frac{3a^2}{4c^2}l_1l_2}{\sqrt{(h_1^2+k_1^2+h_1k_1+\frac{3a^2}{4c^2}l_1^2)(h_2^2+k_2^2+h_2k_2+\frac{3a^2}{4c^2}l_2^2)}} \\
\end{align*}
\]  
(3.2)

\[
\begin{align*}
d_{hkl} &= \frac{1}{\sqrt{\frac{1}{3} \left( \frac{h^2+k^2+k^2}{a^2} \right)^2 + \left( \frac{1}{c^2} \right)^2}} \\
\end{align*}
\]  
(3.3)
3.6.3 Scanning electron microscopy

SEM is one of the most powerful techniques for studying the morphology of materials. A SEM instrument generates a beam of electrons that hits a material where these electrons undergo a series of elastic and inelastic collision with the atoms of the material (Goldstein et al., 2017). The collisions generate signals which are detected in the microscope to form an image. In SEM measurements, the brightness of the SEM image is determined by the inclination angle of the surface materials, so they are commonly used to show the morphology of materials. In this study, a Merlin Compact field emission scanning electron microscope (Carl Zeiss NTS GmbH, Germany) working at a voltage of 15 KV was used to observe the morphology of ettringite samples or hydration products of ČSA and PC paste. Before examination, each sample was sputter coated with gold in a vacuum chamber to make it electrically conductive.

3.6.4 Thermogravimetric analysis

TG is a useful tool for measuring the changes of sample weight both qualitatively and quantitatively. It is able to identify the presence of substances according to the weight loss occurring in a typical temperature range (Gabbott, 2008). Therefore, it was employed to identify the decomposition temperature of ettringite, thus determining the thermal stability of ettringite. It was demonstrated that the thermal stability of ettringite depends on how easily the 32 molecules of
crystalline water within the structure can be removed under heating, which can
be determined from TG and derivative thermogravimetry (DTG) results (Jimenez
and Prieto, 2015).

Because a self-generated water vapour pressure can affect the practical
decomposition temperature of ettringite during heating (Zhou et al., 2004), the
crucible, loaded with about 22 mg sample of ettringite (or 40 mg of ČSA paste)
was covered by a lid with a tiny hole on before it was tested in the TG instrument.
In this way, the water vapour pressure generated as H$_2$O is lost from ettringite
can only escape slowly through the small open hole, hence keeping as moisture
as much as possible in the crucible. It was reported that the dehydration of
gypsum and hemihydrate can be differentiated by a similar approach (Hudson-
Lamb et al., 1996). Measurement was carried out with a heating ramp from 25 to
300°C at a rate of 1 °C·min$^{-1}$, followed by a cooling ramp from 300 to 25°C at a
rate of 40°C·min$^{-1}$. In all cases, a purge of nitrogen at 20 mL·min$^{-1}$ was kept
throughout the whole experiment. After each test, the TG data was processed
into DTG results (Scrivener et al., 2015). The TG machine used was a NETZSCH
TG 209 F1 Libra supplied by a German company.

The number of water molecules lost from the ettringite was calculated from the
mass loss occurred from the first TG peak which is associated with the water lost
during the decomposition of ettringite (Grounds et al., 1985b, Carmona-Quiroga
and Blanco-Varela, 2013, Zhang and Saito, 2000). It should be noted that the total number of water molecules present in the synthesised ettringite was determined by adding the number of water molecules in the monosulfate and gypsum as well as the number of water molecules loss. The details of the calculation were as follows: firstly, the start and end temperatures for ettringite decomposition were determined by the second derivative to DTG (DDTG); Secondly, the weight loss between the start temperature and end temperature was calculated; finally, based on the decomposition reaction of ettringite as shown in equation (3.4) below, the total number of water molecules (n) existing in the ettringite can be calculated using equation (3.5).

$$3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot n\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O} + 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + (n-16)\text{H}_2\text{O}$$  \hspace{1cm} (3.4)

$$n = \frac{305W_{AFT}+144}{9(1-W_{AFT})}$$  \hspace{1cm} (3.5)

In this equation, $W_{AFT}$ stands for the weight loss of ettringite from the first peak of the TG curve.

### 3.6.5 X-ray photoelectron spectroscopy

XPS is a surface analysis technique that gives information on the elemental composition in the parts per thousand range, empirical formula, chemical and electronic state of the elements that exist within a material. XPS spectra are
obtained by irradiating a material with a beam of X-rays while concurrently measuring the kinetic energy and number of electrons that escape from the top 0 to 10 nm of the material being analysed (Knop - Gericke, 2012, Wagner, 2011). The kinetic energy of each element reflects its bonding state. The full width at half maximum (FWHM) indicates the chemical state changes and physical influences (Watts and Wolstenholme, 2003). The bonding state of elements of ettringite was investigated by XPS (ESCLAB 250Xi, Thermo Fisher Scientific Company, USA). Al Kα (hv=1486.6 eV) X-rays were used and energy resolution was 0.10 eV. In this measurement, adventitious carbon was utilised as the energy referencing method and powder samples were used.

3.6.6 Solid-state nuclear magnetic resonance spectroscopy

Solid state nuclear magnetic resonance (SSNMR) spectroscopy is an important research tool for the characterisation and structural analysis of materials. $^{27}$Al is a high sensitivity NMR active nucleus that yields broad lines over a wide range of chemical shifts which show the environment of aluminium in its chemical bonds (Scrivener et al., 2015, MacKenzie and Smith, 2002). The $^{27}$Al spectra of the powder samples were obtained with a solid state nuclear magnetic resonance spectrometer (Bruker Avance III). The resonance frequency used in this study was 400 MHz, with a spinning rate of 10 KHz. Spectra were obtained after irradiation of the sample with a $^{11/2}$ pulse (0.97 µs). All measurements were
taken at room temperature with saturated aluminium nitrate solution as the external standard.
Chapter 4 Microstructure and Thermal Stability of Ettringite Synthesised under Microwave Heating

4.1 Introduction

Like steam curing, the process of manufacturing precast concrete products under microwave heating would require two stages: (a) the first stage should occur at ambient conditions, which is meant to provide the concrete products with sufficient strength gain so as to facilitate their handling; (b) the second stage involves heating the concrete specimens using microwave heating, during which concrete is expected to gain a high level of strength, reaching the desired strength for construction purpose. During the first stage, cement reacts with water at room temperature to form a certain amount of ettringite together with some other hydration products. The crystal structure and thermal stability of ettringite formed at this stage are well documented in the literature, and these are explained at length in Chapter 2. However, when concrete samples are moved to the second stage where microwave heating is involved, there exists two open questions: first, it remains unclear what will happen to ettringite crystals formed previously at ambient conditions as soon as they come in contact with electromagnetic heating; second, the characteristics of the ettringite forming during the second stage is unknown to date. The latter question is the main focus of this chapter where the stability of ettringite formed during the microwave heating is reported, whilst the
former will be dealt with in the next chapter where ettringite already formed is exposed to microwave heating.

The ettringite samples were precipitated in a microwave and thereafter dried and characterised using a variety of characterisation techniques. As a reference, ettringite was also synthesised at room temperature and under conventional heating. In general, throughout this chapter, the followings are being examined.

(i) the changes microwaves cause to the morphology and crystal structure of ettringite;

(ii) the extent to which microwave heating changes the thermal stability of ettringite;

(iii) the extent to which microwaves alter the chemical state and binding energy of the constituent elements of ettringite.

### 4.2 Sample preparation

The ettringite was prepared following the methodology developed by Struble (1986), in which the aqueous solution of Ca(OH)$_2$ is reacted with that of Al$_2$(SO$_4$)$_3$.18H$_2$O. The synthesis method is similar to the method of synthesising pure ettringite described in Section 3.3.1, except 800ml 10% sucrose solution was used to replace 800 ml deionized water. The synthesis duration was 24 hours. The temperature of the reaction was fixed at either room temperature (25°C) or
maintained at 60, 70 or 80°C, respectively. In the latter three cases, the samples were heated by using either a microwave or a conventional heating system (see details in Section 3.4). The details of ettringite synthesised under different conditions and sample IDs used in this chapter are shown in Table 4.1.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Heating method</th>
<th>Heating temperature (°C)</th>
<th>The total synthesis time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFt-SRT24</td>
<td>Room temperature</td>
<td>25</td>
<td>24</td>
</tr>
<tr>
<td>AFt-SM6024</td>
<td>Microwave heating</td>
<td>60</td>
<td>24</td>
</tr>
<tr>
<td>AFt-SC6024</td>
<td>Conventional heating</td>
<td>60</td>
<td>24</td>
</tr>
<tr>
<td>AFt-SM7024</td>
<td>Microwave heating</td>
<td>70</td>
<td>24</td>
</tr>
<tr>
<td>AFt-SC7024</td>
<td>Conventional heating</td>
<td>70</td>
<td>24</td>
</tr>
<tr>
<td>AFt-SM8024</td>
<td>Microwave heating</td>
<td>80</td>
<td>24</td>
</tr>
<tr>
<td>AFt-SC8024</td>
<td>Conventional heating</td>
<td>80</td>
<td>24</td>
</tr>
</tbody>
</table>

**Note**: in the sample IDs, AFt stands for ettringite; S: synthesis; M: Microwave heating; C: conventional heating; RT, 60, 70 and 80: the synthesis temperature are room temperature (25°C), 60°C, 70°C and 80°C, respectively.

After ettringite was synthesised, each sample was characterised by XRD, TEM, SEM, TG, XPS and NMR (refer to details explained in Section 3.6). The effect of microwave heating on the crystal structure, morphology, ettringite decomposition, binding energy of elements and $^{27}$Al nucleus of ettringite is reported and discussed in the following sections.
4.3 Results

4.3.1 Effect of microwave heating on the crystalline structure of ettringite

Figure 4.1 shows the XRD patterns of ettringite synthesised under different heating conditions.
Figure 4.1 XRD patterns of ettringite synthesised with microwave and conventional heating at 60 (a), 70 (c) and 80°C (e), whereas (b), (d) and (f) show the changes of the (0001) d-spacings of the corresponding samples by enlarged main peak of ettringite (~9.0° 2θ).

In Figure 4.1(a), at room temperature, the products formed consist primarily of ettringite with only a small trace of gypsum. The reason why gypsum is in the
sample could be because the 24-hour duration used here to synthesise ettringite is not long enough for the reactants to fully convert to ettringite, leading to the formation of gypsum that is highly likely is an intermediate phase (Zhang and Saito, 2000). Similar result was previously reported in the study by Struble (1986) who proposed the method for synthesising ettringite, in which sucrose was used to enhance the solubility of Ca(OH)$_2$ and prevent any formation of CaCO$_3$ in some cases. The specific role of sucrose addition was also verified by other research (Norman et al., 2013, Komatsu et al., 2009, Poellmann et al., 1990).

At 60°C, under both microwave and conventional heating, a small amount of gypsum and monosulfate is present in addition to ettringite. Theoretically, the target product should be pure ettringite as the raw materials for synthesis are stoichiometric. However, it is important to note that synthesising ettringite in solution is a slow process involving dissolution and precipitation reactions (Baur et al., 2004, Van Santen, 1984). It is known that the solubility of Ca(OH)$_2$ decreases as temperature increases (Shackelford et al., 2016). The reduction in the solubility of Ca(OH)$_2$ would, in turn, slows down the precipitation of ettringite which depends on the concentrations of ionic species (Al$^{3+}$, SO$_4^{2-}$, Ca$^{2+}$ and OH$^-$) dissolved in the solution (Terai et al., 2007), leading to the formation of more gypsum. Another reason may be that as temperature increases, the solubility of gypsum in the temperature range of 0-100°C initially increases and then decreases, which reaches the maximum value at 40°C (Innorta et al., 1980,
Blount and Dickson, 1973). At 60°C, the solubility of gypsum is 1.92 g/L, slightly lower than the value at 20°C (2.00 g/L), causing more gypsum precipitation (James, 1992). When ettringite samples are prepared at 70 and 80°C, the solubility of Ca(OH)$_2$ and gypsum is further reduced compared to that at 60°C, favouring more gypsum precipitation. In addition, as temperature is increased from 60 to 80°C, the thermal stability of ettringite may be reduced, resulting in the decomposition of ettringite to form some monosulfate and gypsum (Mehta, 1972). These can explain the fact that the ettringite coexists with gypsum and monosulfate in the final product when ettringite is synthesised at 60, 70 and 80°C. The XRD results in Figure 4.1 further confirm that as the heating temperature is increased from 60 to 80°C, the intensity of ettringite peaks decreases, while the intensity of gypsum and monosulfate peaks increases.

The above results show that, the higher the temperature, the less the ettringite and the more the gypsum. Additionally, trace amount of monosulfate was also detectable above 60°C. This is more pronounced for the ettringite samples synthesised under microwave heating than for those synthesised under conventional heating, at a given temperature. This may be due to the non-thermal effects that microwave brings about besides the thermal effects (see more detailed discussion in Section 4.4).
It is not easy to identify the subtle differences from a broad XRD trace, so the main peak of ettringite at around 9.0° 2θ was amplified for all samples, as shown in Figure 4.1 (b), (d) and (f). When the 2θ is converted to D spacings, the interplanar spacing of ettringite decreases slightly as the temperature rises under conventional heating, changing from 9.75 Å at room temperature to 9.73 Å at 80°C. Additionally, at any given temperature, the interplanar spacing of microwave-synthesised ettringite samples has shifted to lower values compared to conventional heating-synthesised ettringite samples, e.g. at 70°C, the interplanar spacing of microwave-synthesised ettringite is 9.71 Å, while the interplanar spacing of conventional heating-synthesised ettringite is 9.73 Å. In the meantime, it is clear to see that the full width at half maximum (FWHM) of the main peak of ettringite synthesised under microwave heating is smaller than that synthesised under conventional heating, at any given temperature. These may be due to the non-thermal effect of microwave, which will be discussed in detail in Section 4.4.

The lattice parameters of ettringite calculated from the XRD patterns are shown in Figure 4.2.
Figure 4.2 Calculated lattice parameters of $a$ (a) and $c$ axes (b) of ettringite synthesised under microwave and conventional heating at 60, 70 and 80°C

The calculated parameters of the ettringite sample synthesised at room temperature are $a=11.1348$ Å and $c=21.3775$ Å. It should be noted that as ettringite belongs to the hexagonal crystal system, the $a$ axis is equal to the $b$ axis, therefore, in the following sections, only the $a$ axis is shown. It should be mentioned that the values are in close agreement with the values for ettringite that were 11.2250 Å and 21.4670 Å in the literature, in which the ettringite was synthesised by dissolving 13.63 g Al$_2$(SO$_4$) in 40 mL H$_2$O and 13.4 g CaO in 890 mL of an aqueous 10% sugar at 24°C (McMurdie et al., 1986). It can be seen from Figure 4.2 (a) that with the increase of the synthesis temperature, both heating methods reduce the $a$ axis of ettringite. In addition, compared to the conventional heating, the microwave heating reduces the lattice size of ettringite more in the $a$ direction. Moreover, the higher the temperature, the shorter the lattice parameter in the $a$ axis — a trend which is in consistent with the findings in the literature (Hartman et al., 2006, Bannister, 1936). From Figure 4.2 (b), the
lattice dimension in the c axis of ettringite also shows similar trends as those found for the a axis. This may be due to the loss of zeolitic water locating between the columns of ettringite structure under heating conditions (Zhou and Glasser, 2001, Guimarães et al., 2016).

From the XRD results, it can be concluded that when ettringite is synthesised at 70°C, there is a clear difference in the lattice size of ettringite between a sample synthesised under microwave heating and the one under conventional heating. To further identify any potential effects microwave has on the lattice parameters, binding energy of elements as well as the $^{27}$Al nucleus environment in ettringite, samples synthesised at room temperature and at 70°C using microwave and conventional heating were further characterised by TEM, XPS and NMR.

The electron diffraction patterns of each sample, examined using TEM, are presented in Figure 4.3. All the electron diffraction patterns were recorded from the same zone axis [2200] for the sake of comparison. The corresponding reflection crystal planes and zone axis are schematically illustrated in Figure 4.4. The crystal structure of ettringite is presented in Figure 4.5.
Figure 4.3 Electron diffraction patterns of ettringite synthesised at room temperature (a), at 70°C under microwave (b) and conventional heating (c)

Figure 4.4 Schematic diagram of corresponding reflection crystal faces with the electron beam paralleled to [220] zone axis
The diffraction patterns shown in Figure 4.3 were analysed using the method explained in Section 3.6.2, in combination with the schematic diagram of corresponding reflection crystal faces (Figure 4.4) and crystal structure of ettringite (Figure 4.5). From the electron diffraction pattern of ettringite synthesised at room temperature as shown in Figure 4.3 (a), the calculated lattice constants of $a$ and $c$ are 11.123 Å and 21.177 Å, respectively. In comparison, for the ettringite sample synthesised under microwave heating at 70°C, $a$ and $c$ are 10.998 Å and 19.944 Å, and under conventional heating at 70°C, 11.114 Å and 20.292 Å, respectively. Overall, the ettringite has shrunk in both $a$ and $c$ directions when heated at 70°C, with more shrinkage taking place under microwave heating. This is in agreement with the change noted for the $a$ and $c$ dimensions of ettringite when dehydrated under conventional heating (Bannister, 1936, Zhou et al., 2004) (Zhou et al., 2004). These results are also similar to the calculated lattice
parameters of ettringite from XRD results. The corresponding crystal morphology of each sample observed under TEM is displayed in Figure 4.6.

![Figure 4.6 TEM micrograph of ettringite at room temperature (a) or at 70°C under microwave (b) and conventional heating (c)](image)

In Figure 4.6 (a), the crystals of ettringite synthesised at room temperature are in the form of long hexagonal prisms, but for the samples synthesised at 70°C, the prisms are shorter, as shown in Figure 4.6 (b) and (c), being more pronounced for the sample synthesised under microwave heating as shown in Figure 4.6 (b). These results all indicate that microwave affects the size of ettringite crystals, hence altering their morphology in addition to the thermal effects.
4.3.2 Effect of microwave heating on the morphology of ettringite

To compare the morphology of the ettringite synthesised under different heating conditions, all the samples were further examined by SEM and the SEM images are presented in Figure 4.7.

Figure 4.7 SEM micrographs of ettringite synthesised at room temperature (a), under microwave (b,d,f) and conventional heating (c,e,g) at 60, 70 and 80°C, respectively
At room temperature, as shown in Figure 4.7 (a), the sample are composed of small solid barrel-shaped crystals, approximately 0.1 to 0.2 µm in diameter, with a length to diameter ratio (L/C) of around 4.0 to 6.0. The ettringite crystals are small in size compared to what generally formed in PC concrete which are typically 2 to 4 µm in diameter and 20-30 µm long (Association, 2001). This is likely due to the presence of sucrose, which enhances the solubility of Ca(OH)$_2$, and thus accelerates the nucleation of ettringite (Myneni et al., 1998, McMurdie et al., 1986). Nevertheless, the morphology observed here is still typical of ettringite crystals (Moore and Taylor, 1970, Taylor, 1973, Poellmann et al., 1990), and it is very similar to the morphology of the ettringite synthesised by Goetz-Neunhoeffer et al. (2006) through mixing a solution of Ca(OH)$_2$, Al$_2$(SO$_4$)$_3$·18H$_2$O and sucrose at a pH around 12.5. In their study, the pH value was adjusted by adding sodium hydroxide. Although similar materials were used in the current study to synthesise ettringite, a pH value of 10.5 was maintained instead of 12.5. Nevertheless, similar ettringite morphology was observed even though the crystal size of ettringite is smaller.

When ettringite is synthesised at 60°C under microwave [Figure 4.7 (b)] or conventional heating [Figure 4.7 (c)], the typical hexagonal prism morphology of ettringite can be clearly observed, with the crystals showing a high degree of similarity with the samples obtained at room temperature. Additionally, there is
also no major differences in the morphology of ettringite synthesised under microwave and conventional heating.

However, at 70°C, the ettringite synthesised [Figure 4.7 (d) and (e)] are 0.2-0.6 \( \mu \text{m} \) in length, slightly shorter and thicker than those synthesised at room temperature and 60°C, with some even in a distorted spherical shape. This effect is more noticeable in the samples synthesised under microwave heating [Figure 4.7 (d)] as compared to that of conventional heating [Figure 4.7 (e)].

Finally, at 80°C, the ettringite formed is in the form of platelet shape, regardless of the heating method adopted. This morphology resembles that of the monosulfate (Baur et al., 2004, Taylor, 1997, Mehta, 1969), indicating that the ettringite becomes less stable and starts to show features of monosulfate. This also confirms the previous result that the c value of ettringite decreased as the synthesis temperature rose from 60 to 80°C.

### 4.3.3 Effect of microwave heating on the thermal stability of ettringite

Thermal analysis was used here to determine the temperature at which ettringite decomposes. The TG and DTG patterns of each sample are shown in Figure 4.8.
As can be seen in Figure 4.8, all the DTG patterns consist of three major peaks as also being noted by other researchers (Zhang and Saito, 2000, Meller et al., 2009, Wang et al., 2016): (i) the first peak at around 80-90°C, is associated with the dehydration of ettringite; (ii) the second peak at around 105-115°C could be attributed to the decomposition of gypsum; and (iii) the third peak at about 180-215°C is related to the decomposition of monosulfate.
The peak temperature of the decomposition of ettringite synthesised under different conditions from DTG patterns is summarised in Figure 4.9.

![Figure 4.9 Summary of peak temperatures of the decomposition of ettringite synthesised under microwave and conventional heating at 60, 70 and 80°C](image)

The most striking observation is that the peak temperature of the decomposition of ettringite has shifted to lower temperatures with the increase of synthesis temperature. This finding shows that the ettringite produced at high temperatures is thermally less stable. Moreover, the samples synthesised with microwave is also consistently less stable than those from conventional heating at any given temperature.

To further compare the thermal stability of the ettringite synthesised under different conditions, the number of water molecules present in the synthesised ettringite was determined using the calculation procedure shown in Section 3.6.4. The results are plotted in Figure 4.10.
Figure 4.10 Water molecules contained in the ettringite synthesised at room temperature, and under microwave and conventional heating at 60, 70 and 80°C.

It can be seen in Figure 4.10 that as the synthesis temperature is increased, the number of water molecules existing in the ettringite crystal decreases. Furthermore, at any given temperature, microwave heating further decreases the number of water molecules in the ettringite than with conventional heating. The results derived from the DTG data show that elevated temperatures decreases the thermal stability of synthesised ettringite, and at a given temperature, microwave heating leads to more reduction in the thermal stability of synthesised ettringite than conventional heating.

4.3.4 Effect of microwave heating on the binding energy of elements in ettringite

The binding energy and FWHM data of the Al 2p, Ca 2p and S 2p spectra of ettringite are plotted in Figure 4.11.
From Figure 4.11, it can be seen that the binding energies of the Al 2p, Ca 2p and S 2p of ettringite synthesised at room temperature are 72.25, 345.62 and 167.17 eV. These values are close to those quoted for ettringite in the literature (Comans et al., 1996) where the ettringite studied was small needle-like crystals removed from an assemblage of ettringite crystals embedded in a chalk deposit.

As shown in Figure 4.11 (a), the binding energy of the Al 2p of ettringite synthesised at 70°C by both heating methods is lower than that of ettringite
synthesised at room temperature, with the Al 2p spectra binding energy of ettringite synthesised under microwave heating even slightly lower than that of ettringite synthesised under conventional heating. This indicates that increasing the synthesis temperature to 70°C reduces the binding energy of Al 2p, and this phenomenon is more pronounced with the microwave-synthesised sample. One possible explanation is the rearrangement of electrons of Al in [Al(OH)₆]³⁻ to the low-spin state under microwave heating (Pozar, 2009) induces chemical environment alterations around Al, hence reducing the binding energy of Al 2p. As for the FWHM data, the value of ettringite synthesised under microwave heating is the lowest amongst the three samples. This may be another indicator of the chemical environment changes of Al 2p under microwave heating (Carlson, 1978).

We can see from Figure 4.11 (b) that the same trend occurs with the binding energy of Ca 2p as those happened with Al 2p, viz. when synthesised at high temperature, the binding energy of Ca 2p in ettringite decreases, with microwave heating causing more reduction than conventional heating. However, the FWHM of the ettringite synthesised under microwave heating is almost the same as that of the ettringite synthesised under conventional heating at 70°C, both of which are lower than that of ettringite synthesised under room temperature. In Figure 4.11 (c), similar results were found for the binding energy and FWHM data of S 2p.
These changes in the binding energies and FWHM data of Al 2p, Ca 2p and S 2p indicate that microwaves may have additional effects besides the function of dielectric heating during the formation of ettringite.

### 4.3.5 Effect of microwave heating on $^{27}$Al nucleus in ettringite

Figure 4.12 shows the $^{27}$Al-NMR spectra of the ettringite synthesised at room temperature as well as the ettringite synthesised under both microwave and conventional heating at 70°C.

![Figure 4.12](image)

**Figure 4.12** $^{27}$Al NMR spectra of ettringite synthesised under microwave and conventional heating at 70°C. Figure (a) shows the the patterns over 200-(250) ppm range, whereas (b) shows enlarged range 25-0 ppm for clarity.

The $^{27}$Al peaks for ettringite synthesised under microwave and conventional heating have the same chemical shift at about 13 ppm associated with ettringite (Shimada and Young, 2004), but are both smaller than that of the ettringite synthesised under room temperature. This indicates that at high temperatures the environment surrounding the $^{27}$Al nucleus may change, leading to a decrease
in the $^{27}$Al-NMR resonance (Ogorodnikova et al., 1983, Huheey et al., 2006). Furthermore, at 70°C, the resonance band of $^{27}$Al-NMR in ettringite synthesised under microwave heating has shifted to a higher chemical shift compared to that synthesised under conventional heating. This implies that when microwave heating is applied, it may have a non-thermal effect besides its thermal effect, which might reduce the electron density around Al nucleus, thus resulting in a higher chemical shift than with conventional heating (Lambert and Mazzola, 2002). These findings are in good agreement with the XPS results.

### 4.4 Discussion

The results from XRD, TEM, SEM, TG/DTG, XPS and NMR all show that when the microwave heating is applied in synthesising ettringite, microwaves exert additional effects beyond its thermal effect.

The compounds used in the current study to synthesise ettringite are calcium hydroxide (Ca(OH)$_2$) and aluminium sulphate (Al$_2$(SO$_4$)$_3$·18H$_2$O). These, together with the ettringite to be formed are all poor microwave absorbers due to their very low dielectric constants that are about 0.96, 1.80 and 2.0 (see Section 3.5.5), respectively. Hence, it is expected that they are poor electrical conductors in the microwave field. It is known that poor electrical conductors are often heated by surrounding dielectric substances (Huheey et al., 2006, Gupta and Leong, 2008).
The water molecules in the synthesis solution are very polar with a dielectric constant of 77.29 measured at 20°C under a microwave frequency of 2.45 GHz. Therefore, water is a good absorber of microwaves, playing a pivotal role in determining the dielectric properties of the synthesis solution. When ettringite is synthesised under microwave heating, the water molecules would be forced to re-orientate and vibrate following the alternating high frequency electric field (Makul et al., 2009). The vibration causes friction between the water molecules, converting electromagnetic energy into thermal heat energy, which leads to heating the synthesis solution (Makul et al., 2014a, Chandrasekaran et al., 2013).

In addition to the above dielectric heating of microwave, microwaves act additional effects. This could be attributed to the non-thermal effects as also identified by Zuo et al (2013) who investigated the microstructure evolution and densification kinetics of α-alumina by using microwave sintering at 2.45 GHz and by Red’ko et al. (2017) studying the mechanism and possibilities of defect reorganization in III-V compounds. In the following, details about how microwave heating works during the process of synthesising ettringite at 60, 70 and 80°C are discussed.

As reviewed in Chapter 2, microwave can enhance the mass transport, so the mobility of ions can be increased and thus diffusion rates under microwave heating (Hinrikus et al., 2015, Li et al., 2010, Nomanbhay and Ong, 2017).
Consequently, the rate of nucleation formation of ettringite under microwave heating can be sped up, which might be faster than under conventional heating, at a fixed temperature, resulting in smaller ettringite crystals (Callister and Rethwisch, 2005, Jhung et al., 2007a). This can be used to explain why the full width at half maximum (FWHM) of the main peak of ettringite synthesised under microwave heating is smaller than that synthesised under conventional heating, as shown in XRD results.

In addition, due to the possible non-thermal effect of microwave that might increase the Arrehenius pre-exponential factor $A$ (Binner et al., 1995) or decrease the activation energy $E_a$ (Fini and Breccia, 1999, Nomanbhay and Ong, 2017) in the Arrhenius’ equation, the decomposition rate of ettringite could be increased. In other words, ettringite under microwave heating is more prone to decompose than under conventional heating. In addition, when the temperature is above 70°C, the dehydration of ettringite may play a dominant role in the solution reactions during the synthesis process. Therefore, more water molecules may be lost from ettringite synthesised under microwave heating than under conventional heating, resulting in more shrinkage in the $a$ and $c$ axes, correspondingly, at a given temperature. These were verified by the calculation results of water molecules existing in ettringite under different heating conditions, which were derived from TG data as well as XRD and TEM results.
As reported by Moore and Taylor (1970), the inter-columnar waters are linked to the columns of ettringite by hydrogen bond and the apical water molecules on the calcium coordination polyhedral are observed to form hydrogen bonds with other calcium coordination polyhedral as well as with columns of sulfate tetrahedral and water molecules. More water is lost from ettringite synthesised under microwave heating than conventional heating which means that more hydrogen bonds are broken. It is reported that the hydrogen bond network plays a significant role in stabilising the ettringite structure and provides a connective framework for the columnar structure (Hartman and Berliner, 2006). Therefore, a greater collapse of hydrogen bonds would lead to less stability of ettringite. This can be seen from the DTG results, showing that the peak temperature for the decomposition of ettringite synthesised under microwave heating was lower than that with conventional heating, at any given temperature. Ettringite with less stability is easier to decompose to form monosulfate and gypsum. This can explain why there is an increase in the XRD peaks of gypsum and monosulfate when ettringite is synthesised under microwave heating than conventional heating, at 70 or 80°C. It can also account why when the ettringite is synthesised above 70°C, more irregular shapes and platelet shapes associated with monosulfate (Baur et al., 2004) can be seen in the presence of microwaves than in the conventionally heated samples.
In addition, a greater water loss would lead to an increase in the loss of oxygen atoms for hydrogen bonding in the ettringite structure, decreasing the bridging moiety of Al-O, Ca-O and S-O bonds, thus reducing the binding energy of Al 2p, Ca 2p and S 2p electrons in ettringite (Callister and Rethwisch, 2005, Watts and Wolstenholme, 2003). This was shown by the XPS results, revealing that when ettringite is synthesised at 70°C under microwave heating, the binding energy of the Al 2p, Ca 2p and S 2p electrons of ettringite is slightly lower than those from conventional heating. As manifested in the NMR results, after heating at 70°C, the peak area of the $^{27}$Al-NMR signal from ettringite synthesised under microwave heating becomes smaller and has a higher chemical shift compared to the ettringite synthesised under conventional heating. These NMR results demonstrate the possibility of a lower electron density distribution around the Al nucleus (Huheey et al., 2006). This can be attributed to greater loss of oxygen from the ettringite structure under microwave heating that would result in a reduction of covalent bonds, decreasing the shared electron pairs, thus leading to a lower electron density distribution around Al nucleus compared to the conventional heating.

### 4.5 Conclusions

In this chapter, ettringite was synthesised under microwave and conventional heating at 60, 70 and 80°C for 24 hours, and then the microstructure and thermal
stability of each sample were characterised by XRD, TEM, TG, XPS and NMR. From this study, the following main conclusions were drawn:

- At a given temperature, the ettringite crystals synthesised under microwave heating are smaller than those synthesised under conventional heating. This can be attributed to the enhancement of the release of ions into solution under microwave heating, resulting in a faster rate of nucleation of ettringite than under microwave heating.

- At the same temperature, ettringite crystals shrink more under microwave heating than under conventional heating, whilst more damage occurs to the ettringite crystals synthesised during microwave heating. This may be because that microwave heating causes more water to be lost from ettringite than conventional heating.

- Ettringite synthesised under microwave heating is thermally less stable than that from conventional heating. This may be due to that microwave heating increases the probability of the collision of molecules and atoms, causing a decrease in the activation energy needed for ettringite decomposition. This leads to more water lost from ettringite, giving rise to further collapse of the hydrogen bonds, thus destabilising the ettringite.
Chapter 5 Microstructure and Thermal Stability of Synthetic Ettringite and Metal Ion-doped Ettringite Exposed to Microwave Heating

5.1 Introduction

Chapter 4 has shown that microwave heating affects the microstructure and thermal stability of ettringite synthesised directly under microwave heating at different temperatures in several ways with main findings: (i) at a given temperature, ettringite crystals shrink more when microwave heated than from conventional heating; (ii) ettringite synthesised under microwave heating is thermally less stable than that from conventional heating. However, it is unclear if the same observations will occur when ettringite is synthesised at room temperature before being exposed to microwave heating. In addition, as mentioned before, ettringite formed during the hydration of PC is usually doped with metal ions such as Fe, Cr and Mn. To date, although there are a few documents on the crystal structure and thermal stability of these three metal ion-doped ettringite as illustrated in Chapter 2, no research has been performed when they are exposed to microwave heating at different temperatures. Therefore, this chapter will be focused on the influence of microwave heating on pure ettringite and metal ion-doped (Fe, Cr and Mn) ettringite synthesised at room temperature and subsequently exposed to microwave heating. Conventional heating was
used a reference to heat the synthetic pure ettringite and metal ion-doped ettringites.

The samples obtained were characterised using XRD, TEM, SEM, TG, XPS and NMR to examine the following:

(i) the changes caused by microwaves on the crystal structure and morphology of synthetic pure ettringite and metal ion-doped ettringite;

(ii) whether or not synthetic pure ettringite and metal ion-doped ettringite exposed to microwave heating are thermally stable;

(iii) the extent to which microwave heating changes the chemical state and binding energy of the constituent elements of synthetic pure ettringite and metal ion-doped ettringite.
5.2 Microstructure and thermal stability of synthetic ettringite exposed to microwave heating

5.2.1 Sample preparation

In this section, ettringite synthesised at room temperature (see details in Section 3.5.2) was then exposed to microwave and conventional heating at 60, 70 and 80°C for 8 hours. The details of synthetic ettringite exposed to microwave heating and sample ID used are shown in Table 5.1. For all the ettringite samples exposed to microwave and conventional heating, they will be called synthetic ettringite in the following sections.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Heating method</th>
<th>Heating temperature (°C)</th>
<th>The total heating time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFT-RT</td>
<td>Room temperature</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>AFT-M6008</td>
<td>Microwave heating</td>
<td>60</td>
<td>8</td>
</tr>
<tr>
<td>AFT-C6008</td>
<td>Conventional heating</td>
<td>60</td>
<td>8</td>
</tr>
<tr>
<td>AFT-M7008</td>
<td>Microwave heating</td>
<td>70</td>
<td>8</td>
</tr>
<tr>
<td>AFT-C7008</td>
<td>Conventional heating</td>
<td>70</td>
<td>8</td>
</tr>
<tr>
<td>AFT-M8008</td>
<td>Microwave heating</td>
<td>80</td>
<td>8</td>
</tr>
<tr>
<td>AFT-C8008</td>
<td>Conventional heating</td>
<td>80</td>
<td>8</td>
</tr>
</tbody>
</table>

Note: in the sample IDs, AFT: synthetic ettringite; M: microwave heating; C: conventional heating; RT: the synthesis temperature is room temperature (25°C); and the samples were heated to 60°C, 70°C or 80°C.
5.2.2 Effect of microwave heating on the crystalline structure of synthetic ettringite

The XRD patterns of synthetic ettringite exposed to microwave and conventional heating at different temperatures are displayed in Figure 5.1.
Figure 5.1 XRD patterns of synthetic ettringite exposed to microwave and conventional heating at 60 (a), 70 (c) and 80°C (e), whereas (b), (d) and (f) show the changes of the (0001) d-spacings of the corresponding samples with an enlarged main peak of synthetic ettringite (~9.0° 2θ).

It can be clearly seen that ettringite is the only phase present in the room temperature-synthesised sample (AFt-RT) that has not been exposed to any
high-temperature treatment. The pattern agrees well with the XRD patterns of ettringite reported by Shimada and Young (2001) where pure ettringite was prepared by mixing solutions (250mL) of 0.04 mol/L \( \text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} \) and a 0.32mol/L \( \text{Ca(OH)}_2 \) at room temperature for 24 hours. The molar ratio \( \text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} \) to \( \text{Ca(OH)}_2 \) (1:8) is lower than that used in the current study (1:6) based on Equation (3.1). For the samples heated at 60°C, either by microwave or conventional heating, only ettringite peaks were identified, too, showing that the synthetic ettringite can be stable up to 60°C. For the synthetic ettringite samples that are heated at 70 and 80°C, the peaks of gypsum and monosulfate as well as ettringite are identified. This suggests that ettringite has begun to decompose to monosulfate and gypsum when the temperature is 70°C or higher, irrespective of the heating method. Similar results have been reported in other researches (Ghorab et al., 1980, Grounds et al., 1985a, Shimada and Young, 2001). In addition, when the temperature is increased from 70 to 80°C, the intensity of ettringite peaks further decreases, whereas the intensity of gypsum and monosulfate peaks increases. This is more noteworthy for the samples exposed to microwave heating than those exposed to conventional heating.

In order to distinctly observe the very small difference between the XRD results, the main peak of ettringite, at around 9.0 2\( \Theta \), in all samples was amplified in Figure 5.1 (b), (d) and (f) where the x axis has been converted from 2\( \Theta \) to D spacings. We can see that when the samples are heated, the interplanar spacing
of the synthetic ettringites exposed to heat treatments become smaller, compared to that of the sample without being exposed to any heat treatment. For the ettringite exposed to microwave heating, the intensity of the ettringite peak is lower than that of ettringite exposed to conventional heating and the interplanar spacing has shifted to lower values than that exposed to conventional heating.

The average lattice parameters of ettringite calculated using the XRD patterns are shown in Figure 5.2.

**Figure 5.2** Calculated lattice parameters of a (a) and c axes (b) of synthetic ettringite exposed to microwave and conventional heating at 60, 70 and 80°C

The calculated parameters of ettringite synthesised at room temperature (AFt-RT) are \(a=11.2828\) Å and \(c=21.4275\) Å. These values are very similar to the values of ettringite that was reported previously (Bannister, 1936, Moore and Taylor, 1970, Manzano et al., 2012).
It is well-established that the dehydration of ettringite is normally accompanied by lattice shrinkage, mainly in the $a$ axis, arising from the loss of water and motion of columns (Zhou et al., 2004). In Figure 5.2, it can be seen that both heating methods reduce the $a$ and $c$ axes. With microwave heating reducing the $a$ and $c$ axes of ettringite more than conventional heating except for the $c$ axis value of ettringite heated at 60°C. This result is consistent with the literature (Hartman et al., 2006, Bannister, 1936). This contraction may be due to the loss of zeolitic water existing between the columns of ettringite structure when exposed to heating (Zhou and Glasser, 2001).

The XRD results show a clear difference in the lattice dimensions of ettringite between the samples exposed to microwave and conventional heating at 70°C. To further identify any potential effects microwave heating has on the lattice parameters, binding energy of elements and the $^{27}$Al nucleus environment in ettringite, ettringite samples synthesised at room temperature and then exposed to microwave and conventional heating at 70°C were further characterised by TEM, XPS and NMR.

TEM was used to examine the ettringite synthesised at room temperature and synthetic ettringite heated at 70°C. The electron diffraction patterns of each sample are shown in Figure 5.3. All the electron diffraction patterns were collected from the same zone axis [2201].
Figure 5.3 Electron diffraction patterns of ettringite synthesised at room temperature (a), synthetic ettringite exposed to microwave (b) and conventional (c) heating at 70°C

The diffraction patterns were analysed using the method stated in Section 3.6.2, combining with the schematic diagram of corresponding reflection crystal faces (see Figure 4.4) and crystal structure of ettringite (refer to Figure 4.5). From the electron diffraction pattern of ettringite synthesised at room temperature as presented in Figure 5.3 (a), the calculated lattice constants of $a$ and $c$ are 11.342 Å and 21.225 Å, respectively. For the synthetic ettringite sample exposed to microwave heating at 70°C, $a$ and $c$ are 11.123 Å and 19.964 Å, while for the synthetic ettringite exposed to conventional heating at 70°C, 11.141 Å and 20.504 Å, respectively. In general, when exposed to 70°C, the lattice constants of $a$ and $c$ of the synthetic ettringite become shorter and are more pronounced with conventional heating. This agrees with the changes of the $a$ and $c$ axes of ettringite when dehydrated in the previous studies exposed to conventional heating (Bannister, 1936, Zhou et al., 2004). These results show similar trends
as those of the calculated lattice parameters of ettringite from XRD results. The corresponding crystal morphologies seen by TEM are exhibited in Figure 5.4.

![Figure 5.4 TEM micrograph of ettringite synthesised at room temperature (a), synthetic ettringite exposed to microwave (b) and conventional heating (c) at 70°C](image)

It can be seen from Figure 5.4 (a) that the crystals of ettringite synthesised at room temperature are intact, long hexagonal prisms. However, when the synthetic ettringite samples are exposed to 70°C, some lumpy particles have stuck to the crystal surface of ettringite. Furthermore, there are more lumpy particles on the crystal surface of synthetic ettringite exposed to microwave heating [Figure 5.4 (b)] than that exposed to conventional heating [Figure 5.4 (c)]. This indicates that at the same temperature, microwave treatment has caused more damage to the crystals of ettringite.
5.2.3 Effect of microwave heating on the crystalline morphology of synthetic ettringite

The synthetic ettringite samples exposed to microwave heating were examined by SEM and were compared with the samples exposed to conventional heating at the same temperature. All the SEM images are shown in Figure 5.5.

Figure 5.5 SEM micrographs of ettringite synthesised at room temperature (a), synthetic ettringite exposed to microwave (b,d,f) and conventional heating (c,e,g) at 60, 70 or 80°C
It can be seen that at room temperature [Figure 5.5 (a)] and 60°C [Figure 5.5 (b) and (c)], the samples are intact hexagonal prisms, typical of the morphology of ettringite. This indicates that up to 60°C, the synthetic ettringite remains stable, irrespective of the heating method. However, when the synthetic ettringite is heated at 70°C, some slim hexagonal platelet shapes due to monosulfate phase (Baur et al., 2004, Taylor, 1997, Mehta, 1969) have been identified in the synthetic ettringite sample exposed to microwave heating (AFt-M7008) as shown in Figure 5.5 (d), whereas no platelet shapes appear in the synthetic ettringite sample exposed to conventional heating (AFt-C7008) as shown in Figure 5.5 (e). Like the XRD results, this different morphology identified in the synthetic ettringite samples exposed to microwaves at 70°C further confirms that besides the thermal effect of microwaves, there is some other effect from the microwave that may affect the morphology of ettringite. However, at 80°C, platelet shapes appear in the samples of synthetic ettringite exposed to both microwave (AFt-M8008) and conventional heating (AFt-C8008), as seen from Figure 5.5 (f) and (g).

### 5.2.4 Effect of microwave heating on the thermal stability of synthetic ettringite

Figure 5.6 displays the TG and DTG curves of the samples discussed above.
Figure 5.6 TG and DTG patterns of ettringite synthesised at room temperature, synthetic ettringite exposed to microwave and conventional heating at 60 (a), 70 (b) and 80°C (c)

In all the samples, three peaks are clearly observed from 25 to 300°C, which are attributed to the dehydration of ettringite, gypsum and monosulfate in order. This is in agreement with the other research (Meller et al., 2009, Wang et al., 2016). The three corresponding peaks in the current study are at about 85-105°C, 100-115°C, 210-230°C, respectively.

The peak temperature of the decomposition of ettringite in the DTG patterns are plotted in Figure 5.7 to distinctly compare the difference between them.
Figure 5.7 Summary of the peak temperatures of the decomposition of synthetic ettringite samples exposed to microwave and conventional heating at 60, 70 and 80°C

From Figure 5.7, it is interesting to see that at 60, 70 or 80°C, the peak temperature of the decomposition temperature of synthetic ettringite exposed to microwave heating is shifted to lower temperatures compared with that of the synthetic ettringite exposed to conventional heating, e.g. at 70°C, the peak temperature of the decomposition of synthetic ettringite exposed to microwave heating is 92.8°C, while that of the synthetic ettringite exposed to conventional heating is 97.8°C. This finding confirms that microwave-heated sample is consistently less stable than the conventionally heated sample at a given temperature.

The number of water incorporated in the synthetic ettringite was calculated in light of the calculation procedures that were described in Section 3.6.4. The calculated results are shown in Figure 5.8.
Figure 5.8 shows that with the increase of temperature from 60 to 80°C, the number of water molecules decreases from 32 to 28. The synthetic ettringite exposed to microwave heating has less water than that exposed to conventional heating, e.g. at 70°C, the synthetic ettringite exposed to microwave heating has 29.5 water molecules, whereas that exposed to conventional heating has 31 water molecules.

5.2.5 Effect of microwave heating on the binding energy of elements in synthetic ettringite

To investigate the effect of microwave heating on the chemical environment of elements Al, Ca and S, the synthetic ettringite exposed to microwave heating at 70°C for 8 hours (AFT-M7008) was examined by XPS, and then compared with room temperature-synthesised ettringite (AFT-RT) and the synthetic ettringite
exposed to conventional heating at 70°C for 8 hours (AFt-C7008). The data of binding energy and FWHM data of Al 2p, Ca 2p and S 2p spectra are displayed in Figure 5.9.

![Figure 5.9 Binding energy and FWHM of Al 2p (a), Ca 2p (b) and S 2p (c) spectra of ettringite synthesised at room temperature, synthetic ettringite exposed to microwave and conventional heating at 70°C](image)

The binding energy of Al 2p, Ca 2p and S 2p electrons of ettringite synthesised at room temperature are 72.98, 346.11 and 167.95 eV. When heated at 70°C, the binding energies of the Al 2p, Ca 2p and S 2p electrons of synthetic ettringite are lower than that of the synthetic ettringite not exposed to any heat treatment (AFt-RT). Similar trends occur in the data of FWHM. These findings indicate that
heating may change the chemical environment around the elements Al, Ca and S in ettringite (Wagner, 2011), which will be detailed in the discussion section. Moreover, both data show that for the synthetic ettringite exposed to microwave heating the energies are lower than those of the synthetic ettringite exposed to conventional heating. This suggests that microwave heating causes further changes to the chemical environment around each element compared with conventional heating, at a given temperature.

5.2.6 Effect of microwave heating on the $^{27}$Al NMR nucleus in synthetic ettringite

Figure 5.10 shows the $^{27}$Al-NMR spectra of ettringite synthesised at room temperature and synthetic ettringite exposed to microwave and conventional heating at 70°C.
Figure 5.10 $^{27}\text{Al}$ NMR spectra of ettringite synthesised at room temperature, synthetic ettringite exposed to microwave and conventional heating at 70°C. Figure (a) shows the patterns over 200-(-250) ppm range, whereas (b) shows 25-0 ppm for the sake of clarity.

The $^{27}\text{Al}$ NMR peaks for synthetic ettringite exposed to both heating treatments look almost the same; and are smaller than those for ettringite synthesised at room temperature. This indicates that at 70°C, synthetic ettringite shows a trend of decomposition, leading to a reduction in the peak area at round 13 ppm. This is consistent the NMR results in the literature (Shimada and Young, 2001), revealing that when the water in ettringite was reduced, the main peak became broader. The $^{27}\text{Al}$ peak area of synthetic ettringite exposed to microwave heating is smaller than that exposed to conventional heating. Furthermore, the resonance band of $^{27}\text{Al}$ in synthetic ettringite exposed to microwave heating has a slightly higher chemical shift than that exposed to conventional heating. This further supports the argument that when microwave heating was applied, it may have a non-thermal effect besides its thermal effect which leads to a higher chemical shift than from conventional heating. The higher chemical change may be related
to lower electron density around Al (Ogorodnikova et al., 1983). These findings agree well with the XPS results.

5.2.7 Discussion

All the results from XRD, TEM, SEM, TG/DTG, XPS and NMR show that when microwave heating was used to heat the synthetic ettringite, additional chemical changes are noted in addition to the thermal effect of heating. The mechanism of microwave heating working on the synthetic ettringite is detailed as follows.

The synthetic ettringite paste adopted in this investigation is made up of synthetic ettringite and water. The dielectric constant of synthetic ettringite is only 2.0 as shown in Section 3.5.5. It is not a good microwave absorber according to references (Huheey et al., 2006, Shackelford et al., 2016). A detailed description about the mechanism of the dielectric heating of water was discussed in Section 4.4. Therefore, when exposed to microwave heating at 60°C, water molecules are firstly heated promptly followed by the ettringite crystals (Council, 1994, De la Hoz et al., 2005). It is well documented that once the temperature of ettringite reaches a threshold value of decomposition, the two zeolitic water molecules located between the (Ca₆[Al(OH)₆]₂·24H₂O)⁶⁺ columns begins to be lost, followed by the other water molecules bonded to calcium, leading to broadening of the XRD peak of ettringite and a contraction of the a and c axes of ettringite (Skoblinskaya and Krasilnikov, 1975, Hartman and Berliner, 2006, Guimarães et
This phenomenon applies to the synthetic ettringite exposed to microwave heating at 60, 70 and 80°C, and was shown by XRD, TEM and TG results.

In addition to the thermal effect, non-thermal effects were found in other studies, such as reducing the activation energy (Shibata et al., 1996) or increasing the Arrhenius pre-exponential factor $A$ (Binner et al., 1995) in the Arrhenius' equation, and are dependent on the vibration frequency of the atoms at the reaction interface, along with enhanced mass transport (Blanco and Auerbach, 2002, Herrero et al., 2008, Horikoshi and Serpone, 2013, Hinrikus et al., 2015, Li et al., 2007). These can be attributed to the fact that under a microwave field, the rotation of dipoles increases the probability of colliding of molecules and atoms.

Due to the possible reduction of activation energy or an increase of the Arrhenius pre-exponential factor, the decomposition rate of synthetic ettringite might increase. This could result in less crystallinity of ettringite and greater loss of water from the structure of ettringite, giving rise to more contraction along the $a$ and $c$ axes of ettringite than under conventional heating, at any particular temperature, which is seen from the results of XRD, DTG and TEM.

At any particular temperature, the water loss from the synthetic ettringite sample exposed to microwave heating was more than that exposed to conventional
heating as displayed in Section 5.2.4, so the structure contains at least one less water molecule. It is well established that the hydrogen bond network in ettringite clearly plays a significant role in stabilizing and coordinating the structure of ettringite (Hartman and Berliner, 2006). Therefore, the greater water loss from ettringite exposed to microwave heating than that exposed to conventional heating, at a given temperature, indicates that more hydrogen bonds were broken, and thus the stability of synthetic ettringite exposed to microwave is less than that exposed to conventional heating. This can explain why the peak temperature of synthetic ettringite exposed to microwave heating was consistently lower than that exposed to conventional heating when heated at 60, 70 and 80°C. As a result, at any given temperature, the synthetic ettringite exposed to microwaves is more prone to decompose to form monosulfate and gypsum compared to that exposed to conventional heating. This is in consistent with the XRD and SEM results at 70 and 80°C.

Greater water loss would result in an increase in the loss of oxygen atoms in ettringite structure, decreasing the bridging moiety of the Al-O, Ca-O and S-O bonds, thus reducing the binding energy of the Al 2p, Ca 2p and S 2p electrons in ettringite (Smith et al., 2006). This was verified by the XPS results which showed that at 70°C under microwave heating, the binding energy of the Al 2p, Ca 2p and S 2p electrons of synthesised ettringite have shifted to lower values compared to those under conventional heating. The XPS results agree with the
statement that the absorption of microwave photons cannot induce any chemical bond breaking due to the inadequate energy, but under microwave heating, the polar molecules vibrate at the frequency of the microwaves, which may affect the strength of the bond or alter the distribution of electrons around atoms (Stuerga and Gaillard, 1996, Meredith, 1998). The NMR results show that, at 70°C, the resonance band of $^{27}$Al-NMR in synthetic ettringite exposed to microwave heating has a higher chemical shift value compared to the sample exposed to conventional heating. This demonstrates that greater loss of oxygen from ettringite structure under microwave heating results in a reduction of covalent bonds, decreasing the shared electron pairs, thus leading to a lower electron density distribution around Al nucleus compared to the conventional heating (Huheey et al., 2006, Levitt, 2001).
5.3 Microstructure and thermal stability of metal ion-doped ettringite exposed to microwave heating

5.3.1 Sample preparation

This section investigates the influence of microwave heating on the microstructure and thermal stability of Fe- ettringite, Cr- ettringite and Mn- ettringite. The three metal ions doped ettringites were firstly synthesised at room temperature before being exposed to microwave and conventional heating at 60, 70 and 80°C for 8 hours. The details on synthesis and heating treatment can be seen in Chapter 3. The sample details of synthetic Fe- ettringite, Cr- ettringite and Mn- ettringite exposed to microwave heating are presented in Tables 5.2-5.4. All heat treated samples were characterized by XRD, TEM, SEM, TG, XPS and NMR. The three metal ion-doped ettringite samples will be called synthetic Fe- ettringite, Cr- ettringite and Mn- ettringite in the subsequent sections.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Heating method</th>
<th>Heating temperature (°C)</th>
<th>Heating time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-AFT-RT</td>
<td>Room temperature</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>Fe-AFT-M6008</td>
<td>Microwave heating</td>
<td>60</td>
<td>8</td>
</tr>
<tr>
<td>Fe-AFT-C6008</td>
<td>Conventional heating</td>
<td>60</td>
<td>8</td>
</tr>
<tr>
<td>Fe-AFT-M7008</td>
<td>Microwave heating</td>
<td>70</td>
<td>8</td>
</tr>
<tr>
<td>Fe-AFT-C7008</td>
<td>Conventional heating</td>
<td>70</td>
<td>8</td>
</tr>
<tr>
<td>Fe-AFT-M8008</td>
<td>Microwave heating</td>
<td>80</td>
<td>8</td>
</tr>
<tr>
<td>Fe-AFT-C8008</td>
<td>Conventional heating</td>
<td>80</td>
<td>8</td>
</tr>
</tbody>
</table>
Table 5.3 Details of Cr- ettringite exposed to microwave heating

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Heating method</th>
<th>Heating temperature (°C)</th>
<th>Heating time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr-AFt-RT</td>
<td>Room temperature</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>Cr-AFt-M6008</td>
<td>Microwave heating</td>
<td>60</td>
<td>8</td>
</tr>
<tr>
<td>Cr-AFt-C6008</td>
<td>Conventional heating</td>
<td>60</td>
<td>8</td>
</tr>
<tr>
<td>Cr-AFt-M7008</td>
<td>Microwave heating</td>
<td>70</td>
<td>8</td>
</tr>
<tr>
<td>Cr-AFt-C7008</td>
<td>Conventional heating</td>
<td>70</td>
<td>8</td>
</tr>
<tr>
<td>Cr-AFt-M8008</td>
<td>Microwave heating</td>
<td>80</td>
<td>8</td>
</tr>
<tr>
<td>Cr-AFt-C8008</td>
<td>Conventional heating</td>
<td>80</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 5.4 Details of Mn-ettringite exposed to microwave heating

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Heating method</th>
<th>Heating temperature (°C)</th>
<th>Heating time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn-AFt-RT</td>
<td>Room temperature</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>Mn-AFt-M6008</td>
<td>Microwave heating</td>
<td>60</td>
<td>8</td>
</tr>
<tr>
<td>Mn-AFt-C6008</td>
<td>Conventional heating</td>
<td>60</td>
<td>8</td>
</tr>
<tr>
<td>Mn-AFt-M7008</td>
<td>Microwave heating</td>
<td>70</td>
<td>8</td>
</tr>
<tr>
<td>Mn-AFt-C7008</td>
<td>Conventional heating</td>
<td>70</td>
<td>8</td>
</tr>
<tr>
<td>Mn-AFt-M8008</td>
<td>Microwave heating</td>
<td>80</td>
<td>8</td>
</tr>
<tr>
<td>Mn-AFt-C8008</td>
<td>Conventional heating</td>
<td>80</td>
<td>8</td>
</tr>
</tbody>
</table>

**Note:** in the sample IDs, Fe-AFt, Cr-AFt and Mn-AFt stand for synthetic Fe-ettringite, Cr-ettringite and Mn-ettringite, respectively; M: microwave heating; C: conventional heating; RT: the synthesis temperature is room temperature (25°C); and samples were heated to 60, 70 or 80°C.
5.3.2 Effect of microwave heating on the crystal structure of synthetic Fe- ettringite, Cr- ettringite and Mn- ettringite

The results obtained from the XRD analysis of the synthetic Fe- ettringite, Cr- ettringite, Mn- ettringite samples exposed to the distinct heating treatments are plotted in Figures 5.11-5.13.
Figure 5.11 XRD patterns of synthetic Fe-ettringite exposed to microwave and conventional heating at 60 °C (a), 70 °C (c) and 80 °C (e), with (b), (d) and (f) showing the changes of (0001) d-spacings of the corresponding samples in the enlarged main peak of synthetic Fe-ettringite (~9.0° 2θ)
Figure 5.12 XRD patterns of synthetic Cr-ettringite exposed to microwave and conventional heating at 60 (a), 70 (c) and 80°C (e), with (b), (d) and (f) showing the changes of (0001) d-spacings of the corresponding samples by enlarged main peak of synthetic Cr-ettringite (~9.0° 2θ)
Figure 5.13 XRD patterns of synthetic Mn-ettringite exposed to microwave and conventional heating at 60 (a), 70 (c) and 80°C (e), with (b), (d) and (f) showing the changes of (0001) d-spacings of the corresponding samples from the enlarged main peak of synthetic Mn-ettringite (~9.0° 2θ)
In the room temperature-synthesised samples (Fe-AFt-RT, Cr-AFt-RT and Mn-AFt-RT), only Fe-ettringite, Cr-ettringite and Mn-ettringite are identified respectively, indicating that all the three metal ion-doped samples are pure with few impurities. As the three metal ion-doped ettringites belong to ettringite group, the structure of metal ion-doped ettringite is very similar to pure ettringite. The main reflections of each sample are very close to those of pure ettringite, but the XRD peaks are broadened with some peak shifts (Collepardi et al., 1979, Möschner et al., 2009, Wieczorek-Ciurowa et al., 2001, Norman et al., 2013, You et al., 2007b). This is because the radii of the dopant ions (Fe, Cr and Mn) are bigger than Al ion, leading to the broadening XRD peaks of metal ion-doped ettringite compared with pure ettringite.

At 60°C, only peaks due to Fe-ettringite, Cr-ettringite and Mn-ettringite are detected in the corresponding samples irrespective of the heating method. At 70°C, in the synthetic Fe-ettringite and Cr-ettringite samples, only Fe-ettringite and Cr-ettringite peaks are identified, whereas in the synthetic Mn-ettringite sample, peaks of Mn-ettringite, gypsum and Mn-monosulfate are observed. At 80°C, in the synthetic Fe-ettringite sample, only the Fe-ettringite peak is identified. But in the synthetic Cr-ettringite sample, Cr-ettringite, bassanite as well as Cr-monosulfate co-exists and similarly, in the synthetic Mn-ettringite, peaks of Mn-ettringite, gypsum and Mn-monosulfate appear.
As the temperature is increased from 60 to 80°C, the intensity of the Fe-ettringite peak decreases significantly. At any given temperature, the intensity of Fe-ettringite peak in the sample exposed to microwave heating is always slightly less than that in the sample exposed to conventional heating.

For the synthetic Cr-ettringite sample at 80°C, bassanite and Cr-monosulfate are present coming from the decomposition of Cr-ettringite. Likewise, for the synthetic Mn-ettringite sample, when the temperature is increased beyond 70°C, the Mn-ettringite decomposes to form gypsum and Mn-monosulfate.

All these results point to the fact that when exposed to high-temperature treatment, the thermal stability of three ion-doped ettringite samples become less stable than the room temperature-synthesised samples. At any given temperature, the three microwave heated metal ion-doped ettringite samples are less stable than the samples exposed to conventional heating.

In order to observe the small differences between the samples caused by the two distinct heating treatments, and hence identify the potential effects caused by microwave heating, the main peaks of Fe-ettringite, Cr-ettringite and Mn-ettringite at around 9.0 2Θ in all samples were amplified as shown in [Figure 5.11 (b), (d) and (f)], [Figure 5.12 (b), (d) and (f)] and [Figure 5.13 (b), (d) and (f)]. It can be clearly seen that at a fixed heating temperature, the interplanar crystal spacing of
Fe-ettringite, Cr-ettringite and Mn-ettringite exposed to microwave heating has shifted to lower values with lower intensities compared to that of the corresponding conventionally heated samples.

The lattice parameters of the three metal ion-doped ettringite were calculated from the corresponding XRD patterns and the results are plotted in Figures 5.14-5.16.

Figure 5.14 Calculated lattice parameters of a (a) and c axes (b) of Fe-ettringite exposed to microwave and conventional heating at 60, 70 or 80°C

Figure 5.15 Calculated lattice parameters of a (a) and c axes (b) of Cr-ettringite exposed to microwave and conventional heating 60, 70 or 80°C
Figure 5.16 Calculated lattice parameters of $a$ (a) and $c$ axes (b) of Mn-ettringite exposed to microwave and conventional heating conditions at 60, 70 or 80°C

As the three metal ion-doped ettringites belong to ettringite group, they have similar properties to that of pure ettringite. The data displayed in Figures 5.14-5.16 show that like pure ettringite, microwave heating at any temperature has reduced the $a$ axis dimensions of three metal ion-doped ettringites more than for the conventionally heated samples. Also, the higher the temperature, the shorter the lattice in the $a$ axis, which is consistent with the trend reported in the literature (Hartman et al., 2006, Bannister, 1936). The $c$ axis lattice dimension of the three metal ion-doped ettringite samples also show similar trends as those found for the $a$ axis, except for samples exposed to 60°C. These changes are likely to be caused by the loss of inter-columnar water and apical water when subjected to elevated temperatures. The difference between the microwave and conventionally heated sample results indicate that microwaves not only play a role of heating, but can also have an additional effect that can modify the crystal structure of the three metal ion-doped ettringites.
The XRD results clearly show a difference in the lattice dimensions of each ion doped ettringite sample exposed to microwave and conventional heating. To further identify the effects of microwave heating has on the lattice parameters of the three metal ion-doped ettringite samples, the binding energy of elements as well as the $^{27}$Al nucleus environment in ion-doped ettringite sample were further characterised by TEM, XPS and NMR, for samples synthesised at either room temperature or heated to 70°C using microwave and conventional heating. Fe-ettringite could not be measured by NMR as Fe$^{3+}$ is paramagnetic and can disturb the NMR measurements (Knop - Gericke, 2012).

The electron diffraction patterns of Cr-ettringite and Mn-ettringite are presented in Figures 5.17-5.18. All the electron diffraction patterns were collected from the same zone axis [220̅].

![Figure 5.17 Electron diffraction patterns of Cr-ettringite synthesised at room-temperature (a), synthetic Cr-ettringite exposed to microwave and conventional heating](image)

Figure 5.17 Electron diffraction patterns of Cr-ettringite synthesised at room-temperature (a), synthetic Cr-ettringite exposed to microwave and conventional heating
The diffraction patterns shown in Figures 5.17-5.18 were analysed using the method explained in Section 3.6.2, combined with the schematic diagram of corresponding reflection crystal faces (Figure 4.4) and the crystal structure of ettringite (Figure 4.5). From the electron diffraction pattern of synthesised Cr-ettringite in Figure 5.17 (a), the calculated lattice constants of $a$ and $c$ of Cr-ettringite are 11.282 and 21.491 Å. When heated by microwaves to 70°C, the values for $a$ and $c$ are 11.203 and 21.402 Å respectively, whilst for conventional heating at 70°C, $a$ and $c$ are 11.221 and 21.454 Å.

From Figure 5.18 (a), the calculated $a$ and $c$ lattice constants of Mn-ettringite synthesised at room temperature are 11.182 and 22.231 Å. Similarly, for the synthetic Mn-ettringite exposed to microwave heating at 70°C [Figure 5.18 (b)], $a$ and $c$ are 11.143 and 21.524 Å, and for that exposed to conventional heating at 70°C [Figure 5.18 (c)], the $a$ and $c$ dimensions are 11.163 and 21.681 Å.
The above results show that both the $a$ and $c$ axes in Cr-ettringite and Mn-ettringite have shrunk when heated at 70°C, with more shrinkage occurring under microwave heating. These results agree very well with the results of a previous study that investigated the changes of a natural specimen of ettringite upon dehydration using X-ray techniques (Hartman et al., 2006). They found that the $a$-axis decreased from 11.24 to 8.4 Å and the $c$-axis was reduced from 21.45 to 10.21 Å at 90°C. These results are similar to the lattice parameters of Cr-ettringite and Mn-ettringite calculated from XRD patterns. The corresponding TEM micrograph of each sample is exhibited in Figures 5.19-5.20.

![Figure 5.19 TEM micrograph of Cr-ettringite synthesised at room temperature (a), synthetic Cr-ettringite exposed to microwave and conventional heating at 70°C](image)

![Figure 5.20 TEM micrograph of Mn-ettringite synthesised at room temperature (a), synthetic Mn-ettringite exposed to microwave and conventional heating at 70°C](image)
As shown in Figures 5.19-5.20 (a), the TEM micrograph of Cr-ettringite and Mn-ettringite synthesised at room temperature show the crystals appear as long intact hexagonal prisms. However, when heated at 70°C, the crystals of Cr-ettringite and Mn-ettringite look shorter than the samples synthesised at room temperature. In addition, some very small irregular shapes have appeared. More damage has occurred on the samples exposed to microwave heating than on those exposed to conventional heating. These TEM results once again demonstrate that microwave exposure may have additional effects besides its role of heating, causing more changes on the crystal structure of ettringite than the conventional heating at the same temperature.

5.3.3 Effect of microwave heating on the morphology synthetic Fe-ettringite, Cr-ettringite and Mn-ettringite

The SEM images of metal ion-doped ettringite samples under different conditions are shown in Figures 5.21-5.23.
Figure 5.21 SEM micrographs of Fe-ettringite synthesised at room temperature (a), synthetic Fe-ettringite exposed to microwave heating (b,d,f) and conventional heating (c,e,g) at 60, 70 and 80°C, respectively.
Figure 5.22 SEM micrographs of Cr-ettringite synthesised at room temperature (a), synthetic Cr- ettringite exposed to microwave heating (b,d,f) and conventional heating (c,e,g) at 60, 70 and 80°C, respectively.
Figure 5.23 SEM micrographs of Mn-ettringite synthesised at room temperature (a), synthetic Mn-ettringite exposed to microwave heating (b,d,f) and conventional heating (c,e,g) at 60, 70 and 80°C, respectively.

When synthetic Fe-ettringite, Cr-ettringite and Mn-ettringite are exposed to microwave and conventional heating at 60°C, intact hexagonal columnar morphology is observed, the same as the typical morphology of ettringite prepared by using a solution of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and a slurry of CaO in water at 4°C in a PE bottle (Baur et al., 2004). No difference is observed between the
same samples exposed to microwave and conventional heating at 60°C, showing that the three samples remain stable at 60°C irrespective how they are heated.

When heated by microwaves at 70°C, several short irregular shaped crystals are observed in the three synthetic metal ion-doped ettringite samples as shown in Figures 5.21-5.23 (d), whereas crystals in the three samples heated conventionally remain as intact hexagonal prisms as displayed in Figures 5.21-5.23 (e).

At 80°C, some amorphous morphology is observed in all three synthetic metal ion-doped ettringite samples exposed to both microwaves [Figures 5.21-5.23 (f)] and conventional heating [Figures 5.21-5.23 (g)], with more amorphous morphology in the samples exposed to microwave heating. These results agree with the XRD and TEM results.

5.3.4 Effect of microwave heating on the thermal stability of synthetic Fe-ettringite, Cr-ettringite and Mn-ettringite

As stated in Section 4.2, the decomposition of ettringite was followed by thermal analysis. The TG and DTG patterns of the synthetic Fe-ettringite, Cr-ettringite, Mn-ettringite samples exposed to the distinct heating treatments are presented in Figures 5.24-5.26.
Figure 5.24 TG and DTG patterns of Fe-ettringite synthesised at room temperature, synthetic Fe-ettringite exposed to microwave and conventional heating at 60 (a), 70 (b) and 80°C (c)
Figure 5.25 TG and DTG patterns of Cr-ettringite synthesised at room temperature, synthetic Cr-ettringite exposed to microwave and conventional heating at 60 (a), 70 (b) and 80°C (c)
Figure 5.26 TG and DTG patterns of Mn-ettringite synthesised at room temperature, synthetic Mn-ettringite exposed to microwave and conventional heating at 60 (a), 70 (b) and 80°C (c)

In the DTG curves of Fe-ettringite synthesised and synthetic Fe-ettringite exposed to 60°C [Figure 5.24 (a)], only one peak (around 92.5-98.5°C) is identified, which is assigned to the decomposition of Fe-ettringite. This is in agreement with the DTG data of Fe-ettringite presented in the literature (Csizmadia et al., 2001). However, at 70°C and above [Figure 5.24 (b) and (c)], a very small shoulder appears in the DTG curves of samples exposed to high temperatures at around 105°C and a very tiny peak appeared at about 220°C,
which are attributed to the decomposition of gypsum (Paulik et al., 1992) and the decomposition of Fe-monsosulfate, respectively. The gypsum and Fe-monsosulfate could have been formed from the decomposition of Fe- ettringite at temperatures beyond 70°C under microwave or conventional heating. These results suggest that when Fe- ettringite is heated to 70°C and above, either by conventional or microwave heating, the ettringite sample begins to decompose, thereby leading to more gypsum being formed compared to room temperature.

In the DTG curves of Cr- ettringite synthesised at room temperature as well as all the synthetic Cr- ettringite samples exposed to 60, 70 and 80°C, either by microwave or conventional heating, only two peaks are observed, which are ascribed to the decomposition of Cr- ettringite (around 100-105°C) and Cr- monosulfate (about 225-230°C). The DTG figure is very similar to that of Cr- ettringite prepared by using solutions of Cr2(SO4)3·18H2O and CaO calcined from CaCO3 at room temperature (Wieczorek-Ciurowa et al., 2001). However, no clear peak for the decomposition of gypsum was present in their trace. One possible reason may be that the decomposition peak of gypsum overlaps with the decomposition peak of Cr- ettringite.

In the DTG curve of the Mn-ettringite synthesised at room temperature and all the synthetic Mn-ettringite samples exposed to 60, 70 and 80°C irrespective of heating type, three peaks are observed, which are attributed to the decomposition
of Mn-ettringite (about 100-105°C), gypsum (111-117°C) and Mn-monosulfate (215-225°C).

To compare the peak temperature of the decomposition of three metal ion-doped ettringites exposed to 60, 70 and 80°C under microwave and conventional heating, the peak temperature of each sample from DTG patterns is summarized in Figure 5.27.

![Figure 5.27 Summary of peak temperatures of the decomposition of synthetic Fe-ettringite (a), Cr-ettringite (b) and Mn-ettringite exposed to microwave and conventional heating at 60, 70 and 80°C](image)
From Figure 5.27, it is interesting to note that the peak temperatures of all samples of the synthetic Fe-ettringite, Cr-ettringite and Mn-ettringite exposed to microwave heating are always lower than their counterparts exposed to conventional heating at a given temperature, indicating that the samples exposed to microwave heating are less stable. This difference can be attributed to the non-thermal effects of microwave treatment which may relate to an increase in the Arrehenius pre-exponential factor or a reduction in the activation energy (Stuerga et al., 2006), accelerating the decomposition of metal ion-doped ettringite.

The number of water molecules present in the synthetic Fe-ettringite, Cr-ettringite and Mn-ettringite was calculated according to the procedures stated in Section 3.6.4 in Chapter 3 and the results are shown in Figure 5.28.
It can be seen in Figure 5.28 that with the increase of the temperature, the number of water molecules existing in each metal ion-doped ettringite decreases. At any given temperature, microwave heating decreases the number of water molecules in the ion-doped ettringite more than conventional heating. For example, at 80°C, Fe-ettringite exposed to microwave heating has 28 water molecules, while that exposed to conventional heating has 29 water molecules; for Cr-ettringite exposed to microwave and conventional heating, the water molecules are 28 and 28.5, respectively; for Mn-ettringite, the sample exposed to microwave heating
has 28 water molecules, whereas the sample with conventional heating has 28.5 water molecules.

5.3.5 Effect of microwave heating on the binding energy of elements in synthetic Fe-ettringite, Cr-ettringite and Mn-ettringite

The binding energy and FWHM data of the Al 2p, Ca 2p and S 2p electron spectra are presented in Figures 5.29-5.31.
Figure 5.29 Binding energy and FWHM of Al 2p (a), Ca 2p (b) and S 2p (c) spectra of Fe-ettringite synthesised at room temperature, synthetic Fe-ettringite exposed to microwave and conventional heating at 70°C
Figure 5.30 Binding energy and FWHM of Al 2p (a), Ca 2p (b) and S 2p (c) spectra of Cr-etttringite synthesised at room temperature and synthetic Cr-etttringite exposed to microwave and conventional heating at 70°C
Figure 5.31 The binding energy and FWHM of Al 2p (a), Ca 2p (b) and S 2p (c) spectra of Mn-ettringite synthesised at room temperature, synthetic Mn-ettringite exposed to microwave and conventional heating conditions at 70°C

From Figures 5.29-5.31 (a), it can be observed that the binding energy of the Al 2p electrons centres around 72 eV in the synthetic Fe-ettringite, Cr-ettringite and Mn-ettringite samples exposed to both conventional and microwave heating. This is lower than that in the corresponding samples synthesised at room temperature. In comparison, the binding energy of the Al 2p electrons in the synthetic Fe-ettringite, Cr-ettringite and Mn-ettringite samples exposed to microwave heating is subtly lower than the counterparts exposed to conventional heating.
Figures 5.29-5.31(b) show that the binding energies of the Ca 2p electrons in the synthetic Fe-ettringite, Cr-ettringite and Mn-ettringite samples exposed to 70°C are lower than that of corresponding room temperature-synthesised samples. Also, the binding energy of Ca 2p electron in any synthetic ion-doped ettringite exposed to microwave heating is slightly lower than that exposed to conventional heating.

Like the Al 2p and Ca 2p, the binding energy of S 2p electrons in the synthetic Fe-ettringite, Cr-ettringite and Mn-ettringite samples heated at 70°C has shifted to a lower value compared with Fe-ettringite, Cr-ettringite and Mn-ettringite synthesised at room temperature as shown in Figures 5.29-5.31(c). Moreover, the binding energy of S 2p electron of the synthetic ion-doped ettringite exposed to microwave heating is lower than its counterpart exposed to conventional heating. This shows that high temperature treatment reduces the binding energy of S 2p electrons, with microwave heating giving a greater reduction in the binding energy.

A similar trend occurs in the binding energy of Al 2p, Ca 2p and S 2p electrons suggests that microwaves may have both thermal and non-thermal effects.
5.3.6 Effect of microwave heating on the $^{27}$Al nucleus in synthetic Fe- ettringite, Cr- ettringite and Mn- ettringite

To study the influence of different heating conditions on the chemical environment of $^{27}$Al nucleus, the metal ion-doped ettringite (Fe-ettringite, Cr-ettringite and Mn-ettringite) synthesised at room temperature and metal ion-doped ettringite exposed to microwave and conventional heating at 70°C for 8 hours were examined by NMR and the results are shown in Figures 5.32-5.34.

![Figure 5.32](image)

Figure 5.32 $^{27}$Al NMR spectra of synthetic Fe-ettringite exposed to microwave and conventional heating at 70°C. Figure (a) shows the patterns over 200-(-250) ppm range, whereas (b) shows 25-0 ppm for clarity.
Figure 5.33 $^{27}$Al NMR spectra of synthetic Cr-etàtringite exposed to microwave and conventional heating at 70°C. Figure (a) shows the the patterns over 200-(-250) ppm range, whereas (b) shows 25-0 ppm for clarity.

Figure 5.34 $^{27}$Al NMR spectra of synthetic Mn-etàtringite exposed to microwave and conventional heating at 70°C. Figure (a) shows the the patterns over 200-(-250) ppm range, whereas (b) shows 25-0 ppm for clarity.

Figure 5.32 shows that the $^{27}$Al peaks of synthetic Fe-etàtringite samples exposed to conventional and microwave heating at 70°C are almost the same, with the peak area centred around 13 ppm and much smaller than that synthesised at
room temperature. This implies that a high temperature may change the environmental surrounding the $^{27}$Al nucleus, giving a disordered structure leading to a decrease in the $^{27}$Al-NMR resonance (Huheey et al., 2006). The $^{27}$Al peaks of synthetic Fe-ettringite exposed to microwave heating are almost the same as those of synthetic Fe-ettringite exposed to conventional heating.

From Figures 5.33-5.34, we can see that the area of the $^{27}$Al peaks of synthetic Cr-ettringite and Mn-ettringite exposed to microwave and conventional heating at around 13 ppm are all smaller than those of the room temperature synthesised sample. This shows that high temperature may change the environmental surrounding of the $^{27}$Al nucleus, leading to a reduction in the amount of $^{27}$Al-NMR resonance. In addition, at 70°C, the resonance band of $^{27}$Al in the microwave heated synthetic Cr-ettringite and Mn-ettringite samples has a higher chemical shift than in the corresponding conventionally heated samples. This suggests that when microwave heating is applied, it generates a non-thermal effect besides its thermal effect, which results in a higher chemical shift than conventional heating. These findings are in good accordance with the XPS results, once again demonstrating the existence of non-thermal effect of microwave heating.
The results from XRD, TEM, SEM, TG/DTG, XPS and NMR all indicate that when microwaves are employed to heat synthetic Fe-ettringite, Cr-ettringite and Mn-ettringite, the microwaves act to produce both thermal and non-thermal effects. Both effects have been reported in a number of studies (Tompsett et al., 2006, Kaewwichit et al., 2017, Li et al., 2001, Binner et al., 1995, Menezes et al., 2012, Zhu and Chen, 2014).

The three synthetic metal ion-doped ettringite pastes are composed of synthetic metal ion-doped ettringite and water. As the three metal ion-doped ettringite belongs to ettringite group, the structure of metal ion-doped ettringite is very similar to pure ettringite, but their lattice parameters are different. This is because the radii of the Fe$^{3+}$, Cr$^{3+}$ and Mn$^{2+}$ are bigger than that of Al$^{3+}$ (Huheey et al., 2006), so when the three ions substitute for Al$^{3+}$ to form ion-doped ettringite, the structure of ion-doped ettringite is similar to ettringite but the c axis of the ion-doped samples is generally longer than that of ettringite.

Like ettringite, Fe-ettringite, Cr-ettringite and Mn-ettringite are also poor microwave absorbers, because their measured dielectric constants are very low, 1.90, 1.72 and 1.56 respectively. Hence, they act as poor electric conductors in the microwave field. Poor electric conductors are often heated by close proximity to dielectric substances (la Hoz et al., 2006). As stated previously, water
molecules are good microwave absorbers, so when synthetic ion-doped ettringite pastes are exposed to microwaves at 60°C, the water molecules in the synthetic ion-doped ettringite samples are heated promptly (see details in Section 4.4) in turn heating the synthetic ion-doped ettringite samples (Huheey et al., 2006, Gupta and Leong, 2008).

It is well known that once the temperature reaches the critical value of decomposition, two zeolitic water molecules located between the (Ca₆[(Fe/Cr/Mn, Al)(OH)₆]₂·24H₂O)⁶⁺ columns are lost, followed by the other water molecules bonded to calcium. This water loss from ettringite results in broadening of the XRD peaks as well as shrinkage of the a and c axes of ettringite (Skoblinskaya and Krasilnikov, 1975, Hartman and Berliner, 2006, Guimarães et al., 2016). This will also apply to the synthetic metal ion-doped ettringite exposed to microwave heating, as seen from XRD, TEM and TG results.

When the temperature is increased, the conductivity of metal ion-doped ettringite might also increase, leading to an increase in the dielectric properties that allows better coupling with microwaves (Gupta and Leong, 2008). This may affect the non-thermal effects of microwaves, increasing the Arrehenius pre-exponential factor A (Binner et al., 1995) or decreasing the activation energy Eₐ (Fini and Breccia, 1999) in the Arrhenius’ equation, so the decomposition rate of metal ion-doped ettringite might be increased. These can lead to more water lost from the
structure of ettringite, and therefore more shrinkage in the $a$ and $c$ axes of ettringite than that occurs under conventional heating at all elevated temperatures. These have been verified by the results of XRD, DTG and TEM.

At the same temperature, more water is lost from the microwave heated synthetic metal ion-doped ettringite samples than those exposed to conventional heating as shown in Section 5.3.4. As discussed in Section 4.4, this water loss from ettringite leads to collapse of the hydrogen bonded network of water molecules. It was reported that the hydrogen bond network in ettringite clearly plays a significant role in stabilizing the structure of ettringite (Hartman and Berliner, 2006). More water loss means more broken hydrogen bonds and thus less stability. This can explain why the decomposition temperatures of the synthetic metal ion-doped ettringite exposed to microwave heating are consistently lower than those exposed to conventional heating at 60, 70 and 80°C. Consequently, at a particular temperature, a synthetic metal ion-doped ettringite heated by microwaves is more prone to decompose to form monosulfate and gypsum than that exposed to conventional heating. This has been demonstrated by the XRD and SEM results at 70 and 80°C.

Similar to pure ettringite, a greater water loss would result in an increase in the loss of oxygen atoms in the structure of metal ion-doped ettringite, decreasing the bridging moiety of Al-O, Ca-O and S-O bonds, thus reducing the binding
energy of Al 2p, Ca 2p and S 2p electrons in metal ion-doped ettringites (Smith et al., 2006, Pozar, 2009). This was shown by XPS results. The NMR results also show that, when heated to 70°C, the peak area of the $^{27}$Al-NMR signal in the synthetic metal ion-doped ettringite exposed to microwave heating is smaller and has a higher chemical shift compared to that exposed to conventional heating, which has demonstrated the possibility of a lower electron density distribution around Al nucleus (Huheey et al., 2006). This is because the loss of more oxygen (water) from the structure of metal ion-doped ettringites exposed to microwave heating would result in a reduction of covalent bonds, decreasing the number of the shared electron pairs, leading to a lower electron density distribution around Al nucleus compared to a sample conventionally heated.

5.4 Conclusions

This chapter has in detail investigated the microstructure and thermal stability of synthetic pure ettringite and metal ion-doped ettringites exposed to microwave heating. The main conclusions can be summarised as follows.

- Compared to conventional heating, microwave heating causes slightly more water to be lost from pure ettringite, leading to more shrinkage in all crystal axes of the corresponding samples, and makes them thermally less stable. This may be ascribed to a reduction in the activation energy for the decomposition of ettringite under microwave heating.
• Increasing the temperature augments the extent of structural changes in pure ettringite and this is more pronounced with microwave heating than conventional heating. This may be because more water loss from ettringite under microwave results in an increase in the loss of oxygen atoms in ettringite structure, thus giving rise to small change in the ettringite structure.

• As the radii of Fe$^{3+}$, Cr$^{3+}$ and Mn$^{2+}$ ions are bigger than Al ion, the XRD peaks of metal ion-doped ettringite are more broader than those of pure ettringite. The three metal ion-doped ettringites have similar structures to pure ettringite, so they show a similar trend to the microstructure and thermal stability of pure ettringite when exposed to microwave heating. Namely, compared to conventional heating, microwave heating makes the metal ion-doped ettringites shrink more and become less stable.
Chapter 6 Microstructure and Thermal Stability of Ettringite in Cement Systems Subjected to Microwave Curing

6.1 Introduction

Thus far, this thesis has shown that microwave heating affects the microstructure and thermal stability of synthetic ettringite and metal ion-doped ettringites. In general, compared to conventional heating, at 60, 70 or 80°C, (i) ettringite and metal ion-doped ettringite shrink more when they are formed under or exposed to microwave heating; (ii) microwaved ettringite and metal ion-doped ettringite are thermally less stable. However, it still remains unclear as to whether the observations made so far do in fact occur to the ettringite crystals formed in cement pastes. Therefore, it is imperative to investigate the behaviour of ettringite formed in cement pastes under microwave curing. Two types of cement were used: calcium sulfoaluminate cement (C₃S₄A) and Portland cement (PC).

As ettringite is the main hydration product of C₃S₄A cement, it is expected that the findings of the pure ettringite systems can be applied to the study of ettringite formed in real C₃S₄A cement pastes. Then, the investigation is extended to PC pastes, the main binding material in precast concrete, to provide the reference and basic information for microwave curing precast concrete.
As stated in Chapter 2, in the steam curing precast industry, concrete is normally cured for an initial few hours at ambient conditions, during which some ettringite is formed. Ettringite forms quickly, resulting in some ettringite formed in C₅A (Winnefeld et al., 2017) and PC pastes (Gaviria et al., 2018, Maciel et al., 2019) within one hour, so an initial delay time of one hour before heating was chosen for this study. Following the one-hour delay at room temperature, C₅A and PC pastes samples were subjected to microwave curing at different temperatures for 8 hours. The samples obtained were then characterised using XRD, SEM and TG. As a reference, C₅A and PC pastes samples were also subjected to room temperature and conventional curing. The purpose of this chapter is to study the influence of microwave curing on the crystal structure, morphology of ettringite as well as its thermal stability when it forms in C₅A and PC pastes.

6.2 Microstructure and thermal stability of ettringite in C₅A paste subjected to microwave curing

6.2.1 Sample preparation

In this section, C₅A pastes that had been subjected to one-hour initial delay under ambient conditions and then subjected to microwave and conventional curing at 60, 70 and 80°C for 8 hours were investigated. For C₅A pastes, 25% gypsum by weight of C₅A clinker was used with a water to solid ratio fixed at 0.65. More details on the mixture of C₅A pastes can be seen in Section 3.5.3.
The details of $\text{C}_\text{S}_\text{A}$ pastes subjected to microwave curing and sample IDs used are shown in Table 6.1. Following curing, the samples were characterized by XRD, SEM and TG.

Table 6.1 Details of $\text{C}_\text{S}_\text{A}$ pastes subjected to microwave and conventional curing at 60, 70 and 80°C

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Delay time (h)</th>
<th>Curing condition</th>
<th>Curing Temperature (°C)</th>
<th>Curing Duration (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}<em>\text{S}</em>\text{A}$-D1-RT08</td>
<td>1</td>
<td>Room temperature</td>
<td>25</td>
<td>8</td>
</tr>
<tr>
<td>$\text{C}<em>\text{S}</em>\text{A}$-D1-M6008</td>
<td>1</td>
<td>Microwave curing</td>
<td>60</td>
<td>8</td>
</tr>
<tr>
<td>$\text{C}<em>\text{S}</em>\text{A}$-D1-C6008</td>
<td>1</td>
<td>Conventional curing</td>
<td>60</td>
<td>8</td>
</tr>
<tr>
<td>$\text{C}<em>\text{S}</em>\text{A}$-D1-M7008</td>
<td>1</td>
<td>Microwave curing</td>
<td>70</td>
<td>8</td>
</tr>
<tr>
<td>$\text{C}<em>\text{S}</em>\text{A}$-D1-C7008</td>
<td>1</td>
<td>Conventional curing</td>
<td>70</td>
<td>8</td>
</tr>
<tr>
<td>$\text{C}<em>\text{S}</em>\text{A}$-D1-M8008</td>
<td>1</td>
<td>Microwave curing</td>
<td>80</td>
<td>8</td>
</tr>
<tr>
<td>$\text{C}<em>\text{S}</em>\text{A}$-D1-C8008</td>
<td>1</td>
<td>Conventional curing</td>
<td>80</td>
<td>8</td>
</tr>
</tbody>
</table>

Note: in the sample IDs, $\text{C}_\text{S}_\text{A}$: calcium sulfoaluminate cement; D1: one-hour delay; M: microwave curing; C: conventional curing; RT, 60, 70 and 80: the curing temperatures are room temperature (25°C), 60°C, 70°C and 80°C, respectively.

6.2.2 Effect of microwave curing on the crystalline structure of ettringite formed in $\text{C}_\text{S}_\text{A}$ paste

The XRD pattern of the $\text{C}_\text{S}_\text{A}$ clinkers is shown in Figure 6.1. From Figure 6.1, the identified phases are ye’elemite, larnite, perovskite, mayenite, anhydrite and magnesia as well as a trace amount of ettringite that results from the hydration of a small amount of ye’elemite.
The XRD results of the crystallinity of ettringite in $\text{C}_5\text{A}$ paste samples subjected to microwave and conventional curing conditions are presented in Figure 6.2. Ye’elimite is the major clinker mineral of $\text{C}_5\text{A}$ cement but gypsum significantly affects its hydration properties. Ettringite and monosulfate are the major crystalline hydration products. The XRD peak maxima of ettringite, ye’elimite and gypsum are at $d=9.70$, $3.76$ and $7.60$ Å and after subtraction of background, these are plotted in Figure 6.3 to show semi-quantitatively changes in their amounts during the hydration process. A similar method was previously used in the study on the hydration of $\text{C}_5\text{A}$ cement within 24 hours (Zhang and Glasser, 2002).
Figure 6.2 XRD patterns of $\text{CSA}$ pastes subjected to microwave and conventional curing at 60 (a), 70 (b) and 80°C (c)
Figure 6.3 Changes of the maxima of ettringite (a), ye’elimite (b) and gypsum (c) at d=9.70, 3.76 and 7.60 Å respectively in XRD diagrams

In Figure 6.2 (a), the CŠA paste sample cured at 60°C for 8 hours, following a one-hour delay at room temperature, shows the characteristic diffraction peaks of ettringite, gibbsite, gypsum, Ca₄Al₂O₇·19H₂O, un-hydrated ye’elimite, larnite and perovskite. Compared with the intensity of the ettringite peak in the room-temperature cured CŠA paste (CŠA-D1-RT08), the intensity of ettringite peaks in the heated CŠA pastes is much higher, unlike the peaks of gypsum and ye’elimite which decreases. These findings indicate that when a CŠA paste was cured at 60°C, either by microwave or conventional curing, more ettringite was
formed as the pastes hydrated further, with gypsum and ye’elimite being consumed. This is similar to the findings by other researchers (Wang et al., 2017) who found that heating to 40°C promoted the hydration of CaS A cement. The intensity of the ettringite peaks was higher under conventional curing than that under microwave curing.

After 8 hours curing at 70°C, the gypsum peaks in the CaS A paste subjected to conventional curing (CaS A-D1-C7008) decrease significantly [Figure 6.2 (b) and Figure 6.3 (c)], while the gypsum peaks in the CaS A paste subjected to microwave curing (CaS A-D1-M7008) only slightly decrease, compared to the corresponding samples cured at 60°C by the same curing method. At 70°C the intensity of the ettringite peaks in the CaS A paste cured by both methods reaches the highest value as displayed in Figure 6.3 (a), but is more pronounced with the conventionally cured sample (CaS A-D1-C7008). This suggests that for the conventionally cured CaS A paste, the degree of hydration was higher than that for microwave curing.

Figure 6.2 (c) and Figure 6.3 reveal that at 80°C, the XRD peak intensities of ettringite ye’elimite and gypsum have decreased compared with that at 70°C. In addition, in the sample CaS A-D1-C7008, the characteristic peaks of bassanite appear.
Comparing Figure 6.2 (a), (b) and (c), it can be seen that with microwave curing, as the temperature increases, the intensity of the ettringite peaks increases significantly, while the intensity of the ye’elimite and gypsum peaks decreases noticeably as shown in Figure 6.3 (b) and (c). However, in the C₅A paste samples subjected to conventional curing, the changes in XRD peak intensity of ettringite, ye’elimite and gypsum are larger than those subjected to microwave curing. When the temperature is increased to 80°C, the intensity of the ettringite peak in the samples cured by the both curing methods declines compared with that at 70°C. This may be due to the decomposition of ettringite, resulting in a reduction in its peak intensity. Overall, the XRD results show that within the 8-hour curing by either microwave or conventional curing, below 70°C, the formation of ettringite dominates, whereas when the temperature reaches 80°C, ettringite begins to decompose. However, as the monosulfate coming from the decomposition of ettringite may be X-ray amorphous (Zhou and Glasser, 2001), it was not detected by XRD.

### 6.2.3 Effect of microwave curing on the morphology of ettringite formed in C₅A paste

The SEM images of C₅A paste samples subjected to different curing conditions are exhibited in Figure 6.4.
When the C₃S₄A paste is cured at room temperature as shown in Figure 6.4 (a), the typical hexagonal prismatic morphology expected from ettringite can be clearly observed. This morphology is similar to the ettringite observed in the hydrates of a C₃S₄A paste with W/C ratio of 0.44 cured at 25°C for 8 hours (Zhang and Glasser, 2002). When the curing temperature is increased to 60°C, as shown in Figure 6.4 (b) and (c), there appears more hexagonal prismatic morphology,
which is similar in both the microwave and conventionally cured samples. When the C\(\overline{\text{SA}}\) pastes are cured at 70°C, much more hexagonal prismatic morphology appears in the hydration products. This indicates that the higher curing temperature has accelerated the hydration of C\(\overline{\text{SA}}\) cement, resulting in more ettringite being formed, both under microwave [Figure 6.4 (d)] or conventional curing [Figure 6.4 (e)]. However, when the curing temperature was increased to 80°C, less hexagonal prismatic morphology was identified in the C\(\overline{\text{SA}}\) pastes [Figure 6.4 (f) and (g)] compared to the C\(\text{SA}\) pastes cured at 70°C, particularly with the microwave-cured sample. The SEM results are consistent with the corresponding XRD results at 80°C, where the intensity of the ettringite XRD peaks in C\(\text{SA}\) pastes subjected to microwave curing is lower than that subjected to conventional heating.

6.2.4 Effect of microwave curing on the thermal stability of ettringite formed in C\(\overline{\text{SA}}\) paste

Figure 6.5 displays the TG and DTG patterns of the samples of C\(\overline{\text{SA}}\) pastes subjected to microwave and conventional curing at 60, 70 and 80°C for 8 hours.
Figure 6.5 TG and DTG patterns of C₅A paste samples subjected to microwave and conventional curing at 60 (a), 70 (b) and 80°C (c)

All the patterns are made up of four peaks. This is similar to the previous observations (Winnefeld and Barlag, 2009, Wang et al., 2017, Pelletier-Chaignat et al., 2011, Kaufmann et al., 2016): (i) the first peak around 95-105°C, is associated with the dehydration of ettringite; (ii) the second peak around 110-120°C is due to the decomposition of gypsum; (iii) the third peak (around 150-160°C) is related to dehydration of the monosulfate; (iv) and the fourth peak about 220-235°C is due to the decomposition of Al(OH)₃.
The interesting observation in all the DTG patterns is that the position of the maximum of the ettringite decomposition peak shifts to lower temperatures for samples cured at 60, 70 or 80°C with the higher the curing temperature, the greater the shift. This finding shows that the ettringite in C₃S pastes subjected to high temperatures is thermally less stable. Moreover, at any given temperature, the peak temperature of ettringite subjected to microwave curing is always slightly lower than that subjected to conventional curing. This again suggests that non-thermal effects of microwaves may influence the thermal stability of ettringite formed in C₃S paste.

6.2.5 Discussion

After the C₃S pastes samples have been subjected to one-hour initial curing at room temperature, they are made up of hydration products including a certain amount of ettringite, gibbsite and Ca₄Al₂O₇·19H₂O, as well as un-hydrated ye’elimite, gypsum, larnite and perovskite with water. Thereafter, when the C₃S paste samples are placed into the microwave oven for curing, unreacted free water is heated promptly as a good microwave absorber, leading to the heating of other surrounding components in the paste. The details on the mechanism of dielectric heating of water are discussed in Section 4.4.

It is well documented that an increasing temperature can enhance the hydration rates of cement (Neville, 1995, Taylor, 1997, Hewlett and Liska, 2019). When the
CSA pastes are cured at 60°C, further CSA hydration occurs, accelerated by either microwave or conventional curing, resulting in more ettringite being formed, with more ye’elimite and gypsum being consumed (Wang et al., 2017). This is confirmed by the results of XRD and SEM of both the 60°C and 70°C cured samples. However, the XRD intensity of ettringite peaks in the microwave-cured samples is lower than that in the conventionally cured samples. This could be mainly attributed to the accelerated hydration caused by both the thermal and non-thermal effects of microwave. On one hand, due to its thermal effect, i.e. volumetric heating nature of microwave (Metaxas and Meredith, 1983, Liu, 2019), the hydration of ye’elimite could be instantly enhanced. On the other hand, due to its non-thermal effect under the alternating electromagnetic environment of microwave, the dissolution of anhydrous phases would also be increased (Tompsett et al., 2006, Jhung et al., 2007b). Additionally, it has been reported that the thermal activation energy can be reduced by microwave (Nomanbhay and Ong, 2017, la Hoz et al., 2006). As a result of the above thermal and non-thermal effects of microwave, it could be expected that the rate of release of different ions into the solution is increased while the precipitation of the hydration products is also accelerated. Consequently, when microwave is used to cure CSA cement, a diffusion barrier could have been formed around the anhydrous grains which could slow down the dissolution of ye’elimite, thus reducing its further hydration (Minard et al., 2007). This could possibly explain that the XRD intensity of ettringite in CSA pastes cured by microwave is consistently lower than that in
C₃A pastes conventionally cured at any temperature in the range 60-80°C. However, further detailed microanalysis still needs to be carried out in the future studies in order to verify this hypothesis.

However, it can be noticed from Figure 6.3, regardless of curing methods, the intensity of ettringite peak in the samples cured at 80°C starts to decline compared with that at 70°C. This indicates that curing at 80°C might have exceeded the threshold decomposition temperature of ettringite. This cannot only be supported by the findings in Chapters 4 and 5, but also could be corroborated by the literature. For example, monosulfate was reported as the major product when a C₃A cement paste with a water to cement ratio of 0.44 was hydrated at 85°C between 2 and 24 hours (Zhang and Glasser, 2002). However, surprisingly, only trace amount of weak monosulfate peaks were identified in the XRD pattern of samples at 80°C in Figure 6.2, irrespective of the curing method. One possible reason is that the monosulfate formed could be amorphous and cannot be detected by XRD (ref). Overall, it could be concluded that based on the current results, 70°C could be a threshold value for the decomposition of ettringite under either microwave or conventional curing.

In addition, any possible non-thermal effects of microwaves might increase the Arrhenius pre-exponential factor A (Binner et al., 1995) or decrease the activation energy $E_a$ (Fini and Breccia, 1999, Shibata et al., 1996) in Equation
Chapter 6

(2.14), making the decomposition of ettringite present in C₃A pastes easier than for ettringite that has been conventionally cured. Once ettringite begins to decompose, the two inter-columnar waters are lost first, resulting in collapse of the hydrogen bonds connecting the water with the columns of ettringite, thus destabilising the structure of ettringite (Moore and Taylor, 1970, Hartman and Berliner, 2006). This can account for why the peak decomposition temperature of ettringite formed in microwave-cured C₃A pastes is always slightly lower than that formed in conventionally cured C₃A pastes, at any given temperature, as seen from the results of DTG shown in Figure 6.5.

6.3 Microstructure and thermal stability of ettringite in PC paste subjected to microwave curing

The above study on ettringite in C₃A pastes has shown that microwave heating accelerates the hydration of C₃A cement at 60 and 70°C, but makes ettringite become less stable, compared with conventional heating. In this section, the investigation is extended to PC system.

6.3.1 Sample preparation

In this section, PC pastes with a fixed water to solid ratio at 0.45 (please see Section 3.5.3 for more details) were subjected to one-hour initial delay at ambient conditions and then subjected to microwave and conventional curing at 60, 70
and 80°C for 8 hours, the details of which are shown in Table 6.2. Following curing, the samples were characterized by XRD, SEM and TG. The details of each characterisation are given in Section 3.6.

Table 6.2 Details of PC pastes subjected to microwave and conventional curing at 60, 70 and 80°C

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Delay time (h)</th>
<th>Curing condition</th>
<th>Curing temperature (°C)</th>
<th>Curing duration (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC-D1-RT08</td>
<td>1</td>
<td>Room temperature</td>
<td>25</td>
<td>8</td>
</tr>
<tr>
<td>PC-D1-M6008</td>
<td>1</td>
<td>Microwave heating</td>
<td>60</td>
<td>8</td>
</tr>
<tr>
<td>PC-D1-C6008</td>
<td>1</td>
<td>Conventional heating</td>
<td>60</td>
<td>8</td>
</tr>
<tr>
<td>PC-D1-M7008</td>
<td>1</td>
<td>Microwave heating</td>
<td>70</td>
<td>8</td>
</tr>
<tr>
<td>PC-D1-C7008</td>
<td>1</td>
<td>Conventional heating</td>
<td>70</td>
<td>8</td>
</tr>
<tr>
<td>PC-D1-M8008</td>
<td>1</td>
<td>Microwave heating</td>
<td>80</td>
<td>8</td>
</tr>
<tr>
<td>PC-D1-C8008</td>
<td>1</td>
<td>Conventional heating</td>
<td>80</td>
<td>8</td>
</tr>
</tbody>
</table>

**Note:** in the sample IDs, PC: Portland cement; D1: one-hour delay; M: microwave curing; C: conventional curing; RT, 60, 70 and 80: the curing temperatures are room temperature (25°C), 60°C, 70°C and 80°C, respectively.

### 6.3.2 Effect of microwave curing on the crystalline structure of ettringite formed in PC paste

The XRD patterns of PC paste samples subjected to microwave and conventional curing at different temperatures are shown in Figure 6.6.
After curing at 60°C for 8 hours, X-ray diffraction shows peaks of ettringite, gypsum, portlandite, un-hydrated C₃S, C₂S and C₄AF are present [Figure 6.6 (a)]. The intensity of ettringite peaks in the PC pastes subjected to 60°C curing (PC-D1-M6008 and PC-D1-C6008) is much higher than that in the PC paste cured at room temperature (PC-D1-RT08). The inverse is true for the gypsum and C₃S phases. These findings show that at 60°C, both microwave and conventional curing have accelerated the hydration, leading to more ettringite being formed, with gypsum and C₃S being consumed.

Figure 6.6 XRD patterns of PC pastes subjected to microwave and conventional curing at 60 (a), 70 (b) and 80°C (c)
After 70°C curing of the PC pastes for 8 hours, the peak intensity of the unhydrated C₃S in the PC paste subjected to microwave curing (PC-D1-M7008) is higher than that in the PC paste subjected to conventional curing (PC-D1-C7008). This implies that the PC paste has hydrated more under conventional curing than under microwave curing. Moreover, the peaks of monosulfate appear in the samples subjected to both microwave and conventional curing (PC-D1-M7008 and PC-D1-C7008). This indicates that at 70°C, ettringite has started to decompose to form monosulfate, irrespective of the curing type, which is in agreement with the argument that ettringite is unstable above 70°C (Taylor, 1997, Heinz and Ludwig, 1987).

Figure 6.6 (c) shows when cured at 80°C, the main peak of ettringite at 9.09° 2Θ in the sample subjected to microwave curing (PC-D1-M8008) decreases significantly. Instead, the peak for monosulfate appears, and is more pronounced than in the sample subjected to conventional curing (PC-D1-C8008).

From Figure 6.6 (a), (b) and (c), it can be seen that under microwave curing, as the curing temperature increases, the intensity of the ettringite peaks initially ascends and then declines with the intensity of gypsum and C₃S reduced gradually. For PC paste samples subjected to microwave curing, the rate of change of ettringite, C₃S and gypsum is larger than those subjected to conventional curing. However, when the temperature is above 70°C, monosulfate
begins to appear in the PC paste samples subjected to either microwave (PC-D1-M7008) or conventional curing (PC-D1-C7008). This indicates that above 70°C, ettringite in the PC paste decomposes quickly to form monosulfate (Heinz and Ludwig, 1987, Lawrence, 1995). The peak intensity of monosulfate in the sample subjected to microwave curing is slightly higher than that subjected to conventional curing. The XRD results show that microwave heating has non-thermal effects working on the structure of ettringite crystals besides its thermal effect.

6.3.3 Effect of microwave curing on the morphology of ettringite formed in PC paste

The SEM images of PC paste samples subjected to different curing conditions are shown in Figure 6.7.
In the room temperature-cured sample, ettringite is present as well-formed needle-like products as shown in Figure 6.7 (a). This is very similar to the morphology of ettringite formed when solid gypsum was exposed to C₃A solution for one hour (Mehta, 1976). At 60°C, the morphology of the microwave cured-sample [Figure 6.7 (b)] and conventionally cured sample [Figure 6.7 (c)] look almost the same, with no difference identified for the needle-like ettringite existing
in the both samples. This suggests that at 60°C, the ettringite formed in PC pastes remains almost stable under both microwave and conventional curing. However, when the PC paste was cured at 70°C, the needle-like ettringite appears less dense than at 60°C, with hexagonal platy shapes appearing in the samples cured both by microwave [Figure 6.7 (d)] and conventional curing [Figure 6.7 (e)]. These hexagonal plates are more pronounced with the microwave-cured sample. However, when the curing temperature rose to 80°C, almost no needle-like ettringite was identified in the microwave-cured sample (PC-D1-M8008) [Figure 6.7 (f)] whereas, some short needle-like ettringite remained in the conventionally cured sample (PC-D1-C8008) as shown in Figure 6.7 (g). Like the XRD results, this different morphology of ettringite identified in the microwave-cured PC samples at 70 and 80°C (PC-D1-M7008 and PC-D1-M8008) would, once more, confirm that microwave treatment may also affect the morphology of ettringite in addition to heating.

6.3.4 Effect of microwave curing on the thermal stability of ettringite formed in PC paste

The TG and DTG patterns of PC paste samples subjected to microwave and conventional curing at 60, 70 and 80°C are plotted in Figure 6.8.
The DTG patterns of the room temperature-cured sample are made up of two peaks: (i) the first peak in the range of 80-90°C, which is associated with the dehydration of ettringite and C-S-H gel as the ettringite peak overlaps with the C-S-H gel peak (Qoku et al., 2017, Tobón et al., 2010); (ii) the second peak around 100-110°C, due to the decomposition of gypsum. However, the DTG patterns of PC samples subjected to microwave or conventional curing consist of two peaks at different temperatures. This is similar to the previous reports (Trauchessec et al., 2015, Ramachandran et al., 2002, Gaviria et al., 2018, Maciel et al., 2019): (i)
the first peak (around 70-90°C) is wide and related to decomposition of ettringite and C-S-H gel as well as gypsum (Odler and Abdul-Maula, 1984), and (ii) and the second peak about is around 140-150°C, due to the decomposition of monosulfate.

Comparing the patterns above, it is interesting to see that when the curing temperature is increased, the dehydration peak due to gypsum disappears and instead, the monosulfate peak appears. This indicates that at high temperatures, monosulfate has begun to appear, likely from the decomposition of ettringite. Moreover, as the curing temperature rises from room temperature to 60°C, the first peak area increases and the peak area of microwave-cured sample (PC-D1-M6008) is larger than that of conventionally cured sample (PC-D1-C6008). The DTG results obtained at 60°C indicate that more ettringite and C-S-H gel are formed under microwave curing than under conventional curing. However, when cured at 70°C, the area of the first peak of the microwave-cured sample (PC-D1-M7008) is slightly smaller than that of the conventionally cured sample (PC-D1-M6008), suggesting that the amount of ettringite and C-S-H gel formed is less. As the curing temperature reached 80°C, the area of the first peak of the both samples prepared either by microwave (PC-D1-M8008) or conventional curing (PC-D1-C8008) decreases significantly. This is more pronounced with the microwave-cured sample. These changes indicate that at 60°C, both curing methods have facilitated the formation of ettringite, however, at 70°C or above,
they decelerated the formation of ettringite. Last but not the least, the interesting observation in all DTG patterns is that the position of the first peak has shifted to lower temperatures for samples cured at 60, 70 or 80°C. It also appears that the higher the curing temperature, the larger the shift. This might be due to the fact that ettringite and C-S-H gel in PC pastes subjected to high temperatures is thermally less stable, and is more pronounced in the microwave-cured sample, at a particular temperature. This implies that both thermal and non-thermal effects of microwave act a role in the thermal stability of ettringite and C-S-H gel formed in PC pastes.

6.3.5 Discussion

All the results from XRD, SEM and TG/DTG reveal that when microwave curing was used to cure PC pastes, non-thermal effects occur besides the thermal effects. Both effects have been reported in a number of investigations (Binner et al., 1995, Wroe and Rowley, 1996, Shi, 2017, Kong et al., 2018, Choi et al., 2019).

The PC pastes subjected to one-hour initial curing at room temperature are composed of ettringite, Ca(OH)₂, unreacted gypsum, C₃S, C₂S and C₄AF as well as C-S-H and water. The dielectric constant of the dried PC pastes is only 2.83 as shown in Section 3.5.5, so they are not good microwave absorbers. When the PC paste samples are cured by microwaves, water is heated promptly, and then all the other components in PC pastes are heated. The mechanism of dielectric
heating of water has been detailed in Section 4.4.

It is well known that increasing temperature can enhance the hydration rates of cement (Neville, 1995, Taylor, 1997, Hewlett and Liska, 2019). When PC pastes are cured at 60°C, the hydration of PC paste is facilitated by microwave or conventional curing, resulting in more ettringite being formed, which can be seen from XRD results. However, when the curing temperature is increased to 70°C, peaks of monosulfate begin to appear in the XRD spectra for samples subjected to both microwave (PC-P1-M7008) and conventional curing (PC-P1-C7008). When the temperature is increased to 80°C, the XRD intensity of ettringite in the microwave-cured sample (PC-P1-M8008) is lower than that of ettringite in the conventionally cured sample (PC-P1-C8008) and monosulfate appears. This indicates that 70°C may be the threshold decomposition temperature of ettringite formed in PC pastes, in agreement with that the previously reported (Taylor et al., 2001). Another possible reason is that the accelerated hydration of PC pastes results in more gypsum being adsorbed by the C-S-H gel as it forms, reducing the amount of available gypsum for ettringite formation. Once has reduced to a threshold value, some of the ettringite formed will react with C₃A to form monosulfate. Compared with conventional curing, at a given temperature, microwave curing accelerated the adsorption of gypsum on the C-S-H gel more due to its volumetric heating nature (Rattanadecho et al., 2016).
In addition, as the non-thermal effects of microwaves might increase the Arrenius pre-exponential factor $A$ (Binner et al., 1995) or decrease the apparent activation energy $E_a$ required to initiate the reaction (Fini and Breccia, 1999, Zuo et al., 2014), the decomposition rate of ettringite present in PC pastes might be increased under a microwave field. Once ettringite begins to decompose, water is lost from ettringite, resulting in the collapse of the hydrogen bond connecting the water with the columns of ettringite, thus making the structure of ettringite become less stable (Moore and Taylor, 1970, Hartman and Berliner, 2006). The detailed explanation on the effect of microwave heating acting on the microstructure and thermal stability of ettringite is discussed in Section 4.4 as well as Section 5.2.7 and Section 5.3.7. These explanations can be used to explain why the peak temperature of ettringite and C-S-H gel formed in microwave-cured PC pastes is always slightly lower than that formed in conventionally cured PC pastes, at any given temperature, which can be seen from the results of DTG. This is further confirmed by the SEM results, which show that as the curing temperature is increased from 60 to 80°C, the amount of prismatic hexagonal morphology decreases and the platy prismatic morphology increases, which is more pronounced with the microwave-cured PC sample.
6.4 Conclusions

The microstructure and thermal stability of ettringite formed in C₃A and PC pastes subjected to microwave curing were investigated. The main conclusions can be summarised as follows.

(1) Ettringite formed in C₃A paste

- Due to the volumetric heating nature of microwave, a diffusion barrier could have been formed around the anhydrous grains which could slow down the dissolution of ye’elimite. This decreases the further hydration of ye’elimite, leading to a lower XRD intensity of ettringite peaks compared to conventional curing.

- At 60, 70 or 80°C, the peak temperature of the decomposition of ettringite formed in microwave-cured C₃A pastes is always slightly lower than that of conventionally cured samples. This indicates that the thermal stability of ettringite formed in C₃A paste under microwave curing is less stable than that formed under conventional curing.

(2) Ettringite formed in PC paste

- As the curing temperature is increased from 60 to 80°C, the XRD peak of ettringite initially increases and then decreases. Correspondingly, the prismatic morphology of crystals viewed by SEM looks less and there appears more platy prismatic morphology, which is more pronounced with the microwave-cured sample.
At 60, 70 or 80°C, the peak temperature of the decomposition of ettringite and C-S-H gel formed in microwave-cured PC pastes is always lower than that conventionally cured pastes. This also shows that ettringite and C-S-H gel subjected to microwave curing is less stable than that subjected to conventional curing.
Chapter 7 Conclusions and Recommendations for Future Work

7.1 Introduction

In this chapter, the main findings from this thesis are concluded and highlighted in Section 7.2. Based on the outcome of this research, some recommendations for the future work are then presented in Section 7.3 below.

7.2 Conclusions

Based on the results obtained in this research, some specific conclusions can be drawn from the following aspects.

7.2.1 Microstructure and thermal stability of the ettringite synthesised under microwave heating

The study on the microstructure and thermal stability of the ettringite synthesised under microwave heating was carried out to simulate the effects that microwave radiation may have on the formation of ettringite during the early stage of hydration. The results show that when ettringite is synthesised under microwave heating at 60, 70 and 80°C, the microstructure and thermal stability of ettringite have changed as follows.

- At any given temperature, the ettringite synthesised with microwave heating
forms smaller crystals than those with conventional heating. This may be because microwave heating can enhance the diffusion of ions in solution, accelerating the nucleation formation of ettringite.

- Microwave heating causes more water loss from the ettringite structure, thus leading to more shrinkage in the $a$ and $c$ axes of the ettringite crystals.
- Increasing the synthesis temperature from 60 to 80°C facilitates the formation of more monosulfate and gypsum under microwave heating than under conventional heating.

Therefore, in general, the above would suggest that the ettringite synthesised with microwave heating is less stable than that synthesised with conventional heating.

### 7.2.2 Microstructure and thermal stability of the synthetic ettringite and metal ion-doped ettringite exposed to microwave heating

In a different scenario, pure ettringite and metal ion-doped ettringites (Fe-ettringite, Cr-ettringite, Mn-ettringite) were first synthesised at room temperature, before being exposed to microwave heating at 60, 70 and 80°C. This study was designed to simulate the ettringite formed during the delay period of ambient curing which was then subjected to microwave curing at a targeted temperature. Different metal ions were also doped into the ettringite to simulate the ettringite formed in real cement systems.
The synthetic pure and metal ion-doped ettringites are less stable when heated by microwaves than by conventional heating. All these can be attributed to the decrease of activation energy for ettringite decomposition leading to more water lost from ettringite. This water loss causes the collapse of hydrogen bond that plays an important role for the stability of ettringite, thus making ettringite less stable.

7.2.3 Microstructure and thermal stability of ettringite formed in cement systems subjected to microwave curing

As the ettringite formed in a cement system is more complicated than that synthesised under controlled conditions, this part of the study is mainly focused on investigating the microstructure and thermal stability of the ettringites formed in two type of cements, i.e., calcium sulfoaluminate cement and Portland cement. Based on the results obtained, some specific conclusions can be drawn as follows:

- At a fixed temperature, the peak temperature of the decomposition of ettringite formed in a microwave-cured C₅A₆ paste is always slightly lower than that of a conventional heating cured sample. This indicates microwave cured C₅A₆ is less stable, which could possibly be due to the non-thermal effects of microwave causing more water lost from ettringite.
In the case of the ettringite formed during PC hydration, when the curing temperature is increased to 70°C, monosulfate begins to appear in the samples subjected to both microwave and conventional curing and is more pronounced with the microwave-cured sample. At a given temperature, the peak temperature of the decomposition of ettringite formed in microwave-cured PC pastes is always lower than that conventionally cured.

In conclusion, all the results obtained from the cement samples reveal that the ettringite subjected to microwave heating is always slightly less stable than that subjected to conventional heating. As the samples have all been cured at the same temperature, this difference could be due to the non-thermal effects of microwave. However, the difference in the microstructure and thermal stability between the ettringite formed under the two heating methods is subtle and can be ignored for most practical applications. Ettringites heated by microwaves begin to decompose at 70°C to form monosulfate and gypsum or even bassanite in some cases, which is similar to those heated by conventional heating. Therefore, it is considered that the maximum temperature recommended in the current standards for accelerated curing could be used for microwave curing, although caution should be taken when an additional sulfate source is potentially available internally due to the slightly reduced thermal stability of ettringite under microwave curing.
7.3 Recommendations for future work

7.3.1 Modelling the kinetic process of the decomposition of ettringite under microwave heating

The results of this thesis show that microwave heating does cause more changes to the microstructure and thermal stability of ettringite compared with conventional heating. One possible reason can be attributed to the non-thermal effects that have been discussed in the literature so far. Due to the non-thermal effects, it is difficult to study the kinetic process of decomposition of ettringite under microwave heating only through experiments. Therefore, it will be necessary to carry out some modelling work on the kinetic process of ettringite decomposition under microwave heating.

7.3.2 Influence of pressure and humidity on the thermal stability of ettringite under microwave heating

Pressure and humidity are two crucial factors which influence the water loss from ettringite under conventional heating which again are well documented in the literature as detailed in Chapter 2. However, due to the difference in the mechanism between microwave and conventional heating, the effects of pressure and humidity on the stability of ettringite under microwave heating are likely to vary from that under conventional heating. Therefore, it is worthwhile
investigating how the pressure and humidity might affect the thermal stability of ettringite under microwave heating.

7.3.3 Influence of different pH values on the thermal stability of ettringite under microwave heating

The pH value is also an important factor that affects the thermal stability of ettringite. Several studies have already been conducted to investigate the thermal stability of ettringite when conventional heating is applied. Likewise, it is worth studying how changes in the pH value of the solution surrounding ettringite would influence its thermal stability under microwave heating.

7.3.4 Thermal stability of ettringite in concretes containing various additions under microwave heating

Eventually, microwave heating will be applied to cure precast concrete. As concrete includes sand and stones, the structure and thermal stability of ettringite formed in concrete may be different from those formed in cement pastes. Moreover, additions of supplementary materials, such as fly ash and GGBS, will also affect the setting time of concrete and the pH of pore solution. Thus, it is important to study the thermal stability of ettringite in concretes containing various additions under microwave heating as this will provide some essential information needed for practical applications of microwave curing.
References


BOUKENDAKDJI, M., BROOKS, J. & WAINWRIGHT, P. 1996. Influences of steam curing on strength, shrinkage and creep of OPC and slag concretes.


DAMIDOT, D. & GLASSER, F. P. 1993. Thermodynamic investigation of the CaO \( \text{Al}_2\text{O}_3 \) CaSO\(_4\) H\(_2\)O system at 25°C and the influence of Na2O. Cement and Concrete Research, 23, 221-238.

DANA, J. D. 1997. DANA´S NEW MINERALOGY: THE SYSTEM OF MINERALOGY OF JAMES DWIGHT DANA AND EDWARD SALSbury DANA--8TH EDENTIRELY REWRITTEN AND GREATLY EN LARGED.


GOETZ-NEUNHOEFFER, F. & NEUBAUER, J. 2006. Refined ettringite
(Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O) structure for quantitative X-ray diffraction
analysis. Powder Diffraction, 21, 4-11.

Mineralogical characteristics of Ettringites synthesized from solutions and
suspensions. Cement and Concrete Research, 36, 65-70.

GOLDSTEIN, J. I., NEWBURY, D. E., MICHAEL, J. R., RITCHIE, N. W.,
SCOTT, J. H. J. & JOY, D. C. 2017. Scanning electron microscopy and
X-ray microanalysis, Springer.

GOLDSTEIN, R. J., ECKERT, E. R. G., IBELE, W. E., PATANKAR, S. V.,
SIMON, T. W., KUEHN, T. H., STRYKOWSKI, P. J., TAMMA, K. K.,
BAR-COHEN, A., HEBERLEIN, J. V. R., DAVIDSON, J. H., BISCHOF,
J., KULACKI, F. A., KORTSHAGEN, U., GARRICK, S. & SRINIVASAN,

ligands for specific interaction with crystalline ettringite and
demonstration of a viable mechanism for the setting of cement. Journal

GROUND, T., MIDGLEY, H. & NOWELL, D. 1985a. Thermal and
physicochemical studies on ettringite II. Dehydration and thermal stability.


JHUNG, S. H., JIN, T., HWANG, Y. K. & CHANG, J. S. 2007a. Microwave effect in the fast synthesis of microporous materials: which stage between
nucleation and crystal growth is accelerated by microwave irradiation?

Chemistry–A European Journal, 13, 4410-4417.


KHOYLOU, A., DEBS, M., SHI, S., BAI, Y., FABIAN, M., SUN, T., GRATTAN, K. & MCKINNON, B. Dielectric Properties and Numerical Modelling of
Microwave Heating of Portland Cement/Fly Ash Blends. 2014. 34th Cement and Concrete Science Conference.


LIU, M. 2019. Microwave-based preconditioning for accelerated carbonation curing of cementitious materials. UCL (University College London).


LUDWIG, UGHORAB, H., HEINZ, D., MESKENDAHL, T. & WOLTER, A. On the stability of calcium aluminate sulphate hydrates in pure systems and


METAXAS, A. A. & MEREDITH, R. J. 1983. Industrial microwave heating, IET.


MÖSCHNER, G., LOTTHENBACH, B., WINNEFELD, F., ULRICH, A., FIGI, R. & KRETZSCHMAR, R. Solubility of Fe-ettringite and its solid solutions with


ODLER, I. & ABDUL-MAULA, S. 1984. Possibilities of quantitative determination of the AFt-(ettringite) and AFm-(monosulphate) phases in hydrated cement pastes. Cement and Concrete Research, 14, 133-141.


   Diagnosing delayed ettringite formation in concrete structures. Cement
   and Concrete Research, 38, 841-847.

TOBÓN, J. I., PAYA, J., BORRACHERO, M., SORIANO, L. & RESTREPO, O.
   2010. Determination of the optimum parameters in the high resolution
   thermogravimetric analysis (HRTG) for cementitious materials. Journal of
   Thermal Analysis and Calorimetry, 107, 233-239.

   synthesis of nanoporous materials. Chemphyschem: a European Journal
   of Chemical Physics and Physical Chemistry, 7, 296-319.

TOSUN, K. 2006. Effect of SO3 content and fineness on the rate of delayed
   ettringite formation in heat cured Portland cement mortars. Cement and
   Concrete Composites, 28, 761-772.

TOSUN, K. & BARADAN, B. 2010. Effect of ettringite morphology on DEF-

TRAUCHESSEC, R., MECHLING, J. M., LECOMTE, A., ROUX, A. & LE
   ROLLAND, B. 2015. Hydration of ordinary Portland cement and calcium
   sulfoaluminate cement blends. Cement and Concrete Composites, 56,
   106-114.
TÜRKEL, S. & ALABAS, V. 2005. The effect of excessive steam curing on
Portland composite cement concrete. Cement and Concrete Research,
35, 405-411.

VAIDHYANATHAN, B., BALAJI, K. & RAO, K. 1998. Microwave-assisted solid-
state synthesis of oxide ion conducting stabilized bismuth vanadate
phases. Chemistry of materials, 10, 3400-3404.

Chemistry, 88, 5768-5769.

WAGNER, J. M. 2011. X-ray Photoelectron Spectroscopy (Chemical
Engineering Methods and Technology), Nova Science Publishers
Incorporated.

WANG, P., LI, N. & XU, L. 2017. Hydration evolution and compressive strength
of calcium sulfoaluminate cement constantly cured over the
temperature range of 0 to 80 C. Cement and Concrete Research, 100,
203-213.

WANG, X. B., PAN, Z. H., SHEN, X. D. & LIU, W. Q. 2016. Stability and
decomposition mechanism of ettringite in presence of ammonium sulfate
solution. Construction and Building Materials, 124, 786-793.

by XPS and AES. An Introduction to Surface Analysis by XPS and AES,


ZUO, F., BADEV, A., SAUNIER, S., GOEURIOT, D., HEUGUET, R. & MARINEL, S. 2014. Microwave versus conventional sintering: estimate of
the apparent activation energy for densification of α-alumina and zinc oxide. Journal of the European Ceramic Society, 34, 3103-3110.