Solid-Gel Interactions in Geopolymers

Submitted in total fulfilment of the requirements for the degree of

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by

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&

Bachelor of Science

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“The desire for inner eternal peace is the only path to knowledge”

_Mencius_

(interpreted by William K. Lee)
PREFACE

I hereby declare that, to the best of my knowledge, this thesis is original in its entirety and contains no material which has been previously published by another person, except where due reference is stated. In addition, no part of this work has been submitted for the award of any other degree or diploma in any university.

I certify that the work has been undertaken solely by the candidate and the text of this thesis, exclusive of tables, graphs and bibliography, does not exceed 100,000 words.

William K. Lee

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ABSTRACT

Mineral binders are inorganic polymers that possess bonding properties towards a number of materials such as natural rocks, crushed stones, synthetic mineral wastes and glass wastes. Although the use of mineral binders has dated thousands of years since the Neolithic times (ca. 7000 B.C.), the ‘ultimate’ mineral binder still remains illusive. This is partly because the requirements for such an ultimate material change with people’s perception about its properties as well as its environmental impact. Thus, the once-believed ultimate Portland cement binder is now becoming unacceptable for a number of reasons including poor durability as well as severe environmental impact during production. Thus, an improved mineral binder is required by modern society to serve the same purposes as the existing Portland cement binder, as well as to reduce the current environmental impact caused by Portland cement production.

Geopolymerisation is such a ‘green’ technology capable of turning both natural ‘virgin’ aluminosilicates and industrial aluminosilicate wastes, such as fly ash and blast furnace slag, into mechanically strong and chemically durable construction materials. However, the source materials for geopolymer synthesis are less reactive than Portland cement clinkers and the chemical compositions of these source materials can vary significantly. Consequently, product quality control is a major engineering challenge for the commercialisation of geopolymers.

This thesis is therefore devoted to the mechanistic understanding of the interfacial chemical interactions between a number of natural and industrial aluminosilicates and the various activating solutions, which govern the reactivity of the aluminosilicate source materials. The effects of activating solution alkalinity, soluble silicate dosage and anionic contamination on the reactivity of the aluminosilicate source materials to produce geopolymeric binders, as well as their bonding properties to natural siliceous aggregates for concrete making, are examined. In particular, a new set of novel ‘realistic’ reaction models has been developed for such purposes. These reaction models have been further utilised to develop a novel analytical procedure, which is capable of studying geopolymerisation on ‘real’ geopolymers in situ and in real time. This novel procedure is invaluable for the total understanding of geopolymerisation, which is in turn vital for effective geopolymer mix designs.
TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>PREFACE</td>
<td>iii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iv</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>v</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF REFEREED INTERNATIONAL JOURNAL PAPERS</td>
<td>xiv</td>
</tr>
<tr>
<td>LIST OF SUBMITTED INTERNATIONAL JOURNAL PAPERS</td>
<td>xiv</td>
</tr>
<tr>
<td>LIST OF CONFERENCE AND OTHER PRESENTATIONS</td>
<td>xiv</td>
</tr>
<tr>
<td>LIST OF SYMBOLS</td>
<td>xvi</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xviii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xx</td>
</tr>
</tbody>
</table>

CHAPTER 1  INTRODUCTION  1

CHAPTER 2  CHEMISTRY OF PORTLAND CEMENT HYDRATION AND GEOPOLYMERISATION  4

2.1 Chemistry of Portland Cement Hydration  5

2.1.1 History and Manufacture of Ordinary Portland Cement  5
2.1.2 Ordinary Portland Cement Hydration Reactions  7
2.1.3 Mechanism of Setting Reactions in Ordinary Portland Cement Hydration  9
2.1.4 Silicate Speciation in Hydrating Ordinary Portland Cement Systems  13
2.1.5 Chemical Additives and Mineral Admixtures  15
   2.1.5.1 Effects of inorganic salts  16
   2.1.5.2 Effects of pozzolans  17
2.1.6 The Interface Between Siliceous Aggregates and Ordinary Portland Cement  20
2.1.7 Continual Search for Improved Concrete Binders  24
2.2 Chemistry of Geopolymerisation .................................................. 24

2.2.1 Early History and Definition .................................................. 24
2.2.2 Developments of Geopolymer Technology ............................. 27
2.2.3 Process Optimisation ............................................................... 29
  2.2.3.1 Effects of solids ................................................................. 30
  2.2.3.2 Effects of solutions ............................................................ 31
2.2.4 Chemistry of Geopolymerisation ............................................. 33
2.2.5 Aggregate Inclusion in Geopolymeric Binder ......................... 36

2.3 Solid-Gel Interactions in Geopolymers ........................................ 37

2.4 References ................................................................................... 38

CHAPTER 3  EXPERIMENTAL PHILOSOPHY AND METHODOLOGY  47

3.1 Materials and Characterisation Methods .................................... 48

3.1.1 Sources of Raw Materials ...................................................... 48
3.1.2 Characterisation of Raw Materials .......................................... 49
  3.1.2.1 Solid elemental composition from x-ray fluorescence
          spectroscopy (XRF) ............................................................... 50
  3.1.2.2 Solid mineralogy from x-ray diffraction (XRD) .................. 51
  3.1.2.3 Solid surface area from gas adsorption ............................ 54
  3.1.2.4 Nature of chemical bonds from infrared spectroscopy (IR) .. 57
  3.1.2.5 Solid topography and surface composition from scanning
          electron microscopy (SEM) coupled with energy dispersive
          spectroscopy (EDS) ............................................................... 69
  3.1.2.6 Solution composition from inductively coupled plasma
          optical emission spectroscopy (ICP-OES) ............................ 72

3.2 Geopolymeric Binders and Related Products ............................ 74

3.2.1 Synthesis and Basic Characteristics of Geopolymeric Binders ......... 74
3.2.2 Synthesis of Geopolymeric Mortars ....................................... 78
3.2.3 Synthesis and Basic Characteristics of Geopolymeric Concretes ........ 78
3.2.4 Physical/Mechanical Characterisation of Geopolymeric Products ....... 79
  3.2.4.1 Yield stress measurement by vane rheometer .................... 81
  3.2.4.2 Setting time determination by Vicat needle penetration .......... 82
  3.2.4.3 Compressive strength determination by uniaxial compression ...... 83
3.2.5 Microstructural Characterisation of Geopolymeric Products .......... 84
3.3 Solid-Gel Interactions in Geopolymers ................................................................. 84

3.3.1 Introduction ........................................................................................................ 84
3.3.2 Physical Interactions Between Aluminosilicate Solids and Gels ....................... 85
   3.3.2.1 Macroscopic interfacial bonding strength from interfacial three-point bending ........................................................................................................ 86
3.3.3 Chemical Interactions between Aluminosilicate Solids and Gels ..................... 89
   3.3.3.1 The reaction model and the sampling technique ........................................ 90
   3.3.3.2 Solution analysis ......................................................................................... 94
   3.3.3.3 Solid analysis ............................................................................................. 95

3.4 Experimental Strategic Plan .................................................................................. 95

3.5 References ............................................................................................................. 98

CHAPTER 4 EARLY AGE PROPERTIES OF GEO POLYMERIC BINDERS 104

4.1 Introduction ........................................................................................................... 104

4.2 Materials and Experimental Methods .................................................................... 106
   4.2.1 Materials ........................................................................................................ 106
   4.2.2 Synthesis of Geopolymeric Binders ............................................................... 106
   4.2.3 Characterisation of Geopolymeric Binders ................................................... 109
       4.2.3.1 Physical/mechanical characterisation ...................................................... 109
       4.2.3.2 Microstructural/chemical characterisation .............................................. 109

4.3 Early Age Properties of Geopolymeric Binders ................................................... 109
   4.3.1 Setting ............................................................................................................. 109
   4.3.2 Before Setting ................................................................................................. 114
   4.3.3 After Setting ................................................................................................... 116
       4.3.3.1 Mechanical characteristics ...................................................................... 116
       4.3.3.2 Microstructural/chemical characteristics ................................................. 118

4.4 Mechanistic Considerations on the Effects of Inorganic Salt Contamination ... 120

4.5 Conclusions .......................................................................................................... 123

4.6 References ............................................................................................................. 125
CHAPTER 5  PROPERTIES OF MATURED GEOPOLYMERIC BINDERS  127

5.1 Introduction ................................................................................................................. 127

5.2 Materials and Experimental Methods ............................................................................. 130

5.2.1 Materials ...................................................................................................................... 130
5.2.2 Synthesis of Geopolymeric Binders ............................................................................. 130
5.2.3 Characterisation of Geopolymeric Binders ................................................................. 131
  5.2.3.1 Mechanical characterisation ............................................................................... 131
  5.2.3.2 Microstructural/chemical characterisation ......................................................... 131

5.3 Mature Age Properties of Geopolymeric Binders .......................................................... 132

5.3.1 Compressive Strength and Durability ......................................................................... 132
5.3.2 Sample Crystallinity .................................................................................................... 134
5.3.3 Infrared Vibrational Characteristics ........................................................................... 135
5.3.4 Microscopic Morphology ............................................................................................ 142

5.4 Mechanism of Gel Deterioration Processes in Geopolymeric Binders .......................... 145

5.5 Conclusions .................................................................................................................... 148

5.6 References ....................................................................................................................... 149

CHAPTER 6  PROPERTIES OF GEOPOLYMERIC MORTARS AND CONCRETES  151

6.1 Introduction ...................................................................................................................... 151

6.2 Materials and Experimental Methods ............................................................................. 152

6.2.1 Materials ...................................................................................................................... 152
6.2.2 Synthesis of Geopolymeric Products ......................................................................... 153
6.2.3 Characterisation of Geopolymeric Products ............................................................... 155
  6.2.3.1 Mechanical characterisation ............................................................................... 155
  6.2.3.2 Microstructural characterisation ......................................................................... 155

6.3 General Characteristics ................................................................................................... 155

6.3.1 Salt-Free Systems ....................................................................................................... 155
  6.3.1.1 Mechanical characteristics ............................................................................... 155
  6.3.1.2 Microstructural characteristics ......................................................................... 162
6.3.2 Inorganic Salt-Contaminated Systems ....................................................................... 168
  6.3.2.1 Mechanical characteristics ............................................................................... 168
  6.3.2.2 Microstructural characteristics ......................................................................... 169
### Chapter 7: Chemical Interactions between Glassy Aluminosilicates and Activating Solutions

#### 7.1 Introduction

- Materials and Experimental Methods
  - 7.2.1 Materials
  - 7.2.2 Leaching Experiments
    - 7.2.2.1 Solution analysis
    - 7.2.2.2 Solid analysis
  - 7.2.3 Geopolymeric Binder and Silica Gel Syntheses and Characterisation
    - 7.2.3.1 Silica gel synthesis
    - 7.2.3.2 Geopolymeric binder synthesis
    - 7.2.3.3 Characterisation

#### 7.3 Mass Transfer between Glassy Aluminosilicates and Activating Solutions

#### 7.4 Evidence of Chemical Interactions from the Reacted Solids

- 7.4.1 Change of Crystallinity by XRD
- 7.4.2 Change of Chemical Bonds by FTIR
- 7.4.3 Change of Surface Topography and Compositions by SEM-EDS

#### 7.5 Geopolymerisation in Presence of Soluble Silicates

#### 7.6 Conclusions

#### 7.7 References

### Chapter 8: Anionic-Contaminated Chemical Interactions between Glassy Aluminosilicates and Activating Solutions

#### 8.1 Introduction
8.2 Materials and Experimental Methods ................................................................. 212
  8.2.1 Materials ................................................................................................... 212
  8.2.2 Leaching Experiments ............................................................................ 212
    8.2.2.1 Solution analysis ............................................................................. 212
    8.2.2.2 Solid analysis ................................................................................ 214
  8.2.3 Synthesis and Characterisation of Geopolymeric Binders .................... 214

8.3 Microscopic Chemical Interactions in the Contamination-Free Reaction
  Models .................................................................................................................. 214
  8.3.1 Mass Transfer Across the Fly Ash/Activating Solution Microscopic
    Interface ......................................................................................................... 214
  8.3.2 Evidence of Chemical Interactions from the Reacted Solids ................. 217

8.4 Cl\(^{-}\) & CO\(_3\)^{2-}—Affected Microscopic Chemical Interactions .............. 222
  8.4.1 Mass Transfer between Glassy Aluminosilicates and Activating
    Solutions ....................................................................................................... 222
  8.4.2 Evidence of Chemical Interactions from the Reacted Solids ............... 226

8.5 C\(_2\)O\(_4\)^{2-} & PO\(_4\)^{3-}—Affected Microscopic Chemical Interactions .......... 227
  8.5.1 Mass Transfer between Glassy Aluminosilicates and Activating
    Solutions ....................................................................................................... 227
  8.5.2 Evidence of Chemical Interactions from the Reacted Solids ............... 229
    8.5.2.1 Crystalline phase identification from XRD ..................................... 229
    8.5.2.2 Phase identification from FTIR ...................................................... 230
    8.5.2.3 Sample topography and surface compositions from SEM &
      EDS ......................................................................................................... 231

8.6 Mechanism of Geopolymerisation Using Anions as Reaction Probes ...... 234

8.7 Conclusions ..................................................................................................... 239

8.8 References ....................................................................................................... 240

CHAPTER 9 GEOPOLYMERISATION OF GLASSY
  ALUMINOSILICATES ......................................................................................... 243

9.1 Introduction ...................................................................................................... 244

9.2 Materials and Experimental Methods ............................................................ 246
  9.2.1 Materials ................................................................................................ 246
  9.2.2 Leaching Experiments ............................................................................ 246
    9.2.2.1 Solution analysis ............................................................................. 246
    9.2.2.2 Solid analysis ................................................................................ 246
## 10.6 Conclusions

Conclusions .................................................................................................300

## 10.7 References

References .......................................................................................................301

## CHAPTER 11 CONCEPTUAL MODEL OF SOLID-GEL INTERACTIONS IN GEOPOLYMERS 304

### 11.1 Introduction

Introduction ..................................................................................................305

### 11.2 Initial Brønsted & Ion-Exchange Reactions

Initial Brønsted & Ion-Exchange Reactions ..................................................307

### 11.3 Glassy Aluminosilicates

Glassy Aluminosilicates ...........................................................................309

### 11.4 Crystalline Aluminosilicates

Crystalline Aluminosilicates .......................................................................312

### 11.5 Conclusions

Conclusions .................................................................................................314

### 11.6 References

References .......................................................................................................315

## APPENDIX A LIST OF CHANGES IN RESPONSE TO THE EXAMINERS’ REPORTS 318
LIST OF REFEREEED INTERNATIONAL JOURNAL PAPERS


LIST OF SUBMITTED INTERNATIONAL JOURNAL PAPERS


LIST OF CONFERENCE AND OTHER PRESENTATIONS

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LIST OF SYMBOLS

Notations of Portland Cement Chemistry

A  Al₂O₃
C  CaO
F'  Fe₂O₃
H  H₂O
K  K₂O
M  MgO
N  N₂O
S  SiO₂
S'  SO₃
C₂S  2CaO·SiO₂
C₃S  3CaO·SiO₂
C₃A  3CaO·Al₂O₃
C₄AF  4CaO·Al₂O₃·Fe₂O₃
CSH  Calcium silicate hydrate

Abbreviations of Minerals & Aggregates

A  anorthite ((Na,Ca)AlSi₃O₈)
Alb  albite (NaAlSiO₃)
Au  augite ((Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)₂O₆)
C  clinochlore ((Mg,Fe⁺²)₅Al(Si,Al)₄O₁₀(OH)₈)
F  undifferentiated mica/clay
Kao  kaolinite (Al₂Si₂O₅(OH)₄)
M  mullite (3Al₂O₃·SiO₂)
Q  quartz (SiO₂)
S  siltstone
B  basalt
T  siliceous sand
Symbols of Fracture Mechanics

\( P \)  Load (kN)
\( f_c' \)  Compressive strength (MPa)
\( f_i' \)  Macroscopic interfacial bonding strength (MPa)

Symbols of Solution Chemistry

\([\text{Al}]\)  Concentration of dissolved Al in solution at time \( t \) (mM or M)
\([\text{Al}]_0\)  Concentration of initial dissolved Al in solution (mM or M)
\([\text{Ca}]\)  Concentration of dissolved Ca in solution at time \( t \) (mM or M)
\([\text{Ca}]_0\)  Concentration of initial dissolved Ca in solution (mM or M)
\([\text{Mg}]\)  Concentration of dissolved Mg in solution at time \( t \) (mM or M)
\([\text{Mg}]_0\)  Concentration of initial dissolved Mg in solution (mM or M)
\([\text{Si}]\)  Concentration of dissolved Si in solution at time \( t \) (mM or M)
\([\text{Si}]_0\)  Concentration of initial dissolved Si in solution (mM or M)

= dosage of added soluble silicates (mM or M)

\([\text{OH}^-]\)  Solution alkalinity (mM or M)

\( R_m \)  Dissolved SiO\(_2\)/M\(_2\)O ratio (M = Na or K)

\( t \)  Time (hours)
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 2.1</td>
<td>Typical oxide composition of a Portland cement</td>
<td>6</td>
</tr>
<tr>
<td>Table 2.2</td>
<td>Typical phase composition of a Portland cement</td>
<td>6</td>
</tr>
<tr>
<td>Table 2.3</td>
<td>The various pozzolans</td>
<td>18</td>
</tr>
<tr>
<td>Table 2.4</td>
<td>The applications of the various geopolymeric binders</td>
<td>25</td>
</tr>
<tr>
<td>Table 2.5</td>
<td>Important process parameters in geopolymerisation</td>
<td>30</td>
</tr>
<tr>
<td>Table 3.1</td>
<td>The elemental compositions in mass percentages of the various minerals</td>
<td>50</td>
</tr>
<tr>
<td>Table 3.1</td>
<td>as determined by the method of XRF</td>
<td></td>
</tr>
<tr>
<td>Table 3.2</td>
<td>The characteristic IR vibrational bands of T–O–T (T = Si or Al)</td>
<td>63</td>
</tr>
<tr>
<td>Table 3.3</td>
<td>asymmetric stretching vibrations</td>
<td></td>
</tr>
<tr>
<td>Table 3.3</td>
<td>Characteristic IR vibrational bands of the solid raw materials</td>
<td>68</td>
</tr>
<tr>
<td>Table 4.1</td>
<td>The elemental compositions in mass percentages of the various minerals</td>
<td>107</td>
</tr>
<tr>
<td>Table 4.1</td>
<td>as determined by the method of XRF</td>
<td></td>
</tr>
<tr>
<td>Table 4.2</td>
<td>The compositions in terms of mass ratios of the various Controls</td>
<td>107</td>
</tr>
<tr>
<td>Table 4.3</td>
<td>The classification of the salts at 25°C</td>
<td>108</td>
</tr>
<tr>
<td>Table 4.4</td>
<td>The effects of the anions on the final setting time of the various</td>
<td>110</td>
</tr>
<tr>
<td>Table 4.4</td>
<td>geopolymeric binders at 40°C</td>
<td></td>
</tr>
<tr>
<td>Table 4.5</td>
<td>The final setting time of the various geopolymeric binders at 40°C</td>
<td>113</td>
</tr>
<tr>
<td>Table 4.5</td>
<td>with an inorganic salt dosage of 0.08764 moles</td>
<td></td>
</tr>
<tr>
<td>Table 5.1</td>
<td>The mass compositions of the Control samples</td>
<td>130</td>
</tr>
<tr>
<td>Table 5.2 (a)</td>
<td>The compressive strengths of System III geopolymeric binders</td>
<td>133</td>
</tr>
<tr>
<td>Table 5.2 (b)</td>
<td>The compressive strengths of System V geopolymeric binders</td>
<td>133</td>
</tr>
<tr>
<td>Table 5.3</td>
<td>The relative integrated areas of the IR spectral regions before and after</td>
<td>142</td>
</tr>
<tr>
<td>Table 5.3</td>
<td>thermal treating pulverised geopolymeric binders at 9-months at 105°C for 24 hours</td>
<td></td>
</tr>
<tr>
<td>Table 5.4</td>
<td>The results of the SEM-EDS analyses</td>
<td>144</td>
</tr>
<tr>
<td>Table 6.1</td>
<td>The calculated mass compositions of the geopolymeric products</td>
<td>154</td>
</tr>
<tr>
<td>Table 6.2</td>
<td>The compressive strengths of the geopolymeric products</td>
<td>156</td>
</tr>
<tr>
<td>Table 6.3</td>
<td>The interfacial bonding strength of the rock &amp; geopolymeric mortar sandwich specimens at 28 days</td>
<td>159</td>
</tr>
<tr>
<td>Table 6.4</td>
<td>The SEM-EDS analysis of the siltstone &amp; mortar sandwich specimens at 28 days</td>
<td>167</td>
</tr>
<tr>
<td>Table 6.5</td>
<td>The SEM-EDS analysis of the chloride-induced potassium aluminosilicate crystals from the siltstone &amp; mortar sandwich specimens at 28 days</td>
<td>171</td>
</tr>
<tr>
<td>Table 7.1</td>
<td>The calculated molar compositions of the activating solutions</td>
<td>182</td>
</tr>
<tr>
<td>Table 7.2</td>
<td>The maximum apparent dissolution observed from Gladstone fly ash in the various activating solutions at 20°C</td>
<td>189</td>
</tr>
<tr>
<td>Table 7.3</td>
<td>The results of the SEM-EDS analyses on the unreacted Gladstone fly ash, the reacted fly ash under the various conditions (System I and P after 168 hours), and the geopolymer after 168 hours of curing at 40°C</td>
<td>200</td>
</tr>
<tr>
<td>Table 8.1</td>
<td>The calculated molar compositions of the activating solutions</td>
<td>213</td>
</tr>
<tr>
<td>Table 8.2</td>
<td>The maximum apparent dissolution observed from the reaction models</td>
<td>216</td>
</tr>
<tr>
<td>Table 8.3</td>
<td>Compressive strengths of the various System VII geopolymeric binders at the sample age of 28 days under 20 ± 3°C, 50 ± 5 % relative humidity and atmospheric pressure</td>
<td>235</td>
</tr>
<tr>
<td>Table 9.1</td>
<td>The calculated molar compositions of the activating solutions</td>
<td>247</td>
</tr>
<tr>
<td>Table 9.2</td>
<td>The maximum apparent dissolution observed from the reaction models</td>
<td>250</td>
</tr>
<tr>
<td>Table 10.1</td>
<td>The calculated molar compositions of the activating solutions</td>
<td>275</td>
</tr>
<tr>
<td>Table 10.2</td>
<td>The maximum apparent dissolution and the zero-order dissolution rates, with respect to Si and Al, of the kaolinite and the albite in the activating solutions at 25°C</td>
<td>278</td>
</tr>
<tr>
<td>Table 10.3</td>
<td>The maximum apparent dissolutions of the pulverised basalt and siltstone in the activating solutions at 25°C</td>
<td>298</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 2.1 Schematic illustration of conduction calorimetry results showing the various stages of (a) OPC and (b) C₃S hydration .......................................................... 10

Figure 2.2 Suggested mechanism after the induction period ............................................. 11

Figure 2.3 Basic structure of calcium silicate hydrate ................................................... 13

Figure 2.4 Tobermorite and jennite model structures for calcium silicate hydrate, referred to as C-S-Ha and C-S-Hb respectively ...................................................... 14

Figure 2.5 Influence of curing temperature (25 °C) on silicate polymerisation during alite hydration (time basis) ................................................................. 15

Figure 2.6 Field emission scanning electron micrograph and the distribution of calcium and silicon between C₃S and Beppu white clay (3 days) .................. 20

Figure 2.7 Schematic impression of the interfacial transition zone .................................. 21

Figure 2.8 Zeolite crystallisation mechanisms: (a) solution mediated process (type A); (b) hydrogel reconstruction (type B) ...................................................... 34

Figure 2.9 Zirconia particle coated with sodium silicate at pH = 12 ......................... 36

Figure 2.10 Zirconia particle coated with sodium silicate at pH = 14 ....................... 36

Figure 3.1 Parallel rays reflected from points on neighbouring partially reflecting planes are in phase when Bragg’s law is obeyed ........................................ 51

Figure 3.2 Change in normalised integrated peak intensity at 35.28 °2θ due to the known addition of mullite ................................................................. 53

Figure 3.3 The five types of adsorption isotherm, I to V, in the classification of Brunauer, Deming, Deming and Teller ....................................................... 56

Figure 3.4 Potential energy curves for a diatomic molecule: actual potential (solid line), parabolic potential (dashed line), and cubic potential (dotted line) .... 58

Figure 3.5 Energy level of a diatomic molecule (the actual spacings of electronic levels are much larger, and those of rotational levels are much smaller, than that shown in the figure) ....................................................... 59

Figure 3.6 The structure of silicates. The centre of the atoms (black = silicon or aluminium; white = oxygen) and the tetrahedral coordinating polyhedra are shown here ...................................................... 61
Figure 3.7  Shift of IR bands for faujasite zeolite with Al content in zeolite framework; O, faujasite; Δ, SiO<sub>2</sub> gel; □, Na-X (zeolite); ■, precursor for Na-X ................................................................. 63

Figure 3.8  The effect of network modifier addition on the silicate structure; empty circle represents oxygen; filled circle represents silicon ...................... 64

Figure 3.9  (A) Plot of tetrahedra SiO (asymmetric) stretching vibration vs mole% of Na<sub>2</sub>O. (B) Plot of terminal SiO stretching vibration vs mole% of Na<sub>2</sub>O. (C) Plot of SiOSi (symmetric) stretching vibration vs mole% of Na<sub>2</sub>O. (D) Plot of bending vibrations vs mole% of Na<sub>2</sub>O ........................................ 64

Figure 3.10  The FTIR spectra of the Gladstone fly ash (Gdf), the HR1-grade kaolinite (Kao), the high-purity albite (Alb), the basalt (Bas) and the siltstone (Silt) ........................................................................................................ 67

Figure 3.11  Methods of detecting electrons in a scanning electron microscope: (a) secondary electrons; (b) backscattered electrons, solid state detector; (c) backscattered electrons, scintillation counter; (d) absorbed electron current ........................................................................................................ 70

Figure 3.12  The SE-SEM image of the gold-coated unreacted Gladstone fly ash .......... 71

Figure 3.13  The SE-SEM image of the carbon-coated unreacted HR1-grade kaolinite .. 71

Figure 3.14  The BSE-SEM image of the carbon-coated unreacted albite obtained from Minerals Corporation Limited, Broken Hill, Australia ...................... 72

Figure 3.15  Schematic diagram of a simultaneous ICP system ................................. 73

Figure 3.16  The carbon-coated BSE-SEM image of a typical Gladstone fly ash/HR1-kaolinite geopolymeric binder activated at [MOH] = 6.85 M (Na/K = 0.2) and soluble silicate dosage of [SiO<sub>2</sub>] = 3.26 M after 28 days of curing at 20°C ................................................................. 75

Figure 3.17  The XRD diffractograms of the unreacted Gladstone fly ash/HR1-kaolinite mixture (fly ash/kaolinite = 9) and the as-synthesised geopolymeric binder activated at [MOH] = 6.85 M (Na/K = 0.2) and a soluble silicate dosage of [SiO<sub>2</sub>] = 3.26 M after 28 days of curing at 20°C. K = kaolinite. M = mullite. Q = quartz .................. 76

Figure 3.18  The FTIR spectra of the unreacted Gladstone fly ash/HR1-kaolinite mixture (fly ash/kaolinite = 9) and the as-synthesised geopolymeric binder activated at [MOH] = 6.85 M (Na/K = 0.2) and a soluble silicate dosage of [SiO<sub>2</sub>] = 3.26 M after 28 days of curing at 20°C. The numbers shown in the figure are the kaolinite characteristic vibrational bands .......... 77
Figure 3.19  The carbon-coated BSE-SEM image of a typical Gladstone fly ash/HR1-kaolinite geopolymeric concrete. The geopolymeric binder was activated at \([\text{MOH}] = 6.85 \text{ M (Na/K = 0.2)}\) and soluble silicate dosage of \([\text{SiO}_2] = 3.26 \text{ M}\) after 28 days of curing at 20°C ........................................................ 79

Figure 3.20  The physical characteristics of a geopolymeric product and the 5 stages of geopolymerisation. I = aluminosilicate solid dissolution (alkali-activation). II = polymerisation of the dissolved species including the added soluble silicates. III = gellation of the polymerised aluminosilicates. IV = setting (a) and hardening (b). V = solid-state transformation .............................................................................................. 80

Figure 3.21  The yield stress of a geopolymeric binder synthesised by alkali-activating a Gladstone fly ash/HR1-kaolinite mixture (fly ash/kaolinite = 9) with an activating solution (\([\text{MOH}] = 6.85 \text{ M (Na/K = 0.2)}\) and soluble silicate dosage of \([\text{SiO}_2] = 3.26 \text{ M}\) contaminated with 2% CaCl\(_2\)) at 20°C .............. 81

Figure 3.22  Schematic drawing of a Vicat needle .......................................................... 82

Figure 3.23  The penetration of a geopolymeric binder synthesised by alkali-activating a Port Augusta fly ash/HR1-kaolinite mixture (fly ash/kaolinite = 2) with an activating solution of \([\text{MOH}] = 6.85 \text{ M (Na/K = 0.01)}\) and soluble silicate dosage of \([\text{SiO}_2] = 0.5 \text{ M}\) ................................................................. 83

Figure 3.24  The experimental set-up (not to scale) of the interfacial three-point bending test on a rock aggregate-mortar sandwich specimen .................. 87

Figure 3.25  The schematic drawing of the sampling procedure for separating the alkali-activated aluminosilicate solids from the activating solutions .......... 92

Figure 3.26  Diagram showing pH and concentration of the various solutions studied in relationship to the instability region ..................................................... 93

Figure 4.1  The effect of molar dosage on the setting time of (a) System I and (b) System III geopolymeric binders ................................................................. 111

Figure 4.2  The percentage change in setting time of alkali-activated cements caused by calcium and magnesium salts at the molar dosage of 0.08764 moles ..... 113

Figure 4.3  The yield stress developments of System II geopolymeric binders at an inorganic salt molar dosage of 0.08764 moles at 25°C .................. 115

Figure 4.4  The effects of Ca and Mg salts at a molar dosage of 0.08764 moles on the yield stress ratios of System II geopolymeric binders at 25°C ............. 115

Figure 4.5  The 7-days compressive strengths of System II and System III geopolymeric binders containing (a) potassium salts (b) calcium salts and (c) magnesium salts ........................................................................... 117

xxii
Figure 4.6 The FTIR spectra of III-Control at 1 day and 28 days and III-KNO$_3$ at 7 days ................................................................. 119

Figure 4.7 The IR bands attributable to NO$_3$ molecular vibrations in geopolymeric binders III-KNO$_3$ and III-Mg(NO$_3$)$_2$ at 7-days and in pure KNO$_3$ and Mg(NO$_3$)$_2$-6H$_2$O solids ................................................................. 119

Figure 5.1 Graphical illustration of the definition of ‘durability’ used in this thesis .... 129

Figure 5.2 The FTIR spectra of (a) the solid starting mixture (fly ash/kaolin = 9) and (b) III-Control at the age of 9-months. The arrows indicate where baseline corrections were made .......................................................... 131

Figure 5.3 The XRD diffractograms of the various geopolymeric binders at 9 months. The dotted lines indicate the Ca$_2$SiO$_3$Cl$_2$ crystalline phase, which shows the 2 strongest lines at d-spacing = 3.01 and 3.34 Å ............ 135

Figure 5.4 The FTIR spectra of III-Control and V-Control at 9-months before baseline corrections ................................................................. 137

Figure 5.5 The 9-months baseline corrected FTIR spectra of (a) before thermal treatment, and (b) after thermal treatment at 105°C for 24 hours. x = III-Control, y = III-CaCO$_3$, z = III-CaCl$_2$ .................................................... 138

Figure 5.6 The relative integrated areas of the 810-400 cm$^{-1}$ FTIR spectral region for System III geopolymeric binders before thermal treatment. The relative integrated area was calculated by dividing the integrated area of the spectral region of interest by the integrated area of the T-O-Si stretching vibration region 1380-810 cm$^{-1}$ ........................................ 140

Figure 5.7 The relative integrated areas of the 3700-2700 cm$^{-1}$ FTIR spectral region for System III geopolymeric binders before thermal treatment. The relative integrated area was calculated by dividing the integrated area of the spectral region of interest by the integrated area of the T-O-Si stretching vibration region 1380-810 cm$^{-1}$ ................................................... 141

Figure 5.8 The BSE-SEM micrograph of III-CaCl$_2$ at 9-months. The white dotted circles indicate where the SEM-EDS analyses were performed .................. 143

Figure 5.9 The BSE-SEM micrograph of V-Control at 21-days. The white dotted circle indicates where the SEM-EDS analysis was performed ..................... 144

Figure 6.1 The compressive strengths of the salt-free binders (I) versus the mortars (II) for the geopolymeric systems at two alkali concentrations ([OH$^-$] = 5 and 10 M) for 0, 0.5, 1.0 and 2.5 M of soluble silicates added .................... 157

Figure 6.2 The time evolution of compressive strengths of the salt-free binders (I), the mortars (II) and the concretes (III) for the geopolymeric systems at two alkali concentrations ([OH$^-$]$_0$ = 5 and 10 M) ........................................ 158
Figure 6.3  The binder (I) compressive strength versus mortar (II) compressive strength ($f_{cc}'$) and macroscopic interfacial bonding strength ($f_i'$) for the salt-free geopolymeric systems activated at 5 M OH⁻ at 28 days .......... 160

Figure 6.4  The binder (I) compressive strength versus concrete (III) compressive strength ($f_{cc}'$) and macroscopic interfacial bonding strength ($f_i'$) for the salt-free geopolymeric systems activated at 10 M OH⁻ at 28 days .......... 161

Figure 6.5  The BSE-SEM image of the mica/clay region (F) of the fresh siltstone (S) ................................................................. 163

Figure 6.6  The BSE-SEM image of the sandwich specimen S&II-10-0. F = mica/clay, I = binder I-10-0 and II = mortar II-10-0. The block arrows indicate where SEM-EDS analyses were taken ........................................ 163

Figure 6.7  The BSE-SEM image of the sandwich specimen S&II-10-0. Q = quartz, I = binder I-10-0 and II = mortar II-10-0. The block arrows indicate where SEM-EDS analyses were taken ........................................ 164

Figure 6.8  The BSE-SEM image of the sandwich specimen S&II-10-0.5. Q = quartz, I = binder I-10-0.5 and II = mortar II-10-0.5. The block arrows indicate where SEM-EDS analyses were taken ........................................ 164

Figure 6.9  The BSE-SEM image of the sandwich specimen S&II-10-1. Q = quartz, I = binder I-10-1 and II = mortar II-10-1. The block arrows indicate where SEM-EDS analyses were taken ........................................ 165

Figure 6.10 The BSE-SEM image of the sandwich specimen S&II-10-2.5. Q = quartz, I = binder I-10-2.5, II = mortar II-10-2.5 and T = sand. The block arrows indicate where SEM-EDS analyses were taken ........................................ 165

Figure 6.11 The BSE-SEM image of the sandwich specimen S&II-10-2.5. F = mica/clay, I = binder I-10-2.5 and II = mortar II-10-2.5 ............................. 166

Figure 6.12 The SEM image of the sandwich specimen S&II-5-2.5. Q = quartz, I = binder I-5-2.5 and II = mortar II-5-2.5 and T = sand. The block arrows indicate where SEM-EDS analyses were taken ........................................ 166

Figure 6.13 The SEM image of the sandwich specimen S&II-5-2.5-Cl .......................... 170

Figure 6.14 The SEM image of the sandwich specimen B&II-10-2.5-Cl .......................... 170

Figure 6.15 The SEM image of the sandwich specimen S&II-10-2.5-Cl .......................... 171

Figure 7.1  The effects of alkali cations on the dissolution profiles of Al, Si, Ca and Mg of Gladstone fly ash as a function of time in (a) System A, Na-activating solution, and (b) System I, K-activating solution ............................ 185
Figure 7.2 The effects of soluble silicate dosage on the dissolution profiles of Systems A to H as a function of time for (a) aluminium, (b) silicon and (c) calcium. \([\text{Al}] = \) concentration of Al in the solution at time \(t\). \([\text{Al}]_0 = \) concentration of Al in the initial activating solution. Same notations for Si and Ca .......................................................... 187

Figure 7.3 The effects of soluble silicate dosage on the dissolution profiles of Systems I to J as a function of time for (a) aluminium, (b) silicon and (c) calcium. \([\text{Al}] = \) concentration of Al in the solution at time \(t\). \([\text{Al}]_0 = \) concentration of Al in the initial activating solution. Same notations for Si and Ca ...................................................................................................... 188

Figure 7.4 The XRD diffractograms collected using Cu K\(\alpha\) radiation \((\lambda_{\text{Cu K}\alpha} = 1.54184 \text{ Å})\). \(a = \) unreacted Gladstone fly ash; \(b = \) fly ash reacted under System H for 168 hours; \(c = \) fly ash reacted under System P for 168 hours; \(d = \) System VI geopolymer after 168 hours. \(Q = \alpha\)-quartz. \(M = \) mullite ........................................................................................................... 192

Figure 7.5 The FTIR spectra of Gladstone fly ash reacted under (a) System A to H and (b) System I to P. Each spectrum was taken when maximum apparent Si dissolution was observed from the leaching experiments. \(\text{Gdf} = \) unreacted Gladstone fly ash. \(A = \) fly ash treated under System A. Same notations for B to P ....................................................................................... 193

Figure 7.6 The SE-SEM micrographs of unreacted Gladstone fly ash ........................................ 196

Figure 7.7 The SE-SEM micrographs of the System A-reacted Gladstone fly ash after 168 hours of leaching ................................................................. 196

Figure 7.8 The SE-SEM micrographs of the System B-reacted Gladstone fly ash after 168 hours of leaching ........................................................................... 197

Figure 7.9 The SE-SEM micrographs of the System C-reacted Gladstone fly ash after 168 hours of leaching ................................................................. 197

Figure 7.10 The SE-SEM micrographs of the System H-reacted Gladstone fly ash after 168 hours of leaching ........................................................................... 198

Figure 7.11 The SE-SEM micrographs of the System P-reacted Gladstone fly ash after 168 hours of leaching ........................................................................... 198

Figure 7.12 The BSE-SEM micrographs of the System P-reacted Gladstone fly ash after 168 hours of leaching. The dotted circle indicates the areas (as an example) of where the 15 EDS analyses were taken ........................................ 199

Figure 7.13 The BSE-SEM micrographs of the System VI geopolymeric binder after 168 hours of curing at 40°C. The dotted circle indicates the areas (as an example) of where the 15 EDS analyses were taken ........................................ 199
Figure 7.14  The FTIR spectra of the various solids. Gdf = unreacted Gladstone fly ash. P = System P reacted fly ash after 168 hours of leaching .......................... 203

Figure 8.1  The effects of soluble silicate dosage on the dissolution profiles of Systems A, F, K, P and U reaction models. [Si] = concentration of Si in the solution at time t. [Si0] = concentration of Si in the solution at the start of leaching .................................................................................................. 215

Figure 8.2  The XRD diffractograms of the unreacted Gladstone fly ash (Gdf) and the various reacted solids after 168 hours of leaching under (a) Systems A to E and (b) Systems U to Y (b). Q = α-quartz. M = mullite. W = whewellite ........................................... 218

Figure 8.3  The FTIR spectra of the unreacted Gladstone fly ash (Gdf) and the various reacted solids after 168 hours of leaching under (a) Systems A to E and (b) Systems U to Y (b) .......................................................... 219

Figure 8.4  SE-SEM image of System A-reacted fly ash after 168 hours of leaching. The block arrow indicates where typical SEM-EDS analyses were performed ................................................. 220

Figure 8.5  SE-SEM image of System K-reacted fly ash after 168 hours of leaching .... 220

Figure 8.6  SE-SEM image of System U-reacted fly ash after 168 hours of leaching. The block arrow indicates where typical SEM-EDS analyses were performed .................................................................................................................. 221

Figure 8.7  The leaching characteristics of Systems A to E for (a) aluminium, (b) silicon and (c) calcium. [Al] = concentration of Al in the solution at time t. [Al]0 = concentration of Al at the start of leaching. Same notations for Si and Ca ........................................................................................................ 223

Figure 8.8  The leaching characteristics of Systems F to J for (a) aluminium, (b) silicon and (c) calcium. [Al] = concentration of Al in the solution at time t. [Al]0 = concentration of Al at the start of leaching. Same notations for Si and Ca ........................................................................................................ 224

Figure 8.9  The leaching characteristics of Systems U to Y for (a) aluminium, (b) silicon and (c) calcium. [Al] = concentration of Al in the solution at time t. [Al]0 = concentration of Al at the start of leaching. Same notations for Si and Ca ........................................................................................................ 225

Figure 8.10 SE-SEM image of System V-reacted fly ash after 168 hours of leaching. The block arrow indicates where typical SEM-EDS analyses were performed .................................................................................................................. 227

Figure 8.11 SE-SEM image of System N-reacted fly ash after 168 hours of leaching .... 232

Figure 8.12 SE-SEM image of System O-reacted fly ash after 168 hours of leaching .... 232
Figure 8.13  SE-SEM image of System X-reacted fly ash after 168 hours of leaching. The block arrow indicates where typical SEM-EDS analyses were performed ................................................................. 233

Figure 8.14  SE-SEM image of System Y-reacted fly ash after 168 hours of leaching. The block arrow indicates where typical SEM-EDS analyses were performed ..................................................................................................... 233

Figure 8.15  Yield stress developments of the various System VII geopolymeric binders under 20 ± 3°C, 50 ± 5 % relative humidity and atmospheric pressure ........................................................................................................... 235

Figure 9.1  The Si and Ca dissolution profiles of Systems Q and U reaction models. [Si] = concentration of Si in the activating solution at time t. [Si]₀ = concentration of Si in the initial activating solution. Same notation for Ca ........................................................................................................................................................................... 249

Figure 9.2  The XRD diffractograms of the unreacted fly ash (Gdf) and the various alkali-activated solids (Systems Q and U, IX-Control and XI-Control) after 168 hours of activation ................................................................. 252

Figure 9.3  The FTIR spectra of the unreacted fly ash (Gdf) and the various alkali-activated solids (Systems Q and U, VIII-Control, IX-Control, X-Control and XI-Control) after 168 hours of activation ................................................................................ 252

Figure 9.4  The FTIR spectral deconvolution of the unreacted Gladstone fly ash .......... 254

Figure 9.5  The FTIR spectral deconvolution of the System U-activated fly ash after 168 hours of activation ........................................................................................................................................................................................................... 254

Figure 9.6  The FTIR spectral deconvolution of the IX-Control geopolymeric binder after 48 hours of activation ................................................................................................................................. 255

Figure 9.7  The FTIR spectral deconvolution of the XI-Control geopolymeric binder after 48 hours of activation ......................................................................................................................... 255

Figure 9.8  The calibration curve of the position of the T-O-Si asymmetric stretching principal band versus the extent of alkali-activation for Systems A to H, I to P, Q to U, V to Y and AA after 168 hours of activation in the various reaction models ....................................................................................................................... 257

Figure 9.9  The position of the T-O-Si stretching vibration principal band versus the soluble silicate dosage of Na-activating solutions Systems A to H and K-activating solutions Systems I to P after 168 hours of leaching ............... 258

Figure 9.10  The position of the T-O-Si stretching vibration principal band and the extent of alkali-activation versus the duration of activation for System U-activated fly ash and IX-Control and XI-Control .................................................................................. 259
Figure 9.11  The extent of activation and the compressive strength versus the duration of activation for IX-Control ................................................................. 262

Figure 9.12  The compressive strength versus the relative intensity of the new phase at \(~1105 \text{ cm}^{-1}\) for IX-Control and XI-Control. The numbers within the figure denote the duration of activation when the alkali-activated fly ash was taken for IR analysis ................................................................. 263

Figure 10.1  The sandwich specimen used for examining the interface between rock slices and geopolymer ................................................................. 274

Figure 10.2  The BSE-SEM image of the sandwich specimen. S = siltstone slice, I = I-10-2.5 geopolymeric binder. The locations where the SEM-EDS line analyses were taken were marked as white dotted lines as an example ...... 274

Figure 10.3  The leaching curves of HR1-grade kaolinite in the various soluble silicate-free activating solutions at the solution alkalinity ([OH\(^-\)]) of 0.6 M (Kao 1), 5 M (Kao 3) and 10 M (Kao 5). \([T] = \text{concentration of Si or Al in the reacted activating solution at time } t.\) \([T]_0 = \text{initial concentration of Si or Al in the activating solution} \) ................................................................. 277

Figure 10.4  The plot of log(Si dissolution rate, \(r\)) versus log(solution alkalinity, [OH\(^-\)]). The results shown were obtained from this chapter as well as from Huertas et al. [10.12] ........................................................................... 279

Figure 10.5  The leaching curves of albite in the various soluble silicate-free activating solutions at the solution alkalinity ([OH\(^-\)]) of 0.6 M (Alb 1), 5 M (Alb 3) and 10 M (Alb 5). \([T] = \text{concentration of Si or Al in the reacted activating solution at time } t.\) \([T]_0 = \text{initial concentration of Si or Al in the activating solution} \) ........................................................................................ 281

Figure 10.6  The leaching curves of kaolinite in the various soluble silicate-rich activating solutions at a 0.5 M soluble silicate dosage and at the solution alkalinity ([OH\(^-\)]) of 0.6 M (Kao 2), 5 M (Kao 4) and 10 M (Kao 6). \([T] = \text{concentration of Si or Al in the reacted activating solution at time } t.\) \([T]_0 = \text{initial concentration of Si or Al in the activating solution} \) ................................................................. 283

Figure 10.7  The leaching curves of albite in the various soluble silicate-rich solutions at a 0.5 M soluble silicate dosage and at the solution alkalinity ([OH\(^-\)]) of 0.6 M (Alb 2), 5 M (Alb 4) and 10 M (Alb 6). \([T] = \text{concentration of Si or Al in the reacted activating solution at time } t.\) \([T]_0 = \text{initial concentration of Si or Al in the activating solution} \) ................................................................. 284

Figure 10.8  The change in XRD intensity of the kaolinite peak at \(d\)-spacing = 7.183 Å (\(\lambda_{\text{CuKo}} = 1.54184 \text{ Å}\)) versus solution alkalinity [OH\(^-\)]\(_0\) of the unreacted HR1-grade kaolinite and the reacted kaolinite in the various activating solutions with ([SiO\(_2\)]\(_0\) = 0.5 M) and without soluble silicates ([SiO\(_2\)]\(_0\) = 0 M). The XRD analyses were taken at the 168\(^{th}\) hour ................................................................................................ 285
Figure 10.9  The XRD diffractogram of the unreacted HR1-grade kaolinite (Kao) and the reacted kaolinite in the various activating solutions. Kao 1, 3 and 5 were taken at the 168th hour of leaching whereas Kao 2, 4 and 6 were taken when the maximum apparent Si dissolutions were observed (Table 10.2), i.e. at the 168th hour, the 48th hour and the 4th hour respectively. K = kaolinite. Q = α-quartz  ......... 286

Figure 10.10  The FTIR spectra of the unreacted HR1-grade kaolinite (Kao) and the reacted kaolinite in the various activating solutions. Kao 1, 3 and 5 were taken at the 168th hour of leaching whereas Kao 2, 4 and 6 were taken when the maximum apparent Si dissolutions were observed (Table 10.2), i.e. at the 168th hour, the 48th hour and the 4th hour respectively. The numbers within the graph denote the IR band positions .............................................................. 287

Figure 10.11  The FTIR spectra of the unreacted albite and the reacted albite in the various activating solutions. All the reacted albites Alb 2, 4, 5 and 6 were taken at the 168th hour of leaching. The numbers within the graph denote the IR band positions .............................................................. 288

Figure 10.12  The BSE-SEM images of (a) unreacted albite, (b) reacted albite under Alb 4 for 168 hours and (c) reacted albite under Alb 6 for 168 hours ...................................................................................................... 289

Figure 10.13  The XRD diffractograms of the unreacted albite and the reacted albite in the various activating solutions. All the reacted albites Alb 2, 4, 5 and 6 were taken at the 168th hour of leaching ............................................. 290

Figure 10.14  The results of SEM-EDS line scan across the interface of quartz (Q) and the I-10-2.5 geopolymeric binder (I) from the siltstone-geopolymeric binder sandwich specimen .............................................................. 293

Figure 10.15  The results of SEM-EDS line scan across the interface of anorthite (A) and the I-10-2.5 geopolymeric binder (I) from the basalt-geopolymeric binder sandwich specimen .............................................................. 294

Figure 10.16  The results of SEM-EDS line scan across the interface of augite (Au) and the I-10-2.5 geopolymeric binder (I) from the basalt-geopolymeric binder sandwich specimen .............................................................. 295

Figure 10.17  The results of SEM-EDS line scan across the interface of clinochlore (C) and the I-10-2.5 geopolymeric binder (I) from the basalt-geopolymeric binder sandwich specimen .............................................................. 296

Figure 10.18  The leaching curves of the pulverised basalt in the various activating solutions. [Si] = concentration of Si in the reacted activating solution at time t. [Si]₀ = initial concentration of Si in the activating solution ....... 298
**Figure 10.19** The SEM images of (a) unreacted pulverised basalt using BSE detection, and (b) reacted pulverised basalt under B 6 for 168 hours using SE detection .................................................................................................................. 299

**Figure 10.20** The XRD diffractograms of the unreacted basalt and the reacted basalt in the various activating solutions. All the reacted basalt B 3, 4, 5 and 6 were taken at the 168\textsuperscript{th} hour of leaching .................................................................................................................. 299

**Figure 11.1** The conceptual model of the chemical interactions between aluminosilicate solids and activating solutions. The dashed area represents the true chemical processes of geopolymerisation. ‘a’ to ‘b’ represent the various reaction pathways, which are determined by the nature of the reacting solids and the activating solutions ............................................. 306
PREFACE

I hereby declare that, to the best of my knowledge, this thesis is original in its entirety and contains no material which has been previously published by another person, except where due reference is stated. In addition, no part of this work has been submitted for the award of any other degree or diploma in any university.

I certify that the work has been undertaken solely by the candidate and the text of this thesis, exclusive of tables, graphs and bibliography, does not exceed 100,000 words.

William K. Lee

Many mineral processing technologies utilise the phenomena of mineral-water interactions in a variety of geological and engineered environments. The reactions involved can be broadly summarised as dissolution and precipitation of the solids. As far as the rate and the extent of reactions are concerned, solid mineralogy and solution phase equilibria are the major controlling factors. Therefore, engineering solids, altering solution composition and/or changing reaction conditions, can all be used to process minerals for desirable industrial outcomes. Such examples include concrete making, ceramic production and zeolite synthesis.

Over the last century, hydrated Portland cement has been the most commonly used binder material for concrete making. As solid reactivity of calcareous minerals is greatly enhanced by kilning at high temperature during Portland cement production, neutral water is a good enough co-reactant to produce inorganic gels that readily bind to rock aggregates. These systems have served us well, but not without some drawbacks: Synthesis of high CaO minerals involves high energy and fuel consumption. The major by-product CO$_2$ is a well-known global warming gas. Environmental protection, hence, becomes a strong driving force behind the on-going search for new concrete binder materials.

In the 1940’s, alkali-activation was discovered as an effective method for accelerating latent pozollanic properties of relatively unreactive and calcium-rich aluminosilicate minerals such as blast furnace slag. In these systems, mineral-water interactions were accelerated due to the presence of the alkalis in water. Such binders were thus termed alkali-activated or alkaline cements. Later in the 1970’s, Davidovits used a seemingly similar concept and developed what is now known as geopolymers. Metakaolinite, a low-calcium aluminosilicate produced by calcining kaolinite clay, was activated at room temperature and pressure using soluble silicate-rich alkaline aqueous solutions, or activating solutions. As research continued, Van Deventer and the co-workers found that various natural as well as industrial aluminosilicate
minerals could all give rise to inorganic aluminosilicate gels, or geopolymers, by alkali-activation with soluble silicate-rich activating solutions without further solid pre-processing. These new classes of ‘greener’ materials have already been shown to possess excellent physical and chemical properties, which in some cases are better than the ordinary Portland cement (OPC). Recycling industrial wastes for useful construction end uses is now fast becoming a reality.

Despite excellent research being conducted in the last 15 years, the chemistry of geopolymer synthesis, or geopolymerisation, is still poorly understood. In particular, the role of added soluble silicates in geopolymerisation as well as on the final product properties, is still a subject of intense debate. This thesis, therefore, aims to understand the chemical interactions between aluminosilicate solids and various activating solutions, with and without significant dosages of soluble silicates.

To achieve this goal, a thorough knowledge of the chemical interactions between minerals and aqueous solutions is required before any experimental programme can be proposed. This will be discussed in Chapter 2 by referring to the extensive literature on geopolymer synthesis as well as Portland cement hydration reactions. The general ‘proposed’ processes of geopolymerisation will also be presented in Chapter 2. As will be presented in Chapter 3, low calcium-content coal fly ash was used as the primary solid raw material for geopolymeric binder synthesis throughout this thesis. Siliceous aggregates such as river sand, basalt rock and siltstone were then added to the geopolymeric binders to manufacture geopolymeric mortars and concretes. As this thesis adopts the philosophy that the bonding properties of geopolymeric binders, both internally (or microscopic bonding) or to siliceous aggregates (or macroscopic bonding), are secondary results of the chemical interactions between the various solids and the activating solutions containing varying dosages of soluble silicates, an intimate knowledge of the solid starting raw materials cannot be overlooked. Such knowledge was acquired by the numerous solid characterisation techniques presented in Chapter 3. As will also be discussed in Chapter 3, the study of geopolymerisation from a chemical mechanistic point of view is restricted by the physical nature of the geopolymeric gels. Use of reaction models is inevitable to achieve such an understanding. Designing ‘realistic’ reaction models is of unparalleled importance as the results may be seriously misleading if care has not been taken when designing the models. Hence, by employing the various geopolymer characterisation techniques described in Chapter 3, Chapters 4, 5, and 6 were designed to
obtain the physical/mechanical characteristics of the fly ash-based geopolymeric binders, mortar and concretes, which are necessary for checking the suitability of the reaction models designed in Chapters 7, 8, 9 and 10.

Chapter 7 presents the results obtained from the various reaction models on the chemical interactions between a typical heterogeneous glassy aluminosilicate (Gladstone fly ash) and the activating solutions containing varying dosages of soluble silicates. From these experimental observations, it was proposed that a soluble silicate-rich activating solution should contain higher oligomeric silicates that readily adsorb dissolved Ca$^{2+}$ and thus prevented interfacial precipitation of Ca-containing polysialates, which then promoted mass transfer of the network formers Si$^{4+}$ and Al$^{3+}$ across the microscopic interface between the glassy aluminosilicate and the activating solution. This greatly increased mass transfer of the network formers was attributed to the greater amount of the polysilicate or the aluminosilicate gel (the principal binding phase of geopolymeric products) that was formed in the soluble silicate-rich activating solutions and was found to agree well with the experimental observations obtained from the real geopolymeric binders in Chapters 4 and 5. This hypothesis was further tested in Chapter 8 using various inorganic (KCl and K$_2$CO$_3$) and organic salts (K$_2$C$_2$O$_4$·H$_2$O and K$_2$HPO$_4$) as reaction probes. The results of the reaction models of Chapters 7 and 8 were further utilised to design a novel in situ and in real time analytical procedure to study geopolymerisation on ‘real’ geopolymer samples in Chapter 9.

In Chapter 10, the chemical interactions between crystalline aluminosilicates (kaolinite, albite, pulverised basalt) were further investigated using reaction models similar to those in Chapters 7, 8 and 9. The results obtained as such could be used to mechanistically explain the macroscopic interfacial bonding between siliceous aggregates and geopolymeric binders as presented in Chapter 6. Finally, the thesis will be concluded in Chapter 11 with a conceptual model that describes both the microscopic and macroscopic chemical interactions between various glassy and crystalline aluminosilicates and various activating solutions, which then leads to the observed physical/mechanical/chemical stability properties of the various geopolymeric products. It will also be discussed in Chapter 11 that the secondary products of alkali-activating aluminosilicate solids with ‘soluble silicate-rich’ activating solutions are technically different from those produced from ‘soluble silicate deficient’ activating solutions. ‘Geopolymer’ is chemically, physically and mechanically different from the ‘alkali-activated cement’.
Cement, by definition, is a material with adhesive and cohesive properties that readily binds to mineral aggregates to produce a compact rock-like mass with appreciable strength. Consequently, cement should embrace a large variety of materials synthesised from various solids and/or aqueous solutions. The dominant commercial use of Portland cement in the modern day industry, however, has given a serious misconception to the general public and many civil engineers that Portland cement is the only ‘cementitious’ material capable of making mortars and concretes. For this reason, the materials that can be used to bind mineral aggregates to produce mortars and concretes are referred to as ‘mineral binders’ throughout this thesis. The advantage of this terminology is to show the appreciation of the fact that different mineral binders, such as geopolymers, produced from different reactants ultimately involve different reactions as well as end product properties.

As will be discussed in the chapter, the chemical interactions between minerals and aqueous solutions, though extensively studied, are still not fully understood. The understanding of the chemistry between aluminosilicate solids and alkaline aqueous solutions or alkaline aqueous ‘silicate’ solutions responsible for the synthesis of geopolymers and other geopolymer-related products, is particularly poor. The objective of this chapter, therefore, is to provide a thorough literature review on what is presently known of the major processes existing between (1) minerals and aqueous solutions to produce mineral binders such as Portland cement and geopolymer, and (2) siliceous aggregates and the mineral binders to produce Portland cement-related and geopolymeric mortars and concretes. From here, aspects that are missing from the total understanding of the mineral solid-inorganic gel interactions will be raised, which will be investigated in the remainder of the thesis.
2.1 CHEMISTRY OF PORTLAND CEMENT HYDRATION

2.1.1 History and Manufacture of Ordinary Portland Cement

The first use of mineral binders to produce mortars and concretes is thought to date back to the Neolithic times (ca. 7000 B.C.). The Greeks and the Romans between 400 B.C. and 400 A.D. used a mixture of limestone and pozzolans (e.g. volcanic ash or sedimentary soils) to produce mineral binders and concretes that are still in existence today [2.1, 2.2]. Examples are the Pyramid of Cheops in Cairo, the Pantheon and the Coliseum in Rome, and the Pont du Gard near Nîmes. Unfortunately, the ancient technology for producing extremely durable mineral binders was lost in the Middle Ages. This perhaps is what triggered an on-going search for stronger and more durable mineral binders, a process which is still going on till now. In 1824 A.D., a mineral binder was discovered and patented by a British stonemason, Joseph Aspdin. A mixture of finely ground limestone and clay was calcined in his kitchen stove, which was then ground and mixed with water as well as mineral aggregates to produce concretes that resembled a stone quarried from the Isle of Portland off the British coast. With this invention, Aspdin laid the foundation for today’s Portland cement industry.

From the definition above, it can be seen that Portland cement is made primarily from a mixture of calcareous (calcium-containing, such as limestone or chalk) and argillaceous (alumina and silica-containing clay or shale) minerals [2.3]. The modern manufacturing processes, therefore, essentially consist of grinding these raw materials in certain proportions and burning them in a large rotary kiln. At a temperature of up to 1450°C, the mixture sinters and partially fuses into balls known as clinker. The clinker is then allowed to cool and is ground into fine powders in the size range of 1-100 μm. With the addition of gypsum, which is used to control the setting time (the time required for a paste to solidify and lose its plasticity) of the hydrated binder, the resulting product is the very basic form of the contemporary ordinary Portland cement (OPC). The oxide compositions of a typical commercial OPC clinker are presented in Table 2.1 [2.4].

During manufacturing, the mineral phases of the raw materials are transformed to four major crystalline phases upon cooling. These include tricalcium silicate (3CaO·SiO$_2$ or in cement
Table 2.1  Typical oxide composition of a Portland cement [2.4].

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Shorthand Notation</th>
<th>Mass Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>C</td>
<td>63.0</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>S</td>
<td>22.0</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>A</td>
<td>6.0</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>F'</td>
<td>2.5</td>
</tr>
<tr>
<td>MgO</td>
<td>M</td>
<td>2.6</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>K</td>
<td>0.6</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>N</td>
<td>0.3</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>S'</td>
<td>2.0</td>
</tr>
<tr>
<td>Loss on ignition + impurities</td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100.0</td>
</tr>
</tbody>
</table>

Table 2.2  Typical phase composition of a Portland cement [2.1].

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Mass percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3$S</td>
<td>54.1</td>
</tr>
<tr>
<td>C$_2$S</td>
<td>16.6</td>
</tr>
<tr>
<td>C$_3$A</td>
<td>10.8</td>
</tr>
<tr>
<td>C$_4$AF'</td>
<td>9.1</td>
</tr>
<tr>
<td>Minor compounds</td>
<td>9.4</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
</tr>
</tbody>
</table>

chemistry, C$_3$S), dicalcium silicate (2CaO·SiO$_2$ or C$_2$S), tricalcium aluminate (3CaO·Al$_2$O$_3$ or C$_3$A) and tetracalcium aluminoferrite (4CaO·Al$_2$O$_3$·Fe$_2$O$_3$ or C$_4$AF') [2.1, 2.3]. Because chemical equilibrium is not fully reached during the burning process, varying amounts of amorphous materials also exist in the cooled OPC clinker. The degree of crystallinity of the cooled clinker is controlled by both the rate of cooling as well as the duration of the raw materials being held at the sintering temperature. Although quantitative x-ray diffraction analysis [2.5-8] has been tried, estimation of all the phases in OPC clinker and cement, including crystalline as well as amorphous components, still remain illusive. In fact, proper labelling and/or identification of amorphous materials, not limited to the field of construction materials, is still at its infancy owing to the unavailability of suitable analytical techniques. Therefore, it is general practice to assume that all the amorphous materials have turned into the respective crystalline components. This is done for the sake of easier interpretation, which otherwise, could become too tedious and impractical. The most commonly used calculations for obtaining the ‘potential’ composition of OPC are all based on the work of R. H. Bogue and others. The composition as calculated is often referred to as Bogue’s composition, which is summarised below [2.9].
\[ C_3S = 4.07[\text{CaO}] – 7.60[\text{SiO}_2] – 6.72[\text{Al}_2\text{O}_3] – 1.43[\text{Fe}_2\text{O}_3] – 2.85[\text{SO}_3] \]  
(2.1)

\[ C_2S = 2.87[\text{SiO}_2] – 0.75[3\text{CaO}.\text{SiO}_2] \]  
(2.2)

\[ C_3A = 2.65[\text{Al}_2\text{O}_3] – 1.69[\text{Fe}_2\text{O}_3] \]  
(2.3)

\[ C_4AF’ = 3.04[\text{Fe}_2\text{O}_3] \]  
(2.4)

The terms in the brackets in eq (2.1) to eq. (2.4) represent the mass percentage of the given oxide in a cement. From these equations, a typical phase composition of a Portland cement is shown in Table 2.2 [2.1]. As can be seen, \( C_3S \) accounts for approximately 50% of Portland cement and is the most studied mineral in OPC hydration.

### 2.1.2 Ordinary Portland Cement Hydration Reactions

Ordinary Portland cement (OPC) consists of merely fine powders of silicates and aluminates. Interparticle bonding, from within OPC as well as to mineral fragments such as rocks for concrete making, can only result from chemical reactions between the reactive mineral phases of OPC and water. These reactions are traditionally called ‘cement hydration’ reactions.

From some literature [2.1, 2.2, 2.9-33], the term ‘OPC hydration’ describes all the chemical reactions right from the moment when OPC powders are contacted with water, to the stage where the pastes of OPC and water have become solidified and rigid. It encompasses adsorption of water molecules to cement surfaces (the true hydration) as well as the subsequent hydrolysis (the bond-breaking step that produces water). According to A. M. Neville [2.3], Le Chatelier was the first to observe that, under similar reacting conditions, the products of OPC hydration are chemically the same as the products of hydration of the individual OPC components (\( C_3S, C_2S, C_3A \) and \( C_4AF’ \) etc.). It then comes as no surprise that a great deal of research was conducted prior to the 1970’s to study the hydration reactions of the individual OPC components and to identify the hydration products. The main reactions are summarised below [2.1, 2.3, 2.9-11]:
\[2\text{C}_3\text{S} + 7\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_4 + 3\text{CH}\]  
(2.5)

\[2\text{C}_2\text{S} + 5\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_4 + \text{CH}\]  
(2.6)

\[\text{C}_3\text{A} + \text{CH} + 18\text{H} \rightarrow \text{C}_4\text{AH}_{19}\text{ (calcium aluminate hydrate)}\]  
(2.7)

\[2\text{C}_3\text{A} + 21\text{H} \rightarrow \text{C}_4\text{AH}_8\text{ (hexagonal hydrate)}\]  
(2.8)

where \(\text{H} = \text{H}_2\text{O}\) and \(\text{CH} = \text{Ca(OH)}_2\).

It has to be noted that \(\text{C}_3\text{S}\) and other silicate phases in real OPC clinker are rarely pure and may contain minor compounds, such as MgO, Al\(_2\)O\(_3\), Fe\(_2\)O\(_3\), TiO\(_2\), Mn\(_2\)O\(_3\), K\(_2\)O and Na\(_2\)O, in the solid solution. These oxides have significant effects on the atomic arrangements, crystal forms and hydraulic (dissolution/precipitation) properties of the silicates [2.1]. From a mineral-water interactions’ perspective, the variations in the solid mineralogy of the primary phases can significantly affect the secondary products as produced. Hence, \(\text{C}_3\text{S}_2\text{H}_4\) in (2.5) and (2.6) has been found to be non-stoichiometric in OPC and is therefore usually written as CSH, abbreviated for calcium silicate hydrates [2.1, 2.3, 2.9-11]. Better chemical formulae for describing calcium silicate hydration in real OPC situation should be written as:

\[\text{C}_3\text{S} + (y + z)\text{H} \rightarrow \text{C}_x\text{SH}_y + z\text{CH}\]  
(2.9)

\[\text{C}_2\text{S} + (y + w)\text{H} \rightarrow \text{C}_x\text{SH}_y + w\text{CH}\]  
(2.10)

where \(x + z = 3\) and \(x + w = 2\), but \(w, x, y\) and \(z\) are not necessarily integers. Due to the multiphase nature of CSH, which can be microcrystalline or non-crystalline, a collective term, ‘CSH gel’ (or tobermorite gel), is used to describe the poorly crystalline mixture of the various different forms of CSH’s. On the other hand, CH has always been found to consist of a fixed composition and displays a high degree of crystallinity as in hexagonal plates [2.1, 2.12]. In fact, CH is the only OPC hydration product that is of precisely determined composition. Hence, identification and quantification of CH crystals using techniques such as quantitative x-ray diffraction or loss on ignition are often used as a method for quantifying the extent of OPC hydration.
In hydrated OPC, CSH gel is the major hydration product and makes up approximately 70% of the total volume [2.13]. It has been well accepted [2.1, 2.3, 2.9-16] that it is this CSH gel that provides the bonding between the unreacted OPC particles as well as the other newly produced crystalline phases including calcium hydroxide (CH or portlandite) – the second major product of OPC hydration. The variations in CaO content in the raw materials can also determine how much of the calcium is not included in the CSH, hence the amount of CH available for reactions (2.7), (2.8) and/or others. This should later affect the phase distribution of calcium aluminate hydrates. Furthermore, in the presence of gypsum (CaSO₄·2H₂O), C₃A would react with water to form ettringite and various other sulphate-containing aluminate compounds after a series of subsequent chain reactions from ettringite [2.1, 2.3, 2.9-11]. In short, the products of the hydration reactions in OPC may affect one another and may themselves interact with other compounds. This renders hydrated OPC a chemically very complicated system that is very difficult to study.

### 2.1.3 Mechanism of Setting Reactions in Ordinary Portland Cement Hydration

‘Setting reactions’ describe the reactions that are involved in transforming a hydrated paste in a fluid state to reach a state of plasticity, which is hard and unmouldable. From the last section, it is clear that the multiphase nature of OPC can greatly complicate the reactions involved in hydrated OPC systems. To simplify this problem, the study of setting mechanisms of OPC hydration is normally conducted by ignoring the hydration of the phases that do not directly participate in CSH formation. Consequently, the most studied is the hydration of C₃S [2.13-26], followed by that of C₂S [2.28, 2.29]. Because the hydration is so complicated, even the combined examination of C₃S and C₂S is a rarity [2.30]. Also, due to the fact that reaction (2.10) is much slower than (2.9) [2.1, 2.3, 2.31], it is often assumed that only C₃S is involved in the initial stages of OPC hydration.

Numerous studies have indicated that the mechanism of the early OPC hydration consists of several distinct stages [2.1, 2.3, 2.12]. This is best demonstrated by the kinetic study of the hydration of OPC, as well as the isolated components, using isothermal conduction calorimetry. See Figure 2.1. It has been found that immediately upon contact with water
Figure 2.1  Schematic illustration of conduction calorimetry results showing the various stages of (a) OPC and (b) C₃S hydration [2.12].

(Phase I), a large amount of heat is evolved as ions of calcium and silicon are dissolved away from the dissolving particles [2.32]. Subsequently, the solution pH is reported to reach 12 after just a few minutes [2.12]. A film of CSH surrounding the dissolving particles, also known as Stein hydrate [2.33], or CSH type IV* [2.16], then becomes visible under electron microscopes also within the first few minutes. The Stein hydrate grows in thickness and completely covers the surfaces of the dissolving particles by the end of Phase I. See the schematic representation in Figure 2.2. At this time (~ 15-30 minutes after first contact with water), the growth of the Stein hydrate layer is found to have stopped.

The reaction then enters a so-called dormant or induction phase (Phase II) when cement particles are gradually coagulated [2.34]. It is believed that the dissolved calcium and silicate ions will have to move across the membrane of the Stein hydrate via osmotic transportation during this period [2.1, 2.26]. The rate of reactions is thus diffusion-controlled (barrier layer theory). Consequently, the rate of heat evolution and solid dissolution is much reduced while the concentrations of the dissolved ions gradually build up in the aqueous solution nearby [2.17, 2.18, 2.32]. As the calcium-to-silicate ratio reached in the solution is always well above

* The definition of the various CSH types according to Diamond [2.16] are:
  Type I:  fine fibrous network, 0.5 to 2 µm long and less than 0.2 µm wide, formed in immature pastes after several hours.
  Type II:  reticular network of interconnecting particles, formed in more mature pastes after several days.
  Type III:  continuous network up to 100 nm in size filling the space between grains, formed in very mature pastes.
  Type IV:  fine-grained colloidal gelatinous product formed in the very early stages in Phase I & II of OPC hydration.
Figure 2.2  Suggested mechanism after the induction period [2.21].

3 [2.18], the soluble silicate concentration remains extremely low whereas the calcium concentration in the solution slowly rises until supersaturation. It had been argued previously that the mechanism of CSH formation was of a through-solution type such that nucleation of hydration products was situated in the bulk solution. However, from more recent studies using environmental scanning electron microscopy (ESEM) [2.25, 2.26] and scanning transmission x-ray microscopy (STXM) [2.27], a protective layer topochemical mechanism is more preferred. A hollow and tubular-shaped CSH (CSH type I or second Stein hydrate [2.33]) was found to start nucleating from the outer surface of the Stein hydrate layer at the end of Phase I and continued to grow throughout Phase II. The cause of the tubular CSH formation is still not well understood but could be a result of ion concentration build-up inside the Stein hydrate layer. This generates excessive internal pressure and causes the layer to rupture or to transform into a more permeable one [2.35]. The tubular CSH acts as a transport medium of Ca ions from the dissolving particle to the interstitial solution. After supersaturation has been reached, CH then nucleates at the end of the tubular CSH and the hydration enters Phase III.

Phase III is typified by the appearance and growth of hexagonal CH crystals in the interstitial solution. The rate of heat evolution is found to increase once again after the end of Phase I, which can be largely attributed to CH crystal formation [2.18, 2.36]. It is believed that the lowered ionic activity of calcium in this period (the calcium concentration in the solution drops from supersaturation to the saturation level with respect to CH) can be responsible for the ‘re-initiation’ of cement hydration (delayed nucleation theory). This results in an increased rate of C₃S hydrolysis and all cement grains of less than 5 μm diameter would have become completely hydrated by the end of Phase III [2.3]. From *in situ* morphological studies
it is found that once the CH crystals have reached some critical size, the tubular CSH connecting them to the Stein hydrate would burst and form sheets of CSH resembling CSH type I, II and/or III. The cement particles are now interconnected by CSH gel through chemical bonds (initial set) and the hydrated OPC paste begins to gain strength continuously until it has become solidified and rigid (final set) just before the end of Phase III. Subsequently, the rate of hydration slows down as shown in Phase IV but final equilibrium will never be reached. Even in Phase V, where little heat is evolved and paste hardening is observed, continual dissolution of C$_3$S and C$_2$S and the subsequent precipitations are still evident for years.

It has to be noted that the cause of the induction period, and of its termination, is still unclear and remains debatable. A number of suggestions have been put forward but they all essentially fall into two major categories [2.37]: delayed nucleation theory and barrier layer theory, which have been briefly described above. Both theories recognise the fact that there is nucleation and formation of the Stein hydrate layer on the dissolving particle surfaces and setting only occurs after the formation of CH crystals. However, they disagree on what causes the increased dissolution of OPC clinkers at the start of Phase III, which presumably triggers the start of the setting processes. The above description is merely an attempt of integrating these two contrasting theories together (both contain elements of truth) in reference to the contemporary research of OPC hydration. This general concept of OPC hydration is still unsatisfactory for a number of reasons. For example, there is no clear evidence on how the Stein hydrate layer (and/or the second Stein hydrate) is formed and its role in the overall mechanism of inter-particle bonding between OPC clinker particles is not understood. Is the formation of the Stein hydrate layer or the formation of CH crystal necessary for setting to occur in hydrated OPC systems? Undoubtedly, much research is still required to understand the setting mechanisms of OPC hydration. Perhaps systematic addition of chemical additives and/or mineral admixtures, together with the various methods of characterising the subsequent effects, can be used to better differentiate whether it is delayed nucleation or barrier layer (diffusion-controlled) that controls the setting in hydrated OPC systems.
2.1.4 Silicate Speciation in Hydrating Ordinary Portland Cement Systems

The principal species in CSH formed in real C₃S, C₂S and OPC are chains of silicates, which may contain dimers, pentamers and probably octamers [2.31, 2.38]. According to Tong et al. [2.28], the hydration products of C₃S, C₂S or a mixture of C₃S and C₂S are the same regardless of the solid origins. In any case, no cross-linked silicates have been identified.

In ‘ideal’ systems, the structure of ‘pure’ crystalline CSH has been reasonably well resolved at the atomic level using mainly XRD and NMR techniques as shown in Figure 2.3, which has been proposed to resemble the structure of naturally occurring minerals such as tobermorite and jennite [2.39, 2.40]. According to Faucon et al. [2.41], the structures of tobermorite and jennite are similar in that both consist of chains of ~4-5 bridging silicate tetrahedral units separated by the octahedral calcium oxide layer. They are, however, different in the nature of attachment between the silicate tetrahedral units as shown in Figure 2.4.

In ‘real’ OPC systems, however, the CSH gel produced by OPC hydration consists of both the crystalline and the amorphous polymorphs with varying degrees of aluminate substitutions. The structure of the CSH gel, hence, is very poorly understood mainly due to the lack of analytical methods for the study of heterogeneous and amorphous materials. This is further complicated by the fact that the nature of the silicate anions has been reported to vary with time through the use of trimethylsilylation [2.21, 2.42, 2.43] and solid-state nuclear magnetic resonance (NMR) [2.31, 2.37, 2.44-48].

![Figure 2.3](image)

**Figure 2.3** Basic structure of calcium silicate hydrate [2.41].
Figure 2.4  Tobermorite and jennite model structures for calcium silicate hydrate, referred to as C-S-Ha and C-S-Hb respectively [2.41].

From trimethylsilylation and NMR studies, C₃S and C₂S orthosilicates in OPC have been initially shown to give rise to signals representing monomeric species before hydration. During Phase I & II of OPC hydration, however, the NMR peaks attributable to monomeric silicates have become much broadened, indicating the formation of amorphous reaction product(s) [2.46]. As only monomeric silicates can be found, it is likely that the Stein hydrate formed in Phase I is also monomeric, with a Ca/Si ratio of ~3 [2.17]. When the hydration reaches the end of Phase II, dimeric silicates as well as silicates of higher polymerisation degree start to form [2.42-48] with a Ca/Si ratio of 1.5 to 1.7 [2.38]. The fractions of the total Si as dimers and as polymers increase continuously for 6 months while there is a steady decrease of monomeric species since the start of Phase III. The content of the dimers reaches the maximum at about 6 months and then diminishes. On the other hand, the content of polymers continues to increase for years. The summary of silicate speciation in hydrating OPC with time is summarised in Figure 2.5.

Numerous investigators [2.49, 2.50] have reported that there is a good correlation between the strength of the hydrated OPC and the degree of hydration. As can be seen from Figure 2.5, the average chain length of the formed CSH has been found to increase with the hydration time as
well as with the degree of hydration. Hence, it is possible that the longer the average chain length is, the higher is the observed compressive strength. This has a number of implications and will be discussed in the next section, when mineral admixtures are used to increase the product strength and chemical durability of hydrated OPC.

2.1.5 Chemical Additives and Mineral Admixtures

OPC can give rise to concretes of varying physical as well as chemical properties due to mineralogical variations in the raw materials. Undoubtedly, it is vital to design concrete mixes to tailor-fit a large variety of different engineering applications without excessive modifications to the OPC clinker manufacturing processes. Hence, additions of chemical additives and mineral admixtures have become popular in the construction field to control concrete setting time, to improve workability, to accelerate early strength and to increase product chemical resistance and/or durability.
As C₃S-water interaction can be affected by a wide range of dissolved species through various different mechanisms [2.38], common inorganic salts (CaCl₂, NaCl, CaCO₃ etc.), organic salts (soluble phosphates etc.), organic compounds (sugars etc.), surfactants (alkyl or aryl sulphonate, salts of fatty acids etc.) and pozzolans (silica fumes, blast furnace slag, fly ash etc.) can all be used for creating various desirable engineering outcomes [2.1, 2.3]. Only a few additives and admixtures will be discussed here. These are selected due to their direct effects towards OPC hydration, i.e. primary dissolution of OPC minerals followed by the subsequent secondary phase precipitation.

2.1.5.1 Effects of inorganic salts

The effects of inorganic salt addition can be broadly classified as set acceleration and retardation. A set accelerator accelerates setting processes of OPC so that the time required for a fresh concrete to transform from an elastic and workable state to a plastic and unworkable state is shortened. A set retarder, however, prolongs the time of setting.

According to Taylor et al. [2.38], set acceleration of hydrated OPC by inorganic salt addition can be achieved by changing (a) the phase equilibria; (b) the adsorption phenomena on the dissolving surfaces; and/or (c) the particle growth and gel morphology [2.38]. On the other hand, addition of inorganic salts that are capable of yielding precipitates in a hydrated OPC system can result in set retardation.

By examining the effects of Na₂CO₃ and NaF addition, it becomes clear that Taylor’s generalisation above may not always be true. When these salts are added, the concentration of Ca²⁺ in solution is much reduced in comparison with the hydrated OPC system without any chemical additives. This is because both CO₃²⁻ and F⁻ ions are known to combine with calcium to form insoluble calcium salts. In fact, the soluble Ca²⁺ concentration in both salt-affected systems is essentially the same during the induction period and well into Phase V [2.18]. Yet, Na₂CO₃ is a set accelerator but NaF is a retarder [2.43]. This suggests that it is not the concentration of soluble Ca, or crystallisation of Ca(OH)₂, that is determining the hydration, or the length of induction period, of OPC. It is the nature of the anions that causes the differences to OPC setting. Furthermore, whether increased Si dissolution, due to the presence of CO₃²⁻ at the early stage of OPC hydration (Phase I), could contribute to the acceleratory effect will have to be clarified. Other questions that need to be answered include,
for example, whether anions of the inorganic salts are included in the structures of CSH and/or CH.

The effect of the cations of inorganic salts towards setting is best demonstrated by considering the case of chloride salts. It is found that all alkali and alkaline earth cations can affect OPC hydration to varying extents. The acceleratory effectiveness has been shown to have the following order [2.51]:

$$\text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+} > \text{Li}^+ > \text{Na}^+ > \text{K}^+$$

Calcium chloride is the most effective accelerator. It seems that within the same Periodical Group, the smaller the ionic radius of a cation, the more effective is a salt towards set acceleration. How exactly cations affect hydrated OPC setting is still not well understood. It is possible that setting can be related to solid-state diffusion phenomena. However, it is difficult to fit this into the established mechanism of OPC hydration. Also, it is not sure whether the anion $\text{Cl}^-$ from $\text{CaCl}_2$, or other chloride salts, is structurally included in the products of OPC hydration, which presumably is the reason for a number of observations including (1) shortened induction period; (2) accelerated strength development; (3) new product morphology of CSH; (4) increased surface area of the hydration product(s); (5) lower pH in the pore solution; and (6) lower ultimate strength [2.51, 2.52].

2.1.5.2 Effects of pozzolans

Pozzolans, according to the definition of ASTM C618-93, are siliceous or siliceous and aluminous materials that possess little or no cementitious value in themselves but, in a finely divided form and in the presence of water at ordinary temperatures, they will chemically react with calcium hydroxide to produce compounds possessing cementitious properties. Historically, pozzolans were used as set retarders as well as cheap substitutes for the more expensive OPC clinkers. Nowadays, pozzolans are used as mineral admixtures to effectively reduce the rate of heat evolution generated from OPC hydration. This reduces the chance of thermal cracking within OPC-based concretes. They have also been found to significantly improve product chemical resistance as well as durability of OPC-based concretes [2.1, 2.3, 2.11, 2.53, 2.54]. The use of pozzolans in OPC-based concretes has become so widespread that it is worth a careful examination of the reactions involved.
Table 2.3  The various pozzolans [2.11].

<table>
<thead>
<tr>
<th>Natural</th>
<th>Artificial</th>
</tr>
</thead>
<tbody>
<tr>
<td>volcanic ash,</td>
<td>calcined clay,</td>
</tr>
<tr>
<td>trass (pulverised volcanic overlaying rock known as puffstein),</td>
<td>calcined shale,</td>
</tr>
<tr>
<td>tuffs,</td>
<td>calcined gaize,</td>
</tr>
<tr>
<td>pumicite</td>
<td>pulverised fuel ash (fly ash),</td>
</tr>
<tr>
<td></td>
<td>bauxite,</td>
</tr>
<tr>
<td></td>
<td>granulated blast furnace slag</td>
</tr>
</tbody>
</table>

Table 2.3 includes minerals that may possess pozzolanic activities [2.11]. The natural pozzolans are mostly of volcanic origin but may also include diatomaceous earths, which have lost most of their basic oxides (K₂O, Na₂O, CaO and MgO etc.). The artificial pozzolans are usually products that are obtained by heat treatment of natural materials such as clays, shales and certain siliceous rocks, and pulverised fuel ash (fly ash). The common features of the natural as well as the artificial pozzolans are that (1) they all are silicates of high specific surface areas; and (2) most of these silicates consist of relatively large proportions of glassy phases, which are essentially very porous aerogels of high internal surface area [2.3]. These glassy phases contribute to almost the entire pozzolanic activities of pozzolans. Apparently, thermal history of these materials, such as temperature, duration and/or rate of cooling, which affects the crystallinity of the materials, should play a major role in determining their pozzolanic activities [2.11]. This is not too dissimilar from the case of the OPC clinker production.

The reactions involving pozzolans and lime solutions (the so-called pozzolanic reactions) so far are not well understood at all for the same reason as that of OPC hydration. Variable compositions and phases in the starting solids have rendered the systems hard to characterise using the existing analytical techniques. Consequently, all the major cement chemistry textbooks have failed to address the details of the effects of pozzolan additions to the chemistry of OPC hydration reactions. From the limited information available [2.1, 2.3, 2.11, 2.53, 2.54], pozzolanic reactions can be summarised as:

\[ S + xCH + yH \rightarrow C_xS_{(x+y)} \]  

(2.11)
Note that S denotes SiO$_2$ as reactive silicates inside the pozzolans. Upon contact with alkaline aqueous solution (water plus lime, i.e. CH), the reactive silicates would firstly dissolve. The dissolved silicates then precipitate with dissolved calcium to form calcium silicate hydrate gels of variable compositions, which may or may not be similar to the CSH produced in OPC hydration. Eq (2.11) is by no means the only reaction that can occur. For example, if calcined clay (high in Al and Si contents) was used, a significant amount of Al might also dissolve into the lime solution and form calcium alumino-silicate hydrate(s) [2.11].

According to Ogawa et al. [2.55], the composition of the CSH formed in the vicinity of the pozzolan particles varied with the duration of hydration as well as the composition of the original pozzolan particles. At 3-days hydration, a Ca/Si ratio of ~4 [2.55] could be reached in the CSH formed near the pozzolan particles (in a OPC-only system, the Ca/Si ratio of the CSH surrounding the hydrated OPC clinkers had been reported as 1.7 to 2 after 3 days of hydration [2.38, 2.55, 2.56]). By moving closer to the pozzolan particles, the Ca/Si ratio drops markedly to ~1 at the surface of the pozzolan (the Ca/Si ratio of the pozzolan was well below 0.05) [2.55]. See Figure 2.6 for a graphical presentation. At 91-days, however, it seems the composition of the CSH near the pozzolan particles was almost the same as that formed in a OPC-only system, i.e. ~2, although slightly lower Ca/Si ratio near the pozzolan particles was noted [2.55]. On the other hand, Richardson [2.57] had reported that the Ca/(Si + Al) ratio in OPC-slag blended cement varied from 0.7 to 2.4 after 3 days of hydration. The discrepancy of the reported values of the Ca/Si ratio in the pozzolan-affected CSH could be due to the different calculation and/or analytical methods used as well as the fact that there could be compositional gradients in the blended cements. The closer to the low-calcium pozzolans, the lower was the value of the Ca/Si ratio due to the ineffective diffusion of the dissolved species.

In any case, there is unanimous agreement that the calcium hydroxide crystal (CH) content in the hydrated pastes is lowered in the OPC-pozzolan blended cements due to the presence of pozzolans as compared to the OPC-only system [2.55, 2.58-68]. Increasing the dosage of pozzolans can promote greater CH consumption through pozzolanic reactions such as equation (2.11) [2.63, 2.64]. However, controversies still exist. For example, the occurrence of CH crystals in the hydrating system was reported to be delayed in the presence of pozzolans [2.65, 2.66], whereas others [2.45, 2.59, 2.63] showed that the amount of CH in the
hydrated OPC-pozzolan blends was not lower, but sometimes even higher, than the hydrated OPC-only system at least in the first 1~3 hours. Subsequently, the pozzolans then lowered the CH contents through pozzolanic reactions.

Regardless of the effects on the CH content, it seems that pozzolans initially retard the overall hydration of C₃S in the first 1 to 3 days [2.58, 2.59, 2.67] and then the hydration is accelerated thereafter [2.45, 2.55, 2.64, 2.66]. This can be related to the strength characteristics of OPC-pozzolan blended cements. The strength of OPC-pozzolan blend cement is initially lower but, with time, the strength of the blended cements exceeds that of the OPC-only cement [2.11]. Apart from this, higher calcium silicate hydrate (CSH) content is observed in the OPC-pozzolan blended cements than the OPC-only cement [2.63, 2.66, 2.66]. Products of denser microstructures with apparently different CSH morphologies [2.57], higher overall degree of polymerisation (i.e. higher average chain length) [2.45] and greater cross-linking near the pozzolan surfaces [2.68] have also been reported. This presumably is what constitutes the increase of product strength and durability in OPC-pozzolan blended cements.

2.1.6 The Interface Between Siliceous Aggregates and Ordinary Portland Cement

When a mineral binder is used to bind large mineral fragments, otherwise known as ‘aggregates’, the resulting mixture is called a mortar if the maximum aggregate size is smaller than 5 mm (fine aggregates). If both fine aggregates and course aggregates (> 5 mm) are used,
the finishing product is termed a concrete. As natural crushed stones and siliceous sand are much cheaper than OPC clinker [2.1], process economy has driven the existing construction industry to optimise the use of OPC cement for mortar and concrete manufacture. In general, aggregates are known to occupy at least three-quarters of the volume of a concrete. There is therefore no surprise that the effects of aggregate strength, shape, surface roughness, porosity, moisture content, size distribution and geochemical nature (e.g. the mineralogy) have all been known to play an important part in determining the overall concrete properties such as product physical strength, fracture toughness, chemical resistance and durability [2.1]. As there are many sources of aggregates that are suitable for construction purposes (more detail is given by Neville [2.1]), the following discussion will only concern the siliceous aggregates, which will be investigated in this thesis.

In OPC mortars and concretes, the interface between mineral aggregates and OPC binder is often described as the interfacial transition zone (ITZ) [2.69, 2.70]. The ITZ has been found to universally consist of greater concentrations of large portlandite (CH) crystal plates and long ettringite needles with a lower concentration of CSH gel when compared to the bulk OPC paste. The schematic drawing of the ITZ is presented in Figure 2.7 in reference to De Rooij [2.70], who summarised four of the most respected ITZ models to date [2.71-74]. As CSH gel
is the principal binding phase of OPC materials, the ITZ is generally perceived as the weakest region within OPC mortars and concretes [2.69, 2.70, 2.75-80]. Furthermore, fine micro-sized cracks are also regular features of the ITZ even prior to the application of external loads on OPC concrete [2.1]. This renders the ITZ as the primary defect in concrete and the preferred path for crack propagations. Consequently, it is widely accepted that improving the property of the ITZ will also improve the overall mortar and concrete properties.

From fracture mechanics, OPC concrete has been demonstrated to possess higher fracture toughness (a measure of the amount of energy that is required to induce mechanical failure of materials) than that of the mortar counterpart, which is in turn tougher than that of the binder [2.75]. (As similar trend is also observed on the physical strength of the OPC systems: Concrete is generally stronger than mortar, and mortar is stronger than binder. A strong concrete, however, does not usually possess high fracture toughness [2.1]. An OPC material that possesses a high strength but low fracture toughness is more brittle than the one that possesses a low strength but high fracture toughness.) The increase of fracture toughness through the addition of aggregates has been widely attributed to the inhibition of crack propagation and crack bridging by deflecting cracks around strong aggregates or along weak interfacial regions (the ITZ), when the material is under external stress [2.81, 2.82]. From numerous experimental studies [2.83, 2.84], the formation of microcracks within the ITZ can be prevented by strengthening the ITZ using methods such as silica fume addition. The stress exerted from the external load on the strengthened OPC concrete is thus passed on to the aggregates, which are stronger than OPC binder. This further strengthens and toughens the materials as in the case of high performance concretes (those that are strengthened through the use of silica fume addition as well as reduced water/cement ratio with the aid of water-reducers) [2.77, 2.79, 2.82, 2.83]. Understanding the formation mechanism of the ITZ, therefore, is vital in improving concrete performance.

Although the ITZ was discovered by Farran in the 1950’s [2.85], the processes responsible for its formation still remain poorly understood. Numerous investigators have suggested or implied that, since the ITZ is part of a hydrated OPC binder, the formation mechanism(s) of the ITZ should also resemble that of the normal OPC hydration [2.69, 2.71, 2.86, 2.87]. This is further supported by the observation that when OPC cement and aggregates are just placed in contact with water, a water-rich region containing virtually no OPC cement particles can be easily identified at the aggregate surfaces. The thickness of this water-rich region is roughly
the same as the thickness of the ITZ in the mature OPC mortars and concretes (~50 µm) [2.70]. Dissolved ions, therefore, have to diffuse from the hydrating OPC cement particles to the aggregate surface if the aggregate is chemically inert. As ions such as Ca$^{2+}$, Al$^{3+}$ and SO$_4^{2-}$ are more mobile in hydrating OPC systems than Si$^{4+}$ [2.78], the interfacial products within the ITZ should contain greater concentrations of CH and ettringite than CSH as shown in Figure 2.7.

There is, however, increasing evidence suggesting that aggregates do chemically interact with OPC cement pore solution. Tasong et al. [2.88] recently reported that siliceous rocks, such as basalt and quartzite, and silica sand could absorb ‘significant’ amounts of OH$^-$ and Ca$^{2+}$ from an artificial OPC cement solution (~70 mM (mmoles/litre) of OH$^-$, ~6 mM of Na$^+$, ~36 mM of K$^+$ and ~4 mM of Ca$^{2+}$). Simultaneously, Si$^{4+}$ was found to dissolve from the aggregates initially and then started to precipitate out after a period of time. Their results suggest that heterogeneous nucleation of calcium hydroxide could originate at the aggregate surface, as was also reported by other investigators [2.74, 2.87]. This calcium hydroxide layer is permeable to ions such as Na$^+$, K$^+$, Al$^{3+}$, Si$^{4+}$ and OH$^-$, allowing the dissolution of Si$^{4+}$ etc. from the aggregate to further proceed. After the solubility limit with respect to CSH is reached, calcium silicate hydrate(s) then forms at or near this calcium hydroxide layer at the aggregate surface. This implies that the CSH within the ITZ, and to some degree in the bulk cement paste as well, could contain the Si$^{4+}$ dissolved from both the cement particles and the siliceous aggregates.

As discussed above, the formation of CH within hydrating OPC materials is a result of excessive Ca that is not consumed by the formation of CSH. Additions of pozzolans, therefore, can be expected to significantly reduce the level of dissolved Ca that is allowed to diffuse from the OPC cement particles to the aggregate surfaces. Indeed, there is experimental evidence showing that the CH content of the ITZ can be significantly reduced through the addition of silica fumes and/or fly ash [2.89, 2.90]. Following the reduction of the CH content, the thickness of the ITZ is also reduced. This is reflected by the increased interfacial bonding strength [2.79] and the overall product performance of the modified OPC-based mortars and concretes [2.79].
2.1.7 Continual Search for Improved Concrete Binders

Portland cement-based binder, mortar and concrete products are the most used materials in the modern construction industry, totalling a global production of more than 5 billion tonnes every year. It has been estimated that for each tonne of Portland cement produced, there is at least another tonne of carbon dioxide being released into the atmosphere due to the by-product generation and the energy requirements for raw material calcination [2.1]. Emissions of this harmful ‘Greenhouse Gas’ from the Portland cement industry alone have been estimated to amount to 3-5% of the total emissions due to human activities. Although the cost for manufacturing Portland cement is relatively low (~ 0.050 US dollars per kg *), the massive environmental impact alone is incentive enough to trigger the search for new construction materials such as geopolymers, which can equal, or improve the existing properties of Portland cement-based materials, including durability, chemical resistance, fire resistance and waste encapsulation capability, and eliminate the environmentally unfriendly Portland cement manufacturing processes [2.91]. Below follows a discussion of the process chemistry that is involved in synthesising a new class of mineral binders, geopolymers, and the related mortar and concrete products.

2.2 CHEMISTRY OF GEOPOLYMERISATION

2.2.1 Early History and Definition

The very first paper on the subject of geopolymers and its synthesis method was published by its inventor, Joseph Davidovits et al. in 1979 [2.92]. Geopolymers, according to J. Davidovits [2.91, 2.93] were invented in search for a heat-resistant, non-flammable and non-combustible ‘inorganic polymer’ after numerous plastic-related catastrophic fires in France between 1970 and 1973. The very first geopolymer was synthesised by mixing kaolinite with ground quartz in cold or hot NaOH solution. The resulting mixture was then thermoset at 150 °C to form a block inorganic polymer, the geopolymer [2.92].

* Private discussion with J. S. J van Deventer, Department of Chemical Engineering, The University of Melbourne, 07/10/2002.
A geopolymer, as defined by Davidovits at a later date [2.91, 2.93], is an inorganic polymer with a structural backbone of poly-sialate, which is an abbreviation for poly-silicon-oxo-aluminate. The polysialate network is a framework three-dimensional structure of SiO₄ tetrahedra stacking on top of another in all directions with varying degrees of aluminate substitution. $^{27}$Al MAS-NMR (magic spinning angle-nuclear magnetic resonance) study has revealed that all of the Al$^{3+}$ in the polysialate network is in the IV-coordination. Consequently, cations such as Na, K and Ca are required for charge neutralisation on the negatively charged AlO$_4^-$ tetrahedral units within the polysialate network, which is proposed to have a general formula of:

$$M_n\{(SiO_2)_zAlO_2\}_n\cdot wH_2O \quad (2.12)$$

where M = Na, K and/or Ca, $n$ = degree of polycondensation, and $z$ = degree of aluminate substitution. When $z = 1$, the structure is termed ‘poly-sialate’, or PS; when $z = 2$, it is called poly-sialate-siloxo, or PSS; and when $z = 3$, it is poly-sialate-disiloxo, or PSDS. The varying degrees of aluminate substitution into the three dimensional silicate networks suggest that the three different polysialates should possess different physical and chemical properties. This is reflected by the varying practical applications as listed in Table 2.4.

<table>
<thead>
<tr>
<th>Category</th>
<th>Structure</th>
<th>Charge balancing cation (M)</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly-sialate (PS)</td>
<td>$M_n^+{(Si-O-Al-O-)_n}$</td>
<td>K</td>
<td>Thermal insulation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Na</td>
<td>Fire-resistant</td>
</tr>
<tr>
<td>Poly-sialate-siloxo (PSS)</td>
<td>$M_n^+{(Si-O-Al-O-Si-O-)_n}$</td>
<td>K</td>
<td>Refractory</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Na</td>
<td>Fire-resistant</td>
</tr>
<tr>
<td></td>
<td></td>
<td>K,Ca</td>
<td>Performance cement</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Toxic waste</td>
</tr>
<tr>
<td>Poly-sialate-disiloxo (PSDS)</td>
<td>$M_n^+{(Si-O-Al-O-Si-O-Si-O-)_n}$</td>
<td>K</td>
<td>Tooling composites</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Na</td>
<td>Refractory</td>
</tr>
<tr>
<td></td>
<td></td>
<td>F,K,Na</td>
<td>Fire-resistant</td>
</tr>
</tbody>
</table>
The degree of aluminate substitution in the basic polysialate structure is dependent on the starting material composition and methods of synthesis. Regardless of the degree of substitution, the ideal structures of PS, PSS and PSDS are amorphous to semi-crystalline (not well crystallised). In real geopolymer synthesis, however, the degree of product crystallinity is dependent on the curing conditions. The low temperature-cured products (typically below 100 °C) are all amorphous, giving rise to the usual PS, PSS and PSDS structure(s). Upon hydrothermal curing (e.g. 150-180 °C and 5-10 MPa), however, well-crystallised zeolitic products have been documented to embed within an amorphous matrix consisting of PS, PSS and/or PSDS [2.91].

According to Davidovits [2.91, 2.93], geopolymerisation processes, or the exothermic reactions that are involved in synthesising geopolymers by reacting aluminosilicate(s) with highly alkaline solution(s) (NaOH and/or KOH), can be schematised as below by assuming that the reaction pathway should start from monomeric species, to dimeric, to oligomeric and finally to polymeric, in analogy to organic polymer chemistry:

![Reaction pathway](image)

\[
\text{NaOH/KOH} \\
(Si_2O_5, Al_2O_2)_n + 3nH_2O \rightarrow n(OH)_3-Si-O-Al (\text{-})-(OH)_3
\]

\[(2.13a)\]

**Orthosialate**

\[
\text{NaOH/KOH} \quad | \quad |
\]

\[n(OH)_3-Si-O-Al (\text{-})-(OH)_3 \rightarrow (Na, K)-(\text{-}Si-O-Al (\text{-})-O-)_n + 3nH_2O\]

\[(2.13b)\]

\[| \quad | \quad O \quad \text{O} \quad | \quad | \quad (Na,K)-PS\]

for the Na and/or K charge-balanced poly(sialate), and
NaOH/KOH

\[(\text{Si}_2\text{O}_5, \text{Al}_2\text{O}_2)_{\text{n}} + 2\text{nSiO}_2 + 4\text{nH}_2\text{O} \rightarrow \text{n(OH)}_3\text{Si}^{(-)}\text{O}^{(-)}\text{Al}^{(-)}\text{O}^{(-)}\text{Si}^{(-)}\text{(OH)}_3\]  \hspace{1cm} (2.14a)

\[
\begin{array}{c}
\text{NaOH/KOH} \\
\text{Ortho(sialate-siloxo)} \\
n(\text{OH})_3\text{Si}^{(-)}\text{O}^{(-)}\text{Al}^{(-)}\text{O}^{(-)}\text{Si}^{(-)}\text{(OH)}_3 \\
\end{array}
\]

\[
\begin{array}{c}
\text{NaOH/KOH} \\
\text{(OH)}_2 \\
\text{(Na,K)}-\text{PSS} \\
\end{array}
\]

\[(\text{Na,K})\text{-PSS} \]  \hspace{1cm} (2.14b)

for the Na and/or K charge-balanced poly(sialate-siloxo). In theory, any solids containing significant amount of aluminosilicate(s), including the pozzolans used in Portland cement hydration as shown in Table 2.3, can all be used to synthesise geopolymers from various different reaction conditions for niche industrial applications.

### 2.2.2 Developments of Geopolymer Technology

Since 1979, about 90 journal papers and patents were published on the subject of geopolymers and the related products [2.94]. The practical applications of geopolymers and geopolymer-related products have been greatly diversified throughout the years, from the initial fire-proof thermal insulation panel and coatings [2.95, 2.96] to concrete slabs, roof tiles, fire-resistant mineral resin [2.97], toxic waste immobilisation [2.98, 2.99], and many other construction related products. In many aspects, the uses of geopolymer as mineral binders are compatible with those of the Portland cement, if not better.

The aluminosilicate solids used for geopolymerisation are no longer limited to kaolinite or calcined kaolinite (dehydroxylated kaolinite or metakaolinite) [2.92]. Other aluminosilicate-containing minerals such as fly ash [2.100-102], blast furnace slag [2.103], natural minerals such as stilbite, augite, wollastonite and many others [2.104] have all been successfully applied for geopolymerisation. Simultaneously, sample curing temperature has been greatly
reduced from ≥ 80 °C to below 50 °C for a large part of the more recent applications and fundamental research [2.100-102, 2.105]. A compressive strength of greater than 50 MPa in 28 days is now readily achievable using a range of very different solid raw materials below 50 °C.

The diversification of materials and reaction conditions used for geopolymer synthesis nowadays has driven the industry to broaden the definition of geopolymerisation from that of Davidovits [2.91, 2.93]. Geopolymerisation now encompasses all the chemical processes that are involved in transforming a range of different aluminosilicate and/or silicate solids using various aqueous alkaline solutions, with or without soluble silicates, under varying experimental conditions, into aluminosilicate gels – the principal binding phase of geopolymeric products. By this definition, numerous other minerals binders such as alkali-activated cements [2.106, 2.107], low-temperature synthesised aluminosilicate glasses [2.108, 2.109] and alkali polysialate polymer [2.110] can all be classified as geopolymers, according to Xu [2.94].

According to Davidovits [2.91, 2.93], geopolymerisation of kaolinite and metakaolinite using alkaline polysilicate solutions is originally meant for the ‘complete’ transformation of the solid phase (metakaolinite) to the gel phase, which is stoichiometric with respect to the definitions of poly(sialate), poly(sialate-siloxo) and poly(sialate-disiloxo). Evidence now suggests that when other solids such as fly ash [2.100-102, 2.111], blast furnace slag [2.103] and other natural aluminosilicate minerals [2.104] are used, not all of the solids are dissolved and transformed into aluminosilicate gel(s). Together with the possibility of partial aluminosilicate gel crystallisation under hydrothermal conditions, a ‘modified’ definition of geopolymerisation, therefore, can be depicted as [2.94, 2.112]:

28
As geopolymers were invented with great emphasis on industrial applications, published fundamental mechanistic information on geopolymerisation is very limited especially before 1996. Together with the various research difficulties, which will be elaborated in greater detail in the next chapter, most of the existing publications are still dealing with process optimisation and/or product characterisation.

### 2.2.3 Process Optimisation

As can be seen from the previous sections, the nature of solids used for geopolymerisation is very different from that of Portland cement hydration. In Portland cement industry, the solids have already been processed to a certain composition and mineralogy. Controlling the product properties, therefore, is relatively easy in Portland cement hydration. On the other hand, the geopolymer industry nowadays tends to use whatever is available without much or no furthering processing. The solids used for geopolymerisation include various industrial aluminosilicate wastes and natural virgin aluminosilicate minerals, which may possess very different reactivities from one source to another [2.94]. Controlling the product properties thus becomes a major engineering challenge in geopolymer technology. A thorough understanding of geopolymerisation (the chemical interactions between aluminosilicate solids and aqueous alkaline solutions with or without soluble silicates), and its relationship towards the microstructure and macroscopic properties is essential for optimising process parameters and product properties with good efficiency.
Table 2.5 Important process parameters in geopolymerisation

<table>
<thead>
<tr>
<th>A. Solids</th>
<th>B. Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. chemical composition</td>
<td>a. alkalinity (M₂O/H₂O, or [MOH])</td>
</tr>
<tr>
<td>b. mineralogy</td>
<td>b. Si/alkali cation ratio (SiO₂/M₂O)</td>
</tr>
<tr>
<td>c. microstructure</td>
<td>c. ionic species/electrolytes</td>
</tr>
<tr>
<td>d. particle size</td>
<td></td>
</tr>
<tr>
<td>e. combination of more than 1 solid reactant</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.5 lists some of the most important process parameters of geopolymerisation in reference to some previous investigations [2.91, 2.95, 2.100, 2.104, 2.105, 2.108-100]. Clearly, process optimisation is a very complex task in geopolymer production. Although most of the parameters listed in Table 2.5 have already been examined by various investigators, a much larger data set is still required to solve this process optimisation dilemma. The following is a brief summary and discussion of what has been achieved by some of the most important works in the field.

2.2.3.1 Effects of solids

Xu and Van Deventer [2.104] in 2000 examined the geopolymerisation of 15 natural minerals of widely different chemical compositions and mineralogy. The minerals studied ranged from ortho-aluminosilicates to di-, ring, chain, sheet and framework aluminosilicates. It was found that, through statistical analysis, framework structures were more soluble in aqueous alkaline solutions than ortho-, di-, ring, chain and sheet structures. The solubility of minerals seemed to have a direct relationship with the observed compressive strengths of the geopolymeric binders. A more soluble solid usually gave rise to a stronger product. Furthermore, all of the minerals were found to dissolve through an ion-pair mechanism, meaning the kinetics and the extent of mineral dissolution were dependent on the cationic species in the alkaline solutions. The dissolution of Si and Al was approximately congruent (the dissolution of Si and Al was approximately stoichiometric), despite the fact that Al in IV-coordination was expected to be more reactive in alkaline aqueous solutions than Si in IV-coordination through ab initio
calculations [2.113]. Evidence [2.105] also showed that combination of two or more minerals (such as stilbite in conjunction with kaolinite) in an appropriate ratio was effective in improving the binder compressive strengths. It was therefore speculated that minerals do react differently in alkaline aqueous solutions and some mineral could possess some structural directing effects, which could lead to the formation of a more mechanically strong microstructure.

2.2.3.2 Effects of solutions

The effects of alkaline solutions on mineral dissolution, product compressive strength and waste encapsulation capability have been studied extensively by Van Deventer and co-workers [2.100-102, 2.104, 2.105, 2.113, 2.114], Rahier et al. [2.108, 2.109] and Barbosa et al. [2.110].

Briefly, the effects of alkali cations from the alkaline solution have been well studied. There is unanimous agreement that Na is more effective in promoting aluminosilicate dissolution than K [2.100, 2.104, 2.105, 2.113], and the yield stress of the fresh Na-containing geopolymeric paste is greater than the K-counterpart, meaning the Na-containing paste is more viscous and harder to mix [2.100]. On the other hand, the compressive strength is generally higher in the K-containing systems than Na-counterpart [2.100, 2.104, 2.105, 2.114]. It has also been found that the time of setting and waste immobilisation capability of geopolymeric binders are not dependent on the type of alkali cations in the alkaline solutions [2.98, 2.100].

The solution alkalinity, which can be expressed as M₂O/H₂O, is also an important parameter in determining the product characteristics. Increasing molar M₂O/H₂O is known to induce a greater solid dissolution [2.100, 2.104, 2.105, 2.114]. The compressive strength of the resulting geopolymeric binder, hence, has been observed to increase with increasing M₂O/H₂O ratio until a certain threshold is passed. Over this threshold, the excess alkalis have been suggested to weaken the structure through a still unknown mechanism throughout the literature [2.100, 2.110], which will be investigated in Chapter 5 of this thesis. Rahier et al. [2.108, 2.109] used a range of analytical techniques, including differential scanning calorimetry (DSC), ²⁷Al and ²⁹Si MAS-NMR, Fourier-transform infrared spectroscopy (FT-IR) and XRD, to suggest that although solution alkalinity (M₂O/H₂O) might promote solid
dissolution [2.100, 2.104, 2.105, 2.114], the nature of the reaction product (i.e. the geopolymeric gel) was not affected, or at least before the threshold was exceeded. This means that solution alkalinity is important in controlling how much of the reaction product(s) is produced but it has nothing to do with the nature of the product. In other words, alkalis are reactants, not reaction modifiers.

It is well documented by Davidovits [2.91, 2.93] that the use of high concentrations of soluble silicates in the alkaline solution, or the activating solution, is one of the most critical reaction conditions for synthesising mechanically strong and chemically durable geopolymers. Van Jaarsveld and Van Deventer [2.100], Rahier et al. [2.108] and Barbosa et al. [2.110] further showed that increasing the dosage of soluble silicates at a certain solution alkalinity should at first increase the product compressive strength until a certain concentration is reached. Beyond that concentration threshold, addition of more soluble silicates is detrimental to the product compressive strength. This concentration threshold, however, can be raised by increasing the solution alkalinity [2.108-110]. It therefore appears that it is the molar SiO$_2$/M$_2$O ratio of the activating solution that is critical to the geopolymer synthesis, less the actual amount of soluble silicates being added. The effects of increasing SiO$_2$/M$_2$O ratio on geopolymerisation, according to Rahier et al. [2.109], include:

1. increased compressive strength before a certain threshold was reached;
2. retarded setting and hardening processes if SiO$_2$/M$_2$O ratio is beyond the threshold;
3. increased glass transition temperature (T$_g$), indicating thermal properties of geopolymers can be improved by increasing SiO$_2$/M$_2$O ratio;
4. increased shifts of the $^{29}$Si NMR resonance and IR vibrational bands to the higher energy field, suggesting the chemical bonds and the short-range structure are more polymerised, more cross-linked and less Al-substituted at high SiO$_2$/M$_2$O ratio; and
5. decreased structural crystallinity with higher product homogeneity.

Despite these well-identified effects of SiO$_2$/M$_2$O ratio on metakaolinite-based geopolymer synthesis, a thorough and accepted fundamental explanation about the effects of soluble silicate addition is still lacking. The use of other solid reactants further complicates our fundamental understanding as the SiO$_2$/M$_2$O ratio affects different solids to different extents, although the same trends were observed as those of metakaolinite [2.100]. Obviously, understanding the role of soluble silicates, as presented in the SiO$_2$/M$_2$O ratio, in the overall
geopolymerisation process is extremely important from both a fundamental as well as a process optimisation point of view.

2.2.4 Chemistry of Geopolymerisation

As presented in eq (2.15), geopolymerisation is generally believed to consist of a series of reaction steps including:

1. solid dissolution, which releases both Si and Al species when solids are coming in contact with the activating solutions;
2. polymerisation, possibly through colloidal formation, of the dissolved Si and Al with the soluble silicates from the activating solutions, if added;
3. gellation of the polymerised aluminosilicate;
4. setting and hardening; and
5. solid-state transformation of the aluminosilicate gel.

All of the reaction steps may, or may not, occur simultaneously.

While the solid dissolution step has been extensively investigated by leaching various solids in reaction slurries of much lower solid/solution ratios than the actual geopolymerisation using activating solutions without soluble silicates [2.100, 2.104, 2.105, 2.113, 2.115], all the other reaction steps were proposed by referring to related fields such as soluble silicate chemistry (Iler [2.116]), or zeolite synthesis as suggested by Davidovits [2.91, 2.93].

In most conventional zeolite synthesis, the first step is usually associated with mixing soluble silicate and aluminate, which may be monomeric or polymeric, in aqueous solution to produce the aluminosilicate gel of a desired composition [2.117]. Some of this gel then dissolves as the reactions proceed at a reaction temperature of 60-200 °C after the pH of the aqueous solution is subsequently increased to the alkaline regime. After an induction period in the alkaline environment, where the gel continues to interact with the alkaline solution and the length of which is dependent on the reaction conditions, a crystalline phase, the zeolite(s), then starts to build up. Due to the high number of oligomeric species present in the initial soluble silicate and aluminate solution, the reaction mixture can be very complex, which
subsequently gives rise to various crystalline and amorphous reaction products. Addition of structure-directing templates such as tetrapropylammonium (TPA) cation, hence, has often been practised, which has been proven to be effective in controlling zeolite pore structure and speciation [2.117].

On the basis of solution Si/Al and SiO2/M2O ratios, Derouane et al. in 1981 according to Serrano and Van Grieken [2.117] postulated two extreme reaction mechanisms governing the

**Figure 2.8** Zeolite crystallisation mechanisms: (a) solution mediated process (type A); (b) hydrogel reconstruction (type B) [2.117].
formation and growth of ZSM-5 zeolite where TPA was used as the structural-directing agent. Derouane et al.’s work is still regarded as one of the major contributions towards the understanding of the reaction mechanism(s) involved in zeolite synthesis through heterogeneous nucleation.

As summarised by Serrano and Van Grieken [2.117], ZSM-5 zeolite synthesis starting from type A solution (low Si/Al but high SiO₂/M₂O ratios at a high solution alkalinity (M₂O/H₂O)) was governed by a solution phase ion transport mechanism, or a solution mediated mechanism. In this case, depolymerisation of the silica source, i.e. the aluminosilicate gel as discussed above, was the rate-limiting step. This controlled the supply of the reactants being transported into the solution phase, where nucleation and growth of ZSM-5 took place. See Figure 2.8 (a) for the schematic presentation of the reaction mechanism. As the concentration of Al was higher in the solution phase, the dissolved silicate species from the aluminosilicate gel were exhausted, which in turn promoted further gel dissolution. Furthermore, the preferential adsorption of dissolved silica by the ZSM-5 nuclei instead of alumina was found to increase the crystal growth rate rather than the silica nucleation rate in the solution. Consequently, large crystals with inhomogeneous radial Al distribution (greater silica content at the centre and greater alumina content at the outer) of less numbers were found in the reaction mixture of type A synthesis.

On the other hand, ZSM-5 synthesis starting from type B aqueous alkaline silicate solution (higher Si/Al and lower SiO₂/M₂O ratios at a lower solution alkalinity than type A) appeared to be governed by a solid hydrogel reconstruction mechanism [2.117]. See Figure 2.8 (b). The dissolution of the hydrogel was limited by the low solution alkalinity (typically at a pH of ~11) and the presence of mainly monomeric or low oligomeric silicate species, which was proven by the absence of lower molecular weight silicate oligomers in the solution using solution ²⁹Si-NMR analysis. Zeolite crystallisation in these systems was attributed to the direct and mainly localised hydrogel transformation and recystallisation, which are still poorly understood. The higher silica nucleation rate over the crystal growth rate was believed to cause the formation of many small crystals with homogeneous Al radial distribution.

Clearly, the solution Si/Al, SiO₂/M₂O and M₂O/H₂O ratios are the governing factors that control the reaction mechanisms and the nature of the products formed via the heterogeneous
nucleation route of zeolite synthesis. It is worth noting that although the chemistry of soluble silicates and zeolites has been reasonably well established, these reaction systems can still be very different from the real geopolymerisation processes due to the largely different solid/solution ratios used. *In situ* study and/or a more realistic reaction model, therefore, are needed to better understand the real events involved in the actual geopolymerisation, which should take into account the presence of soluble silicates in the activating solutions.

2.2.5 Aggregate Inclusion in Geopolymeric Binder

Geopolymers can serve as a mineral binder that readily binds to mineral aggregates. However, published information on the geopolymer-based mortars and concretes from a chemical perspective is very limited. In 2000, Phair and Van Deventer [2.115] added a small amount of zirconia to a geopolymeric binder and found that the compressive strength was significantly increased. In the subsequent paper using a reaction model consisting of suspended zirconia particles in alkaline alumino-silicate solutions [2.118], a polysialate layer was identified on zirconia surfaces, which was an aluminosilicate with varying Na/K inclusions. This polysialate layer (subjected to scanning electron microscope, SEM) was found to be denser in high pH environments as shown in Figure 2.9 and Figure 2.10. The varying degree of polysialate formation at different pH was attributed to the differences in the speciation of the soluble silicates, which was dependent on the solution pH. Monomeric and lower oligomeric

---

**Figure 2.9** Zirconia particle coated with sodium silicate at pH = 12 [2.118].

**Figure 2.10** Zirconia particle coated with sodium silicate at pH = 14 [2.118].
soluble silicates at a high pH environment were most effective in producing polysialates on zirconia surfaces. From various adsorption and zeta potential measurements, it was suggested that the mechanism of the interfacial polysialate formation could be attributed to surface adsorption of predominantly monomeric soluble silicates at the hydrated cationic sites of zirconia in alkaline environments. This was followed by growth through surface polycondensation on the existing polysialate layer. According to Phair and Van Deventer [2.115, 2.118], the formation of this interfacial polysialate layer was responsible for the increased compressive strength observed in the zirconia-included geopolymeric product, much like adding aggregates to Portland cement binders to increase product strength and toughness. However, the interface between large mineral aggregates used for construction purposes, such as siliceous sand and crushed natural stones, and geopolymeric binders still remains largely uncharacterised.

2.3 SOLID-GEL INTERACTIONS IN GEOPOLYMERS

From the above discussions, controlling the dosage of soluble silicates used as well as the SiO$_2$/M$_2$O ratio of the activating solutions is of vital importance in process optimisation during the synthesis of geopolymeric binders and the related products. H. Xu [2.94] in her PhD thesis has speculated without experimental proof that, after aluminosilicate gel has been formed at the 3$^{rd}$ step of geopolymerisation (see Section 2.2.4) the dissolved Si and Al from the dissolving solid are allowed to diffuse into the gel phase and precipitate out as new aluminosilicate gel. The concentration build-ups of the dissolved Si and Al in the vicinity of the solid surface are thus minimised. This in turn stimulates further Si and Al dissolution vital for the overall geopolymerisation. Phair and Van Deventer [2.115, 2.118] further indicate that the use of an activating solution at the right SiO$_2$/M$_2$O ratio is critical in providing heterogeneous nucleation of polysialates as well as improving the physical strength of geopolymeric binders. Obviously, understanding the interactions between aluminosilicate solids, such as fine aluminosilicates powders used for geopolymeric binder synthesis, or large mineral aggregates used for the mortar and the concrete manufacture, and alkaline aqueous solutions (with or without significant dosages of soluble silicates), or aluminosilicate gels, is of paramount importance towards successful application of geopolymers.
This thesis, therefore, is dedicated to identify and understand the physical/chemical interactions between aluminosilicate minerals and aluminosilicate gels with much emphasis on the reaction mechanisms involved. Special attention will also be paid to pinpoint the effects of the critical solution process parameters as listed in Table 2.5, i.e. solution alkalinity (M$_2$O/H$_2$O, or [MOH]), SiO$_2$/M$_2$O ratio and the presence of ionic species or common electrolytes. To achieve these project objectives, the geopolymeric binders and the related products would have to be firstly synthesised and characterised as described in Chapter 3. Subsequently, a set of ‘realistic’ reaction models and an \textit{in situ} and in real time analytical procedure were developed for the first time in this thesis to actively study the chemical interactions between aluminosilicate minerals and the various activating solutions or aluminosilicate gels, which is vital in determining the observed physical characteristics of the various geopolymeric binders as well as the related products, as will be discussed throughout the remaining chapters.

2.4 REFERENCES


CHAPTER 3

Experimental Philosophy and Methodology

The central theme of this thesis has been raised and discussed in the last chapter: “To understand the physical/chemical interactions between aluminosilicate minerals (or siliceous aggregates) and aluminosilicate gels.” These aspects are crucial towards process optimisation during the synthesis of geopolymer and the related products. The importance of experimental design, therefore, cannot be overlooked particularly when geopolymeric systems are extremely complex and highly heterogeneous.

This chapter, therefore, will start with detailed descriptions of the raw materials used for the synthesis of the various geopolymeric products, and the analytical techniques used for characterising such raw materials. The chemical and physical characteristics of the geopolymeric binders, mortars and concretes will then be briefly described together with the characterisation techniques involved. This is followed by a discussion, including the advantages and the limitations, of some selective analytical techniques currently available to study the interactions between aluminosilicate solids and alkaline silicate solutions, or aluminosilicate gels. Subsequently, an experimental programme designed to maximise the advantages and minimise the limitations of some of the analytical techniques will be presented with the necessary information attached.

This chapter, and the remaining chapters of this thesis, will show that only a small number of selective analytical techniques are required to yield maximum mechanistic information on the subjects of geopolymerisation as well as the interfacial interactions between siliceous aggregates and geopolymeric binders. This is in contrast to what has been generally perceived among the geopolymer research community, where a large number of techniques have been tried to generate the same results, which is time and resource consuming, or worse, if the combination of techniques is chosen inadequately.
3.1 MATERIALS AND CHARACTERISATION METHODS

3.1.1 Sources of Raw Materials

Fly ash and kaolinite are the only aluminosilicate minerals used for the synthesis of geopolymeric binders throughout the entire thesis. These minerals have been chosen because they represent the central philosophy of material usage in geopolymer technology, i.e. recycling of industrial aluminosilicate wastes and utilisation of virgin aluminosilicate minerals. The coal-origin fly ash from Gladstone, Australia, with a mean particle size \( d_{50} \) of 14.1 \( \mu \text{m} \) has been obtained from Queensland Cement Limited (QCL), Australia. The kaolinite (HR1 grade, \( d_{50} = 0.47 \mu \text{m} \)) has been supplied by Commercial Minerals, Sydney, Australia. Since large quantities of the Gladstone fly ash and the HR1-grade kaolinite are required throughout the duration of the candidature, both the fly ash and the kaolinite have been purchased at the beginning of the candidature. These have been bulk mixed and repackaged separately to ensure raw material consistency. In addition, a coal-origin fly ash obtained from Port Augusta, Australia has also been used, though to a much lesser extent.

Gladstone fly ash, HR1-grade kaolinite, albite, basalt and siltstone have been used for the investigation of the chemical interactions between (alumino)silicate minerals and alkaline silicate solutions or geopolymeric binders. Washed siliceous sand (with a fineness modulus of 2.77 [3.1]; the higher the fineness modulus, the coarser is the sand) has been used for geopolymeric mortar synthesis. Crushed basalt \( d_{99.9} = 12.5 \text{ mm} \) and siltstone \( d_{99.9} = 12.5 \text{ mm} \) have been used as the coarse aggregates for geopolymeric concrete manufacture. Rocks of basalt and siltstone have been chosen due to their abundance in virtually all parts of the earth crust as well as their popularity in the general construction industry. Rocks of basalt with a pale-grey appearance have been obtained from Australian Slate Co., Melbourne, Australia. The siltstone rocks with a greyish appearance have been supplied by Doncaster Quarry, Melbourne, Australia. The albite \( d_{50} = 4.5 \mu \text{m} \) has been obtained from Minerals Corporation Limited, Broken Hill, Australia.

\( \alpha \)-quartz (SiO\(_2\)) of 99.9% purity and mullite (3Al\(_2\)O\(_3\).2SiO\(_2\)) of 99.92% purity from Sigma-Aldrich have been used to quantify the \( \alpha \)-quartz and mullite contents of the Gladstone fly ash as will be discussed in more detail below.
Laboratory grade chemical reagents including NaOH, KOH, KCl, K₂CO₃, K₂C₂O₄·H₂O, K₂HPO₄, KNO₃, CaCl₂, CaCO₃, CaO, Ca(OH)₂, CaSO₃, MgCl₂·6H₂O, MgCO₃, Mg(NO₃)₂·6H₂O, MgO and Mg(OH)₂, have all been obtained from Ajax Chemicals Australia. These chemicals are used to modify the solution chemistry of the aqueous alkaline (silicate) solutions and the geochemistry of the geopolymeric binders.

Sodium silicate (Vitrosol N(N40)®, molar ratio SiO₂/Na₂O = \( Rm = 3.32 \), [SiO₂] = 6.63 moles/L (M)) and potassium silicate (KASIL® 2236(K32), molar ratio SiO₂/K₂O = \( Rm = 3.50 \), [SiO₂] = 5.30 M) have been supplied by PQ Australia. These silicate solutions have been used in conjunction with the chemical reagents listed above to prepare the various activating solutions for geopolymer synthesis. Distilled/deionised water has been used for all solution preparations and dilutions throughout the thesis.

3.1.2 Characterisation of Raw Materials

As in any chemical system, detailed knowledge of the starting raw materials is vital in understanding the reactions and the reaction mechanisms involved in producing the desired final product(s). Knowing the nature of chemical bond(s) and the microstructure(s) of a starting raw material will allow predictions to be made on the required process parameters and conditions. The importance of raw material characterisation in geopolymer technology is no exception. In ill-defined engineering systems, such as geopolymer and the related products, acquiring the right information sometimes is not straightforward, as it is non-economical and time consuming to use all of the analytical techniques available to date. Consequently, the selection of a few analytical techniques suitable for geopolymer technology will have to rely on past experimental and practical experience. Table 2.5 lists some of the most important process parameters in geopolymer technology observed previously. These have been taken into consideration, using the so-called reverse engineering concept, to develop the raw material characterisation programme described below. A discussion of the usefulness of the information gathered from the raw material characterisation in relation to the overall geopolymerisation will be presented in Section 3.2.
3.1.2.1 Solid elemental composition from x-ray fluorescence spectroscopy (XRF)

A Siemens SRS 3000 sequential X-ray fluorescence spectrophotometer was employed to quantify the elemental compositions of all the minerals used in this thesis. This machine generates X-rays by a Ph-anode tube, which are being diffracted by LiF100, LiF110, OVO55 and PET crystals, pass through the powder-fused sample and yield signals that are later picked up by either or both of the scintillation or argon flow counter detectors. Before analysis, all of the minerals were pulverised, if they were not already in the powder form, and dried at 105 °C overnight. Both major and trace elements were analysed on the same powder-fused bead and the detection limit is about 5 ppm for elements heavier than oxygen. In this thesis, each elemental analysis was fully corrected for line interference and matrix effects. The elemental compositions in the oxide form are presented in Table 3.1. The Gladstone fly ash, based on the relatively low calcium content, could be classified as Class F according to the American Society for Testing and Materials (ASTM) definition.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Gladstone Fly ash (wt %)</th>
<th>HR1 Kaolinite (wt %)</th>
<th>Albite (wt %)</th>
<th>Basalt (wt %)</th>
<th>Siltstone (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>50.0</td>
<td>54.5</td>
<td>70.9</td>
<td>48.4</td>
<td>81.3</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>28.0</td>
<td>29.4</td>
<td>17.5</td>
<td>13.8</td>
<td>7.2</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>12.0</td>
<td>1.4</td>
<td>0.07</td>
<td>11.7</td>
<td>4.0</td>
</tr>
<tr>
<td>CaO</td>
<td>3.5</td>
<td>0.2</td>
<td>0.31</td>
<td>9.0</td>
<td>0.9</td>
</tr>
<tr>
<td>MgO</td>
<td>1.3</td>
<td>0.2</td>
<td>0.04</td>
<td>10.3</td>
<td>1.8</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.2</td>
<td>0.1</td>
<td>9.75</td>
<td>3.6</td>
<td>0.9</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.7</td>
<td>0.2</td>
<td>0.43</td>
<td>1.0</td>
<td>1.4</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.7</td>
<td>2.8</td>
<td>0.05</td>
<td>1.9</td>
<td>0.7</td>
</tr>
<tr>
<td>Other minor oxides</td>
<td>0.6</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Combustibles</td>
<td>2.0</td>
<td>11.0</td>
<td>0.75</td>
<td>0.0</td>
<td>1.6</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>
When a beam of monochromatic x-rays is incident on an atom, two processes may occur: (1) the beam may be absorbed, and the electrons of the incident atom may be ejected if they are over-excited, or (2) some or all of the beam may be scattered (or diffracted) [3.2]. If the wavelength of these scattered monochromatic x-rays is not changed (i.e. the x-rays do not lose any energy), the diffraction process is termed an elastic scattering. This elastic x-ray diffraction is what forms the basic principle underlying the modern x-ray diffraction technique (XRD): By bombarding a multi-element material, the elastically diffracted x-rays from different atoms can interfere with each other. This produces a distribution of diffracted x-ray intensities, which is strongly modulated by the diffracted wave interactions. Diffracted maxima, presented as peaks of the XRD diffractograms, can be obtained only if the diffracted x-rays are in phase with one another, which results in constructive interferences. For a given set of lattice planes with an inter-planar distance of $d$, see Figure 3.1, the condition for a diffraction peak to occur follows Bragg’s law [3.3]:

$$2d \sin \theta = n\lambda$$  \hspace{1cm} (3.1)

where $d =$ inter-planar distance, $\theta =$ scattering angle, $\lambda =$ wavelength of the monochromatic x-ray beam and $n =$ an integer representing the order of the diffraction.

---

**Figure 3.1**  Parallel rays reflected from points on neighbouring partially reflecting planes are in phase when Bragg’s law is obeyed [3.4].
If the atoms are arranged in a periodic fashion, as in crystals, the diffracted x-rays will consist of sharp interference maxima, which share the same symmetry as the atomic distribution of the incident material. Crystal structure, therefore, can be deduced based on the diffraction patterns. As the diffraction pattern is also a function of the wavelength of the incident x-ray beam, it is essential to specify the wavelength used. For diffraction purposes, the x-rays are normally in the range of a few angstroms (Å) to 0.1 Å (1 keV to 120 keV), which is comparable to the size of atoms. These energetic x-rays can penetrate deep into a wide range of materials and provide information of the unknown sample including phase identification and structural determination based on the diffraction patterns.

In this thesis, a Phillips PW 1800 diffractometer coupled with a copper anode tube and a graphite monochromator was used. The CuKα x-rays were generated at 30 mA and 40 kV to produce an averaged wavelength of 1.54184 Å. Specimens were step-scanned as random powder mounts from 10 to 70 °2θ at 0.05 °2θ steps and integrated at the rate of 2 s step⁻¹. Before analysis, samples were pulverized to fine powders (< 63 μm) in a ring mill composed of tungsten carbide to avoid contamination. The powders were then mounted in sample holders, compacted and flattened using glass slides. The fact that each crystal phase, including crystal polymorphs, has its own set of characteristic inter-planar distances (otherwise known as d-spacing), has made phase identification using XRD a relatively easy task. Positive phase identification can be made if at least three of the diffraction peaks of the unknown match the standard diffraction pattern of a known crystal phase, which can be obtained from the literature or from a powder diffraction database supplied annually by the committee of the International Centre for Diffraction Data (ICDD). This had been practised throughout the thesis as far as phase identification is concerned.

From XRD analysis, with consideration of the results obtained from XRF elemental analysis, the Gladstone fly ash was found to consist of α-quartz (SiO₂), mullite (3Al₂O₃·SiO₂), hematite (Fe₂O₃), magnetite (Fe₃O₄), lime (CaO) and gypsum (CaSO₄·2H₂O). Both α-quartz and kaolinite (Al₂Si₂O₅(OH)₄) were identified in the HR1 grade kaolinite. The basalt rock was found to comprise predominantly of plagioclase feldspar (albite (NaAlSiO₃), disordered and anorthite ((Na,Ca)AlSi₃O₈), disordered), potash feldspar (sanidine (KAl Si₃O₈), disordered), pyroxene (augite ((Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)₂O₆) and quartz, with minor
quantity of clay (kaolinite). The siltstone rock, on the other hand, comprised predominantly of quartz and chlorite (clinochlore, (Mg,Fe$^{+2})_3$Al(Si,Al)$_4$O$_{10}$(OH)$_8$), with minor quantities of mica (muscovite (KAl$_2$(AlSi$_3$)O$_{10}$(OH)$_2$) and illite (KAl$_2$(AlSi$_3$)O$_{10}$(OH)$_2$), clay (kaolinite) and plagioclase feldspar (albite, disordered). The albite (Minerals Corporation Limited, Broken Hill, Australia) was found to be of very high purity and consists of albite crystallites (NaAlSi$_3$O$_8$) and minor quantity of α-quartz.

XRD analysis can also provide other structural and compositional information of the target material including crystallite size (from the peak width), crystal phase concentration (from the peak height), and the amorphous content (from the intensity of the background hump). Quantitative determination on each of the crystal phases within a target powder sample can also be provided using a Rietveld method [3.5] with the necessary computer softwares, or the method of known additions [3.6].

Using the method of known additions [3.6], the mullite content in the Gladstone fly ash can be estimated by firstly preparing 5 standard samples with compositions of 90.0-10.0, 85.0-15.0, 80.0-20.0, 75.0-25.0 and 70.0-30.0 wt% of fly ash-mullite. In this thesis, the 99.92 wt% pure mullite from Sigma-Aldrich was used as an internal standard. The mullite mass fraction

\[ I = 0.1066X + 0.452 \]

**Figure 3.2** Change in normalised integrated peak intensity at 35.28 °2θ due to the known addition of mullite.
in the 100 wt% fly ash was determined by extrapolating the graph of normalised integrated peak intensity versus the amount of mullite (internal standard) added, to the abscissa as shown in Figure 3.2. The mullite peak used for the quantitative XRD analysis was chosen at 35.28° 2θ because it had been previously shown by White and Case [3.6] as the most sensitive and most accurate peak towards the method of known additions. The normalised integrated peak intensity was calculated by firstly obtaining the integrated intensity difference between the standard sample and the 100 wt% fly ash sample. This difference was then divided by the integrated peak intensity of the 100 wt% fly ash sample. From Figure 3.2, the mullite content of the Gladstone fly ash was estimated to be ~4.2 wt% at the abscissa. Similarly, the quartz content was ~12.3 wt% using the 59.90° 2θ peak.

3.1.2.3 Solid surface area from gas adsorption

Surface area of a material is an important property because it gives an indication of how much surface there is for heterogeneous reactions to take place within a solid-fluid system, as in the case of geopolymerisation.

The adsorption of a gas (the adsorbate) on a solid (the adsorbent) can, in principle, be made to yield valuable information as to the surface area as well as the pore structure of the solid. Briefly, the adsorption is brought about by the attractive forces acting between individual atoms, or ions, of the solid and the molecules of the gas, which are combined results of the ‘dispersion (attractive)’ forces, i.e. the London forces, and the short-range repulsive forces. The total potential energy between two atoms, by adopting the principles of quantum mechanics, can be expressed (in a simplified form) as [3.7]:

\[
\varepsilon (r) = - C r^{-6} + B r^{-12}
\]

where \(\varepsilon = \) potential energy; \(r = \) distance between centres of two atoms; \(C = \) a constant accounting for the effects of instantaneous dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions between two atoms; and \(B = \) a constant accounting for short-range repulsion which arises from the interpenetration of the electron clouds of the two atoms.
The potential energy $\phi(z)$ between a single adsorbate molecule and the surface of the adsorbent at a distance $z$ can be obtained by adding up the individual interaction of each of the atoms $i$ of the adsorbate molecule and each of the atoms $j$ of the adsorbent as [3.7]:

$$\phi(z) = \sum \varepsilon_{ij}(r_{ij})$$  \hspace{1cm} (3.3)

If either the solid or the gas is polar, there will be electrostatic (coulombic) forces coming into play. Eq (3.3) therefore can be rewritten to include the polar effects as [3.7]:

$$\phi(z) = \sum \varepsilon_{ij}(r_{ij}) + \phi_p$$  \hspace{1cm} (3.4)

where $\phi_p = \text{potential energy contributed by the electrostatic forces between polar molecules.}$

When a gas molecule is brought within the vicinity of the solid adsorbent, it is most likely situated at a distance $z$ from the solid surface where the potential energy $\phi(z)$ is at the minimum, i.e. at the equilibrium position.

During adsorption, the quantity of gas taken up by a solid sample at equilibrium is proportional to the sample mass $m$ (i.e. the available surface area for adsorption), the temperature $T$, the gas partial pressure $p$ (i.e. the amount of adsorbate available) and the nature of both the solid and the gas (i.e. the nature of attractive force and potential energy between solid surface and gas molecules). The specific surface area of the solid, therefore, can be calculated as [3.7]:

$$A = n_m a_m L$$  \hspace{1cm} (3.5)

where $A = \text{specific surface area}$, $n_m = \text{moles of adsorbate per gram of adsorbent}$, $a_m = \text{averaged area occupied by a adsorbate molecule in the completed monolayer}$ and $L = \text{Avogadro constant}$.

For a given gas adsorbed onto a particular solid at a fixed temperature below the critical temperature of the gas, $n_m$ can be expressed as:

$$n_m = f(p/p^\circ)_{T,\text{gas,solid}}$$  \hspace{1cm} (3.6)
Figure 3.3  The five types of adsorption isotherm, I to V, in the classification of Brunauer, Deming, Deming and Teller [3.7].

where $p^o = \text{saturation pressure of the gas}$. Eq (3.6) is otherwise known as the gas adsorption isotherm.

In the literature, there are tens of thousands of adsorption isotherms recorded on a wide variety of solids. The majority of these isotherms can be classified into five major groups as shown in Figure 3.3 [3.8]. Type I isotherms are characteristics of microporous ($< \sim 20$ Å) adsorbents. Type II indicates that the solid is non-porous. Type III is representative of a microporous material where the adsorbent-adsorbate interaction is weak. Type IV isotherms are normally indicative of mesoporous (between $\sim 20$ and $\sim 500$ Å) materials. Finally, Type V represents a special case in which the evaluation of either surface area or pore size distribution of the solids is poor possibly due to the weak adsorbent-adsorbate interaction.
To calculate surface area of a solid using eq (3.5), it is necessary to firstly construct an adsorption-desorption curve such as Figure 3.3, and then decide which type of the adsorption isotherms is involved. Subsequently, a mathematical model should be applied to obtain \( n_m \) through eq (3.6), which best describes the adsorption isotherm.

Harris and Sing [3.9] had examined a broad range of nonporous silica and alumina and concluded that, despite the differences in surface areas and crystal structures, the normalised adsorption isotherms of all the materials examined followed the same adsorption-desorption curve using nitrogen as the adsorbate. When the \( p/p^o \) ratio did not exceed 0.3, the Brunauer, Emmett and Teller (BET) equation for multiplayer adsorption was a good mathematical model for approximating the Type II adsorption isotherm, which can be expressed as [3.10]:

\[
\frac{n}{n_m} = \frac{c(p/p^o)}{(1-p/p^o)(1+c-1p/p^o)}
\]

(3.7)

where \( c = e^{(q_1-q_2)/RT} \), and \((q_1-q_2)\) = net heat of adsorption and \( R \) = universal gas constant.

According to the XRF and the XRD analyses, the solid raw materials used in this thesis are highly crystalline, except the two fly ashes, and heterogeneous and consist of various different silica and alumina phases. These solid raw materials, therefore, could be classified as nonporous materials. Consequently, the specific surface areas of these materials, in consideration of Harris and Sing’s observation [3.9], were determined using nitrogen gas as the adsorbate under the condition of \( p/p^o < 0.3 \) with the assumption that all adsorption processes followed Type II isotherm. All specific surface area measurements using the BET method were conducted on a Micromeritics Flowsorb ASAP 2020 instrument. Before analysis, samples were pulverized to fine powders (< 63 \( \mu \)m) in a ring mill composed of tungsten carbide to avoid contamination and dried at 105 °C overnight. The BET surface area thus determined is 4.13 m\(^2\)/g for the Gladstone fly ash, 15.7 m\(^2\)/g for the HR1-grade kaolinite and 0.24 m\(^2\)/g for the albite.

3.1.2.4 Nature of chemical bonds from infrared spectroscopy (IR)

Molecules are compounds that consist of two or more atoms. Through interactions between the electrons of the outermost orbits, a potential energy well such as that shown in Figure 3.4
Figure 3.4 Potential energy curves for a diatomic molecule: actual potential (solid line), parabolic potential (dashed line), and cubic potential (dotted line) [3.11].

As energy is related to frequency of an electromagnetic wave through Eq (3.8) [3.12]:

\[ E_1 - E_2 = h \cdot \nu \]  

(3.8)
where $E_1$ and $E_2$ are the energies (J) of the ground and the excited states respectively, $h$ is the Planck’s constant ($h = 6.626 \times 10^{-34}$ Js) and $\nu$ is the frequency (s$^{-1}$) of the electromagnetic wave, the energy carried by the electromagnetic wave can only be absorbed by the molecule when its frequency matches the energy difference between the ground and the excited states (i.e. $E_1 - E_2$). The frequency (or the wavenumber) of the electromagnetic wave associated with the vibrational excitation lies within the range 12800–200 cm$^{-1}$, corresponding to the infrared (IR) radiation region. In other words, molecular vibrations can be detected and
measured in an infrared spectrum, provided a selection rule other than that of eq (3.8) must be satisfied: The vibrating molecule must produce an oscillating dipole moment [3.11,3.12]. Hence, molecules without a centre of symmetry, which is normally the case in large molecules or amorphous solids, should be infrared active but Raman inactive (which requires molecules to vibrate without producing oscillating dipole moment) [3.12]. It is for this reason that infrared spectroscopy has been chosen over the Raman technique in this thesis to characterise the nature of chemical bonds within the solid raw materials as well as the geopolymeric products.

As stated by Farmer [3.13], the vibrational frequencies observed in an infrared spectrum are dependent on (1) the force constants of the chemical bonds (which measure the strengths of intramolecular bondings), (2) the atomic masses, and (3) the molecular geometry. For molecules that are ionic in nature, the force constants are normally obtained by empirical correlations such as Batsanov and Derbeneva’s equation for ionic crystals [3.14]:

$$k = 4 e^2 Z_A Z_B N / r^3$$

(3.9)

where \( k \) = force constant, \( r \) = bond length, \( Z \) = ionic charge of atoms A and B, \( e \) = electronic charge and \( N \) = coordination number (or bond order). For covalent bonds, the force constants can be obtained by Gordy’s correlation [3.15]:

$$k = a N (x_A x_B / r^2) \times 0.75 + b$$

(3.10)

where \( x \) = electronegativity of atoms A and B, and \( a \) and \( b \) = empirical constants. Hence, as predicted from Eq (3.9) and (3.10), the infrared frequencies observed on a molecule (proportional to \( k^{1/2} \) [3.11]) should increase with increasing intramolecular bonding strength induced by, for example, greater local charge differences between the atoms involved, and vice versa.

For silicates and aluminosilicates under normal conditions, the silicon atom is nearly always bonded to 4 oxygen atoms [3.16]. The silicon atom, with an oxidation state of +4, therefore, is fourth coordinated (\( N = 4 \)) and the resulting structure is said to be a tetrahedron often expressed as \( \text{SiO}_4^{4-} \), or \( \text{SiO}_4 \) as often encountered in the literature. This basic \( \text{SiO}_4 \) tetrahedral unit has a high tendency to polymerise with one to another. Depending on the variations in the
Figure 3.6 The structure of silicates. The centre of the atoms (black = silicon or aluminium; white = oxygen) and the tetrahedral coordinating polyhedra are shown here [3.17].

As aluminium has shared a similar atomic radius with silicon \((r = 1.26 \text{ Å for Al and 1.17 Å for Si})\) [3.19], substitution of an aluminium atom for silicon in a silicate structure to form an
‘alumino-silicate’ is very common in nature or in industrial applications [3.16]. Since aluminium has an oxidation state of +3 [3.20], the aluminosilicate ‘tetrahedral’ units (N = 4, \( \text{Al}^{IV} \text{O}_4^- \)) will carry an extra negative charge for every Al substituted, which will have to be charge-balanced by cations commonly from Group I & II (s-block) or more rarely, from the p and d-blocks such as iron (Fe) [3.21]. According to Loewenstein [3.22], the maximum allowable substitution of an IV-coordinated aluminium for silicon is ~50% for 3-D framework (tecto-) and 2-D network (phyllo-) structures, giving rise to silicon-rich aluminosilicates such as albite (\( \text{NaAlSi}_3\text{O}_8 \)). Within these structures, where tetrahedral units of silicate and aluminate are linked together through shared bridging oxygen(s) (BO), no Al-O-Al bridge should occur according to the Loewenstein aluminium avoidance principle [3.22] and both \( \text{Al}^{IV} \) and Si are termed ‘network formers’. With greater aluminium substitution, the substituted aluminium will become VI-coordinated (N = 6, \( \text{Al}^{VI} \text{O}_6^{3-} \)) to form octahedral units with less cross-linkage as in neso-, cyclo- and ino- aluminosilicates [3.13, 3.23]. The aluminosilicate containing \( \text{Al}^{VI} \) is less cross-linked because the \( \text{Al}^{VI} \) atom is bonded to a greater number of non-bridging oxygen atoms (NBO’s) and requires more charge balancing cations in the structure. Consequently, \( \text{Al}^{VI} \) is a ‘network modifier’.

The substitution of aluminium into a silicate structure has a significant impact on the intramolecular bonding strength within an aluminosilicate. The Al-O bond in pure aluminate has a bond energy of 125 kJ mol\(^{-1}\) at the IV-coordination, whereas at the VI-coordination, the Al-O bond energy is 87 kJ mol\(^{-1}\) [3.36]. Compared to that of the Si-O bond of a pure silica with a bond energy of 466 kJ mol\(^{-1}\) [3.19], the Al-O bond clearly has a smaller bond strength regardless of the coordination state. This is reflected in the IR spectrum as shown in Table 3.2: A fused silica, or a silica gel without any aluminium substitution or any other impurities, is known to exhibit an IR asymmetric stretching Si-O-Si band centred at ~1100 cm\(^{-1}\) [3.27, 3.30]. The IR asymmetric stretching bands of \( \text{Al}^{IV}-\text{O}-\text{Al}^{IV} \) and \( \text{Al}^{VI}-\text{O}-\text{Al}^{VI} \), however, are clearly situated at lower frequencies. With increasing aluminium substitution for silicon-rich phyllo- and tecto- aluminosilicates, the Si-O-T (T = Si or Al\(^{IV}\)) asymmetric stretching vibration band has been observed many times in the past to shift from the original ~1100 cm\(^{-1}\) to a lower frequency as shown in Figure 3.7 [3.33, 3.34, 3.38-40], indicating reduced average vibrational force constants resulting from decreased intramolecular bond strengths.
Table 3.2  The characteristic IR vibrational bands of T–O–T (T = Si or Al) asymmetric stretching vibrations [3.23–35].

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Assignment</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100-900</td>
<td>Asymmetric stretching (Si-O-Si, Si-O-Al)</td>
<td>3.24–34</td>
</tr>
<tr>
<td>1100-1000</td>
<td>Asymmetric stretching (Si-O-Si, alkali cation-modified silicate)</td>
<td>3.24–32</td>
</tr>
<tr>
<td>1100</td>
<td>Asymmetric stretching (Si-O-Si, pure silica)</td>
<td>3.27, 3.30</td>
</tr>
<tr>
<td>900-650</td>
<td>Asymmetric stretching (Al-O-Al, Al(_{13})O(_4) tetrahedra, pure aluminate)</td>
<td>3.23, 3.35</td>
</tr>
<tr>
<td>680-400</td>
<td>Asymmetric stretching (Al-O-Al, Al(_{13})O(_4) octahedra, pure aluminate)</td>
<td>3.23, 3.35</td>
</tr>
</tbody>
</table>

Figure 3.7  Shift of IR bands for faujasite zeolite with Al content in zeolite framework; O, faujasite; Δ, SiO\(_2\) gel; □, Na-X (zeolite); ■, precursor for Na-X [3.39].
Figure 3.8  The effect of network modifier addition on the silicate structure; empty circle represents oxygen; filled circle represents silicon [3.19].

Figure 3.9  (A) Plot of tetrahedra SiO (asymmetric) stretching vibration vs mole% of Na$_2$O. (B) Plot of terminol SiO stretching vibration vs mole% of Na$_2$O. (C) Plot of SiOSi (symmetric) stretching vibration vs mole% of Na$_2$O. (D) Plot of bending vibrations vs mole% of Na$_2$O [3.41].
Apart from Al-substitution, inclusion of cations from Group I & II (s-block, commonly Na, K, Ca and Mg) and/or some metals from the p and d-blocks such as Fe, or more commonly known as ‘network modifiers’, in a silicate structure can also significantly affect the intramolecular bond strengths. Addition of these cations effectively increases the concentration of the NBO’s (−SiO−), which will have to be charge-balanced with the network modifiers as demonstrated in Figure 3.8. As reasoned by Hanna et al. [3.25, 3.26] and indirectly proven by Ferraro and Manghnani [3.41], the interaction between the network modifiers and the NBO’s would have rendered the intramolecular bonding between SiO4 tetrahedral units ‘more ionic’ in nature. Hence, a smaller vibrational force constant should be observed, which has been confirmed by a long list of investigators at normal pressure [3.24-32, 3.42, 3.43] as well as at high pressures [3.41] using various different network modifiers including Li, Na, K, Rb, Cs, Ca, Mg, Fe, Pb, Zn and Sn. Consequently, the frequency of the Si-O-Si asymmetric stretching vibration band should decrease with increasing network modifier content as shown in Figure 3.9, which is equivalent to increasing the degree of silicate network depolymerisation as demonstrated in Figure 3.8.

It is noteworthy that although the effects of network modifier addition or aluminium (AlIV) network substitution on the IR band positions of silicates have been studied extensively, very little has been done to study the ‘combined’ effects of both network modifier (M) addition and aluminium substitution particularly when Al/M ≥ 1 (more specifically, Al/M <1), which is vital towards the total understanding of the overall geopolymerisation processes, as will be investigated and presented in detail in Chapter 9.

An infrared spectrum, apart from the spectral band positions, can also yield other important qualitative information of a molecule through examination of the spectral bandwidths. For example, a very broad bandwidth indicates that the material is highly amorphous and may also be highly heterogeneous [3.13]. As a material acquires increasing degree of structural order through e.g. crystallisation such as zeolite synthesis (i.e. from amorphous to crystalline state), which may not be detected by XRD, the broad band(s) indicative of an amorphous material would firstly become sharpened without apparent band shift [3.13, 3.18]. This is then followed by band splitting, and vice versa. A well-crystallised material, thus, is characterised with sharp and fine spectral bands. This, together with the information gathered from the band positioning and contour, has made infrared spectroscopy an extremely useful tool for the investigation of the short-range order within a mineral. Hence, IR is of paramount importance
when dealing with amorphous materials (such as geopolymers) when XRD technique becomes unsatisfactory [3.18]. This aspect will be elaborated throughout the thesis in the later chapters.

As summarised by V. C. Farmer [3.13], infrared spectroscopy is extremely useful in mineral analysis by:

","1 Identification of minerals of different (but constant) chemical composition.
2 Minerals of constant composition but with different crystal structures, e.g. SiO$_2$ as quartz, cristobalite or tridymite, can be recognised.
3 The technique can allow distinction between minerals that exhibit a range of composition within a group.
4 The technique can be used to distinguish between minerals that vary in both structural modification and chemical composition.

Hence, infrared spectroscopy has been chosen to characterise the nature of the chemical bonds within the raw materials used in this thesis albeit extreme care is required for the assignment of individual spectral bands [3.13, 3.18].

In this thesis, Fourier-transform infrared (FTIR) spectra of pulverised samples were acquired using a Bio-Rad FTS 165 FTIR spectrometer in absorbance mode within the frequency range of 4000-400 cm$^{-1}$. As recommended by numerous investigators [3.11-13, 3.18], KBr was used as the infrared transparent matrix to suspend the samples of interest within the designated frequency range. Pellets of samples (~0.5 mg sample with 250 mg KBr) were prepared using the normal procedure, dried in an oven at 60°C overnight, or at higher temperatures where necessary, and pressed again before spectra were taken, as recommended by Farmer [3.13]. A separate experiment had proven that this procedure was effective in removing physically adsorbed moisture from the samples, which could lower the infrared transmission and interfere with the sensitivity of the analysis. No band shift had been observed due to this procedure at a temperature lower than 250°C. All spectra were obtained with a sensitivity of 8 cm$^{-1}$ and 64 scans per spectrum taken.
Figure 3.10 The FTIR spectra of the Gladstone fly ash (Gdf), the HR1-grade kaolinite (Kao), the high-purity albite (Alb), the basalt (Bas) and the siltstone (Silt).

Figure 3.10 shows the raw materials used for the synthesis of the geopolymer and the related products. As can be seen, only the HR1-kaolinite and the albite were well crystallised and homogeneous with narrow spectral bands and easily distinguishable spectral contours (band positions, intensities and shapes). Although the XRD analysis had shown that both the basalt and the siltstone should comprise of well-crystallised components, the high heterogeneity of these materials had rendered the FTIR spectra poorly resolved. The Gladstone fly ash, as expected, was characterised by a set of very broad spectral bands due to its high amorphous content(s) consistent with the XRD analysis.

The spectral bands of the Gladstone fly ash, the HR1-kaolinite and the albite can be assigned by referring to numerous previous investigations as presented in Table 3.3. The effects of the various activating solutions, with and without soluble silicates, on the nature of the chemical bonds of the various solid raw materials will be briefly discussed later in the chapter, and will be discussed extensively in the remainder of the thesis.
Table 3.3 Characteristic IR vibrational bands of the solid raw materials

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Assignment</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>3699, 3653, 3622 (s)</td>
<td>Kao, stretching vibration (−OH)</td>
<td>3.44</td>
</tr>
<tr>
<td>3600-2200 (s)</td>
<td>Gdf, stretching vibration (−OH, HOH)</td>
<td>3.31, 3.45</td>
</tr>
<tr>
<td>1700-1600</td>
<td>Bending vibration (HOH, molecular water)</td>
<td>3.31, 3.45</td>
</tr>
<tr>
<td>1570-1410</td>
<td>Stretching vibration (O=C=O)</td>
<td>3.46</td>
</tr>
<tr>
<td>1165 (sh), 1138 (sh),</td>
<td>Gdf, asymmetric stretching (Si−O−Si) and Al−O−Si</td>
<td>3.18, 3.47</td>
</tr>
<tr>
<td>1080 (sh), 1077-1074 (s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1162 (sh), 1142 (sh),</td>
<td>Alb, asymmetric stretching (Si−O−Si) and Al−O−Si</td>
<td>3.49, 3.50</td>
</tr>
<tr>
<td>1102 (sh), 1058 (sh),</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1018 (sh), 997 (s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1104(s), 1033 (s), 1010 (s)</td>
<td>Kao, Si−O in-plane vibration</td>
<td>3.44</td>
</tr>
<tr>
<td>915 (s)</td>
<td>Kao, OH bending (Al−OH)</td>
<td>3.44</td>
</tr>
<tr>
<td>882 (sh)</td>
<td>Gdf, Si-O stretching, OH bending (Si−OH)</td>
<td>3.31</td>
</tr>
<tr>
<td>795 (m), 727 (sh), 620 (sh, b), 561 (s)</td>
<td>Gdf, symmetric stretching (Si−O−Si and Al−O−Si)</td>
<td>3.13, 3.18, 3.23, 3.48</td>
</tr>
<tr>
<td>781(sh), 762 (m), 744 (sh), 732 (sh)</td>
<td>Albite, symmetric stretching (Si−O−Si and Al−O−Si)</td>
<td>3.49, 3.50</td>
</tr>
<tr>
<td>698 (m)</td>
<td>Kao, bending (Al−O−Si)</td>
<td>3.44</td>
</tr>
<tr>
<td>650 (s), 611 (sh), 591 (m)</td>
<td>Albite, bending (O-Si(Al)-O)</td>
<td>3.49, 3.50</td>
</tr>
<tr>
<td>539 (sh)</td>
<td>Kao, bending (Al−O−Si)</td>
<td>3.44</td>
</tr>
<tr>
<td>531 (m), 464 (m), 425 (m)</td>
<td>Alb, bending (Si−O−Si and O−Si−O)</td>
<td>3.49, 3.50</td>
</tr>
<tr>
<td>470-466 (s)</td>
<td>Gdf, bending (Si−O−Si and O−Si−O)</td>
<td>3.13, 3.18, 3.23, 3.48</td>
</tr>
<tr>
<td>435 (s)</td>
<td>Kao, bending (Si−O−Si and O−Si−O)</td>
<td>3.44</td>
</tr>
</tbody>
</table>

The abbreviations in parentheses are as follows: s = strong, w = weak, m = medium, sh = shoulder, b = broad, Gdf = Gladstone fly ash, Kao = kaolinite and Alb = albite.
3.1.2.5 Solid topography and surface composition from scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS)

Microscopic imaging has in recent years been recognised as one of the most important analytical techniques ever invented. Several Nobel prizes have been awarded to the inventors of a number of such methods. Scanning electron microscopy (SEM) is certainly one of the greatest inventions of the 20th century. It allows visual examination on a material from millimetres to sub-micron meters to yield definitive topographical information as well as good physical and mechanical descriptions of the microstructures of crystalline as well as amorphous materials, which could not be described successfully by many other techniques. The very short data acquisition time and the very simple sample preparation, which can take the form of powders, blocks or thin sections, are also the most attractive attributes of the SEM imaging [3.51, 3.52].

The basic principle behind scanning electron microscopy is that when a high-energy electron beam is bombarded against a solid sample and penetrates into the material, the electrons can be scattered around the point of incidence to form secondary electrons (SE) [3.51, 3.52]. A small fraction of these scattered electrons may be directed back towards the direction of the electron source, and as such, are termed the backscattered electrons (BSE), which are more energetic than SE’s. These secondary electrons or backscattered electrons can then be picked up by detectors in the arrangements as shown in Figure 3.11 to form the respective images. In general, both the SE and BSE imaging techniques can provide vital images regarding the surface topography of a sample. In SE detection, however, the image is dominated by topographic contrast while in BSE detection, the image is more sensitive to the atomic density, which is a function of the atomic number, and the density of the grains forming the object [3.51-53].

Apart from the electron scattering, the penetrated electrons may also interact with the incident atom of a material to excite an electron from the inner electronic shell of the atom to a higher energy orbital or to eject an electron (ionisation) from the inner electronic shell of the atom if the energy given to the electron is greater than the binding energy of the electron in the atom [3.51, 3.52]. Following the initial electronic excitation, or ionisation, the inner electronic shell will be filled again by the electron falling from the outer shell, or electronic relaxation, which releases energy in a discrete photon equalling the energy difference between the inner and the
outer electronic orbitals similar to that of Figure 3.5. By determining the energy of the photon(s) released, which is in the range of x-ray radiation, the type of the atom may be identified. This forms the basic principle behind the energy dispersive spectroscopy (EDS), or informally known as surface microanalysis [3.51, 3.52]. Combining with SEM imaging, the SEM-EDS analysis is invaluable in phase identification for surface precipitates as a result of chemical interaction between a solid and a solute, as will be exemplified below.

In this thesis, A Philips XL30 SEM coupled with an Oxford Instruments energy dispersive x-ray spectrometer was used for all electron microscopy and chemical microanalysis. As the solid raw materials and the geopolymers and the related products are all poor electrical conductors, these samples had to be gold or carbon coated before analyses were made to yield high quality images as recommended by Sas et al. [3.54].

Figure 3.12 shows the SEM image of the gold-coated unreacted Gladstone fly ash using secondary electron detection. The Gladstone fly ash thus is a mixture of spherical beads, which according to EDS are aluminosilicates with an averaged surface composition (average of 15 analyses from 15 different beads) of 55.1 wt% SiO$_2$, 29.8 wt% Al$_2$O$_3$, 8.2 wt% Fe$_2$O$_3$,
3.5 wt% CaO and other minor oxides, and irregular-shaped quartz with an averaged composition of 99.5 wt% SiO₂ and ~0.5% Al₂O₃. The HR1-grade kaolinite, on the other hand, contains hexagonal platelets of kaolinite of ~0.2 μm thick and varied from ~0.5 to ~2 μm in diameter. As can be seen from Figure 3.13, some of these kaolinite platelets are present as vermiciform aggregates 5 to 10 μm long and ~5 μm in diameter. Finally, the albite obtained from Minerals Corporation Limited, Broken Hill, Australia contains many micron to sub-micron particles adhering to the surface of the larger albite crystals as shown in Figure 3.14. The SEM images of the basalt and the siltstone will be presented in Section 3.2.3.
3.1.2.6 Solution composition from inductively coupled plasma optical emission spectroscopy (ICP-OES)

As presented in Table 2.5, the critical solution process parameters for geopolymerisation may include: (1) solution alkalinity (M₂O/H₂O); (2) soluble silicate/alkali cation ratio (SiO₂/M₂O); and (3) ionic species/electrolytes. Although many analytical techniques can be applied to yield such information, inductively coupled plasma optical emission spectroscopy (ICP-OES) remains one of the most powerful as well as one of the most simplistic methods available due to its capability to analyse over 70 elements with good precision and detection limits (from ppb (ng/mL) to ppm (mg/L)) as well as its simultaneous multi-element detection [3.55-57]. Unfortunately, ICP-OES cannot detect elements such as N, F, Cl, Br and I, which are common solution electrolytes [3.55].

The basic principle of ICP-OES is similar to other spectroscopic techniques such as IR. The atom(s) of the analyte is firstly excited to an ionic excitation state $E_2$ by an energy source, in this case, the inductively coupled plasma of ionised argon gas at a temperature between 8000 to 10,000 K. When the excited atom is returned to the ground state $E_1$, a discrete photon at a ultraviolet (UV) wavelength region carrying the energy equal to $E_1 - E_2$, is emitted. This, photon attributable to ionic emission, is specific to individual atoms and is subsequently
picked up by a high-resolution optical spectrometer capable of distinguishing wavelengths for each element, which forms the basis for the elemental identification as well as quantification of ICP-OES [3.55].

Figure 3.15 shows the basic arrangement of an ICP-OES instrument. The sample, most commonly in the form of an aqueous solution, has to be carried into the plasma by the argon injector gas, which is partly converted into droplets by the helium nebuliser gas. Upon heating at +8000 K, the droplets are nearly completely atomised and result in the formation of aerosols. In practice, any particulate suspension carrying particles of less than 10 μm can be transported by the nebuliser gas without much deposition on the tubings etc. [3.55]. This point will be greatly exploited below as well as in Section 3.3.3.2 of this chapter.
In this thesis, a Perkin-Elmer 3000 machine was used to determine the elemental compositions of Si, Al, Ca, Mg, Fe, Na and K in the various aqueous alkaline (silicate) solutions through the use of ICP-OES. Argon was used as the plasma gas and helium was used as the nebuliser gas. Although three spectral lines were employed to determine the elemental composition of each element (with the exception of Fe, Na and K), only the reading associated with the lowest root mean square standard deviation (RSD) was reported. The spectral lines used were: Si – 212.41 nm, 251.61 nm and 288.16 nm; Al – 237.31 nm, 308.22 nm and 396.15 nm; Ca – 315.89 nm, 393.37 nm and 396.85 nm; Mg – 279.08 nm, 279.55 nm and 280.27 nm; Fe – 238.30 nm and 259.44 nm; Na – 589.00 nm and 589.59 nm; K – 766.49 nm. These spectral lines were chosen by previous experimental experience as well as the recommendation from Thompson and Walsh [3.55].

Before ICP analysis, the Vitrosol N(N40) sodium silicate solution and the KASIL® 2236(K32) potassium silicate solution were diluted to ~400 ppm Si and equilibrated for 2 days due to the reasons presented in Section 3.3.3.1 of this chapter. The Vitrosol N(N40) sodium silicate solution was found to exhibit a molar ratio SiO$_2$/Na$_2$O = $R_m$ = 3.323 and [SiO$_2$]$_{tot}$ = 6.63 M with ~1.2 % Al contamination, in good agreement with the supplier. The KASIL® 2236(K32) potassium silicate solution was characterised by SiO$_2$/K$_2$O = $R_m$ = 3.496 and [SiO$_2$]$_{tot}$ = 5.30 M with ~0.6 % Al contamination, also with good agreement with the supplier.

3.2 GEOPOLYMERIC BINDERS AND RELATED PRODUCTS

3.2.1 Synthesis and Basic Characteristics of Geopolymeric Binders

The synthesis method of geopolymeric binder is similar to that of the OPC binder once the activating solution has been prepared. Extreme care, however, is a necessary requirement in geopolymer synthesis as the activating solution is highly alkaline and corrosive. Even a small drop of the solution would cause serious dehydration of the skin. If such event occurs, immediate washing with excessive amount of water is vital for preventing further injuries. Needless to say, preventive measures such as gloves and safety glasses will have to be worn
Figure 3.16  The carbon-coated BSE-SEM image of a typical Gladstone fly ash/HR1-kaolinite geopolymeric binder activated at [MOH] = 6.85 M (Na/K = 0.2) and soluble silicate dosage of [SiO$_2$] = 3.26 M after 28 days of curing at 20°C.

at all times when handling the activating solution as well as the fresh geopolymeric paste. The geopolymeric products are safe to handle with bare hands after curing overnight.

This section is only concerned with the basic synthesis method of geopolymeric binder. More specific requirements will be presented in the following chapters. Briefly, an activating solution was prepared by firstly preparing the bulk alkaline solution (without soluble silicates) by dissolving the designated amounts of alkali metal hydroxides (NaOH and/or KOH) in distilled/deionised water. Soluble silicates at the designated amounts were then added to the bulk alkaline solution to make up the activating solution, which was then left to equilibrate to room temperature with constant stirring before use. If more than one aluminosilicate powder was used, the solids were mixed at the right proportion in a rotary mixer overnight to ensure solid homogeneity.

Once the activating solution and the solid(s) were prepared separately, the geopolymeric binder was synthesised as follows: After placing the solid(s) at the designated amount in a mixing bowl, the activating solution prepared overnight was then added. The contents of the mixing bowl were mixed in a mechanical mixer for 5 minutes to produce homogeneous paste. This geopolymeric paste was then transferred to a plastic or polystyrene container, which was
Figure 3.17  The XRD diffractograms of the unreacted Gladstone fly ash/HR1-kaolinite mixture (fly ash/kaolinite = 9) and the as-synthesised geopolymeric binder activated at [MOH] = 6.85 M (Na/K = 0.2) and a soluble silicate dosage of [SiO$_2$] = 3.26 M after 28 days of curing at 20°C. K = kaolinite. M = mullite. Q = quartz.

alkali resistant, and cured under atmospheric pressure at the designated temperature and humidity until testing. The geopolymeric paste was demoulded 24 hours after the mixing.

Figure 3.16 shows a typical geopolymeric binder synthesised by activating a Gladstone fly ash/HR1-kaolinite mixture (fly ash/kaolinite = 9) with an activating solution at a solution alkalinity of [MOH] = 6.85 M (Na/K = 0.2) and soluble silicate dosage of [SiO$_2$] = 3.26 M. By comparing to the solid raw materials, see Figures 3.12 and 3.13, the kaolinite particles in the geopolymeric binder have become indistinguishable in the newly formed aluminosilicate gel matrix. However, some small fly ash beads still exist, which may also be attributed to the remain of the reacted larger fly ash beads which shrink due to solid dissolution (or alkali-activation). The very large fly ash beads (≥ ~20 μm) still exist although it seems that the contents originally inside the fly ash sphere have already been leached out, which may be the reason for the formation of the pores specially the larger ones as shown at the lower right corner of Figure 3.16.
Figure 3.18  The FTIR spectra of the unreacted Gladstone fly ash/HR1-kaolinite mixture (fly ash/kaolinite = 9) and the as-synthesised geopolymeric binder activated at [MOH] = 6.85 M (Na/K = 0.2) and a soluble silicate dosage of [SiO$_2$] = 3.26 M after 28 days of curing at 20°C. The numbers shown in the figure are the kaolinite characteristic vibrational bands.

Figures 3.17 and 3.18 include the results obtained from the XRD and the FTIR analyses on the unreacted solid raw materials (Gladstone fly ash/HR1-kaolinite = 9) and the as-synthesised geopolymeric binder, which was activated by a solution of [MOH] = 6.85 M (Na/K = 0.2) and a soluble silicate dosage of [SiO$_2$] = 3.26 M. According to the XRD analysis (Figure 3.17), the kaolinite crystalline phase was completely reacted due to geopolymerisation. Mullite and quartz, on the other hand, had remained largely alkali-resistant as their characteristic XRD peaks were unaffected by geopolymerisation. Furthermore, the aluminosilicate gel formed was x-ray amorphous as no new crystalline peaks could be identified, which was associated with an increase in the background hump at ~30 °C inherent of extensive geopolymerisation [3.58].

The FTIR analysis (Figure 3.18), however, indicates that some kaolinite (whose characteristic vibrational bands are indicated as numbers in Figure 3.18, see also Table 3.3 for their assignments) may still be present in the geopolymeric binder. At this stage, it is not known
what causes the band broadening at the 1200-850 cm\(^{-1}\) region as it can be attributed to a number of different reasons: (1) loss of crystallinity of kaolinite as indicated by the XRD analysis in Figure 3.17; (2) the reacted Gladstone fly ash; (3) the gel formed by the added soluble silicates; (4) the newly formed aluminosilicate gel through geopolymerisation; or (5) a combination of the above. Does the reacted kaolinite participate in geopolymerisation? Is there a phase separation in the geopolymer? To answer these questions, it is necessary to investigate and understand the chemical interactions between the individual minerals (Gladstone fly ash and kaolinite) and the activating solution. It is also required to examine the gel formed from pure soluble silicates without the reaction with aluminosilicate solids etc. Understanding the FTIR spectra collected is of paramount importance in geopolymer optimisation as it is a direct measure of the degree of polymerisation of the aluminosilicate gel formed (see Section 3.1.2.4). This may have a direct relationship with the macroscopic physical strength of the geopolymeric binder formed, which has not been previously examined, as will be presented in Chapters 7, 8 and 9.

### 3.2.2 Synthesis of Geopolymeric Mortars

Geopolymeric mortar synthesis was conducted by firstly preparing a geopolymeric binder as described in Section 3.2.1. Subsequently, a designated amount of siliceous sand (fineness modulus = 2.77) was added to the freshly prepared geopolymeric binder and mixed by a mechanical mixer for a further 5 minutes. The geopolymeric mortar was then transferred to a plastic or polystyrene container, which was alkali resistant, and cured under atmospheric pressure at the designated temperature and humidity until testing. The geopolymeric mortar was demoulded 24 hours after the mixing.

### 3.2.3 Synthesis and Basic Characteristics of Geopolymeric Concretes

A geopolymeric concrete was synthesised by firstly preparing a geopolymeric mortar as described in Section 3.2.2. Subsequently, a designated amount of crushed basalt (or siltstone) was added to the freshly prepared geopolymeric mortar and mixed by a mechanical mixer for a further 5 minutes. The geopolymeric concrete was then transferred to a steel mould and cured under atmospheric pressure at the designated temperature and humidity until testing. The geopolymeric concrete was demoulded 24 hours after the mixing.
Figure 3.19 The carbon-coated BSE-SEM image of a typical Gladstone fly ash/HR1-kaolinite geopolymeric concrete. The geopolymeric binder was activated at \([\text{MOH}] = 6.85 \, \text{M} \) (Na/K = 0.2) and soluble silicate dosage of \([\text{SiO}_2] = 3.26 \, \text{M}\) after 28 days of curing at 20°C.

Figure 3.19 shows a typical image of a geopolymeric concrete synthesised by mixing 1 part of the crushed basalt with 1 part of a geopolymeric mortar, which was prepared by mixing 2 parts of sand with 1 part of a geopolymeric binder synthesised by alkali-activating the Gladstone fly ash/HR1-kaolinite mixture (fly ash/kaolinite = 9) with an activating solution ((MOH] = 6.85 M (Na/K = 0.2) and a soluble silicate dosage of [SiO₂] = 3.26 M). It can be seen that both the coarse and the fine aggregates are evenly distributed within the geopolymer matrix and good cohesion seems to exist between each individual phase.

3.2.4 Physical/Mechanical Characterisation of Geopolymeric Products

As described in Section 2.2.4, a geopolymerisation process can be crudely categorised into five inter-related and inter-overlapped reaction stages as shown in Figure 3.20, which is drawn by considering the experimental results from Chapters 4, 5 and 9. Physically, the initial geopolymeric binder is a mouldable, fluid-like paste, which over time, solidifies/sets and hardens into a hard and rock-like mass highly resistant to external forces. Thus, the physical state of the geopolymeric product is a critical factor for sampling selection, which utterly determines the characterisation techniques capable of being employed. As the initial stages of geopolymerisation can proceed at a very fast rate (setting can be achieved within minutes to
Figure 3.20 The physical characteristics of a geopolymeric product and the 5 stages of geopolymerisation. I = aluminosilicate solid dissolution (alkali-activation). II = polymerisation of the dissolved species including the added soluble silicates. III = gellation of the polymerised aluminosilicates. IV = setting (a) and hardening (b). V = solid-state transformation.

~2 hours), real-time characterisation techniques, or techniques that require very short processing time for information generation, are preferred especially at the very early stages of geopolymerisation (< 3 days). An effective and workable experimental characterisation programme, therefore, demands careful consideration of the physical states of the analyte (geopolymeric products).

In this thesis, the physical characteristics of the various geopolymeric binders before setting were characterised by employing a vane rheometer to measure the yield stress of the mouldable geopolymeric pastes. A Vicat needle was then used to determine the final setting time of the geopolymeric binders. Subsequently, conventional compressive strength testing
Figure 3.21 The yield stress of a geopolymeric binder synthesised by alkali-activating a Gladstone fly ash/HR1-kaolinite mixture (fly ash/kaolinite = 9) with an activating solution ([MOH] = 6.85 M (Na/K = 0.2) and soluble silicate dosage of [SiO$_2$] = 3.26 M contaminated with 2% CaCl$_2$) at 20°C.

was conducted on the hardened products. As the vane rheometer and the Vicat needle cannot accurately measure the yield stress and the setting time of the geopolymeric mortars or concretes, only compressive strength testing was applied to these geopolymeric products, which is sufficient for the purpose of the present investigation. It is important to bear in mind that although mechanical testings are not direct measurements of the chemical processes that are taking place inside a geopolymeric system, they are still important and very powerful tools to back up and reconfirm the results obtained from the chemical measurements. The details of the mechanical characterisation techniques are as the following.

3.2.4.1 Yield stress measurement by vane rheometer

Liddell and Boger [3.59] have stated that the yielding process when rotating a vane inside a paste or a solid suspension involves stretching and breaking of bonds within a network. A yield stress thus provides information on how much force that is required to induce flow by breaking all the bonds within the paste in the vicinity of the surface of the vane. In other
words, the yield stress measurement can be regarded as a measure of how much strength a paste may possess at a given time. When yield stress was plotted against time, strength development of a paste could be determined as shown in Figure 3.21.

The yield stress of early geopolymeric pastes before setting was determined on a Haake vane rheometer using vane C. It was found that fast and thorough mixing of the raw materials and well-controlled curing conditions were essential for good reproducibility. The highest yield stress that could be recorded using a Haake vane rheometer was about 5 kPa. If the yield stress was higher than this value, the sample would have started to move along with the rotating vane. As an experimental observation, when a geopolymeric binder had reached the detection limit of the vane rheometer (5 kPa), the paste would be equivalent to the initial setting time as determined using a modified Vicat needle as below.

3.2.4.2 Setting time determination by Vicat needle penetration

A Vicat needle similar to Figure 3.22 was modified and constructed in this thesis to measure the setting time of geopolymeric binders. The modified Vicat needle essentially consisted of a needle of 1 mm diameter cross-section and 100 g, conforming to ASTM C191&192. A plastic
Figure 3.23 The penetration of a geopolymeric binder synthesised by alkali-activating a Port Augusta fly ash/HR1-kaolinite mixture (fly ash/kaolinite = 2) with an activating solution of [MOH] = 6.85 M (Na/K = 0.01) and soluble silicate dosage of [SiO$_2$] = 0.5 M.

cylindrical container of 75 mm diameter was filled with 50 mm of the freshly prepared geopolymeric pastes. Values of penetration distances were obtained every five to ten minutes as shown in Figure 3.23. The initial setting time was obtained by interpolating the penetration curve at the penetration distance of 25 mm. On the other hand, the final setting time was the time required to reach a penetration distance of 0 mm. At the final setting, geopolymeric binders were in the solid state. Moulding without causing material damage was not possible thereafter. Fast and thorough mixing of the raw materials and well-controlled curing conditions were vital for good reproducibility and accuracy.

3.2.4.3 Compressive strength determination by uniaxial compression

The uniaxial compressive strength results were obtained conforming to ASTM C39 on an ELE compression machine using a loading rate of 1 kN/s. The cylindrical sample dimension was 50 × 100 mm for geopolymeric binders and mortars. Larger samples (100 × 200 mm) were prepared for geopolymeric concretes. All the values presented in this thesis were the averages of three separate tests, with a standard deviation of less than 5%. The top and bottom
sample surfaces were smoothened and made parallel by capping with dental plaster (hydrated gypsum) to increase the accuracy and the precision of the technique.

3.2.5 Microstructural Characterisation of Geopolymeric Products

The microstructural characterisation techniques employed in this thesis for describing the various geopolymeric binders and the related products include (1) XRD analysis to yield the crystal phases present and the inherent microstructure; (2) FTIR characterisation to provide information such as the nature of the chemical bonds as well as the extent of aluminosilicate gel polymerisation; and (3) SEM-EDS to topographically describe the geopolymeric systems as well as to provide the surface compositions of the phases of interest. Among these techniques, only SEM-EDS was applied to study the microstructures of the geopolymeric mortars and concretes. The presence of both the coarse and the fine aggregates was found to prevent confident phase identification by XRD and FTIR analyses. The details of these techniques have been described in Section 3.1 and have been illustrated in Sections 3.2.1 and 3.2.3.

3.3 SOLID-GEL INTERACTIONS IN GEOPOLYMERS

3.3.1 Introduction

As raised in Section 2.3, the principal objective of this thesis is to identify and understand the physical as well as the chemical interactions between (alumino)silicate minerals and aluminosilicate gels. To study the physical interactions, physical/mechanical methods such as interfacial three-point bending can be employed. On the other hand, extensive chemical characterisation is required to follow the chemical processes within the geopolymeric systems. While the acquisitions of the physical characteristics are straightforward, meaningful chemical knowledge is hard to come by because of the very limited analytical methods available to date, which can be largely attributed to the physical constraints inherent to the hardened geopolymeric (aluminosilicate) gel. See Section 3.2.4. The following is a discussion
of the experimental programme designed for the first time to overcome the shortcomings of the current analytical techniques especially on the study of the chemical interactions between (alumino)silicate solids and aluminosilicate gels. As will be demonstrated throughout the thesis, this newly designed experimental programme is not limited to the materials used in this thesis. Other applications may be found in other geopolymeric systems, as well as in Portland cement systems.

Before progressing any further, it has to be noted that there are two types of interfaces existing in a geopolymeric system. The ‘microscopic’ interface is used to describe the interface between an aluminosilicate powder, with a particle size smaller than 150 μm (arbitrarily chosen), and an aluminosilicate gel, or an activating solution. On the other hand, the ‘macroscopic’ interface concerns the interface between larger mineral particles (> 150 μm) and a geopolymeric binder. These definitions will be very useful in the following discussions.

3.3.2 Physical Interactions Between Aluminosilicate Solids and Gels

The term ‘physical interaction between solids and gels’ has been interpreted in this thesis as the ‘interfacial bonding’ that holds the two different phases together. With this definition, the degree of difficulty in selecting an appropriate set of characterisation techniques can be greatly reduced: Information such as interfacial bonding strength as well as the nature and the amount (thickness) of the interfacial product(s) should be sufficient to adequately describe the physical interactions between the two phases. Thus, the characterisation processes adopted in this thesis invariably involve (1) topographical/microstructural examinations; (2) surface compositional analyses; and (3) mechanical interfacial bonding tests.

In this thesis, SEM and EDS techniques were combined to yield valuable topographical as well as surface compositional information on both the microscopic as well as the macroscopic interfaces. See Section 3.3.1 for the respective definitions. See also Section 3.1.2.5 for the detailed discussion on SEM and EDS techniques. In addition, EDS line analysis, which is conceptually the same as EDS dot analyses taken at small and regular intervals along a straight line, was also used to measure the thickness of the macroscopic interface, as opposed to the previous EDS dot measurements on the Portland cement ITZ by Barnes et al. [3.60].
The thickness of the interface can be measured using EDS due to its inherent concentration gradient extending from the solid surface to the bulk gel, as will be discussed in Chapter 10.

In ideal situations, an x-ray diffraction microanalysis (micro-XRD), which involves bombarding a solid surface with a beam of x-rays similar in concept to the conventional XRD analysis but with a much smaller x-ray spot size, should be applied to phase-identify the interfaces between the solids and the gels. This had been practised on the Portland cement systems previously [3.61, 3.62]. Unfortunately, the smallest spot size for micro-XRD analysis (~50 μm [3.63]) is still too large for characterising the interfaces within geopolymeric systems (the interfacial layers between siliceous rocks and geopolymeric binders are thinner than ~5 μm, see Chapter 10). Hence, after a few failed attempts, micro-XRD analysis was excluded in this thesis partly due to obvious economic reasons (the cost of micro-XRD analysis is ~A$250.00 per sample). Similarly, FTIR microspectroscopy with the spot size of 2-0.5 mm [3.12] was also unsatisfactory for such an interfacial analysis. This shortcoming, however, can be partly solved as demonstrated in Chapter 10.

It has to be noted that mechanical testing on the microscopic interfacial bonding strength cannot be achieved because of the difficulty to separate individual powder particle (< 150 μm) and the associated gel for such a purpose. Furthermore, there are no techniques available to mechanically test such a small sample, not even a micro-indentation method [3.64, 3.65]. On the other hand, measurements on the macroscopic bonding strength between coarse aggregates and geopolymeric binders can be obtained by employing the techniques used in concrete fracture mechanics. This will be discussed in greater detail in the following section.

### 3.3.2.1 Macroscopic interfacial bonding strength from interfacial three-point bending

The study of macroscopic interfacial bonding strength in Portland cement technology can be categorised into six broad areas: (1) micro-indentation such as the Vickers technique [3.64, 3.65]; (2) direct tensile (or pull-out) test [3.66, 3.67]; (3) push-out test [3.68]; (4) axial compression [3.69]; (5) shear bond test [3.70]; and (6) three or four-point bending [3.71, 72]. Apart from micro-indentation and three/four-point bending, all the other testing methods require a strong matrix for their measurements. If the mineral binder/mortar is too weak, the
Figure 3.24  The experimental set-up (not to scale) of the interfacial three-point bending test on a rock aggregate-mortar sandwich specimen.

actual fracture may take place inside the binder/mortar matrix instead of breaking at the interface. This is a major drawback for studying an interface of an unknown system such as geopolymers. As discussed above, the macroscopic interface inside a good/strong geopolymeric concrete is about 5 μm thick (see Chapter 10). This further limits the use of the micro-indentation technique on geopolymeric systems (the width of a normal Portland cement ITZ is ~50 μm [3.62]). Consequently, it leaves three/four-point bending as the most suitable method for studying the macroscopic interfacial bonding strength in geopolymeric systems.
In this thesis, three-point bending was preferred because it produced only pure Mode I interfacial fracture in the $y$-direction (see Figure 3.24) without the sliding motion in the $x$-direction (Mode II) or tearing in the $z$-direction (Mode III) [3.73], provided the rock slice was not too thick. See Figure 3.24 for the experimental set-up of the ‘interfacial’ three-point bending adopted in this work. Note that the experimental set-up in Figure 3.24 ensures that the greatest external stress was located at the interface between the rock slice and the geopolymeric mortar. Experimental observations also showed that failures indeed occurred at the interface independent of the strength of the geopolymeric mortars used.

Samples for the macroscopic interfacial bonding strength determination between rock aggregates and geopolymeric mortars were prepared as follows:

A rock slice ($50 \times 25 \times 4.5$ mm) was cut and lightly polished at both sides to minimise variations in surface roughness between different rocks. Subsequently, a plastic strip ($25 \times 4.5$ mm) was glued to one side of the rock slice to introduce an artificial crack. Freshly prepared mortar layers (or sample mortars) of the same compositions (10 mm thick) were then “glued” to either side of the rock slice and cured at $40 \pm 3^\circ$C. The resultant sandwich samples were demoulded after 24 hours and then cured at $20 \pm 3^\circ$C and a relative humidity of $50 \pm 5\%$ under atmospheric pressure until testing. Two days before the interfacial bonding strength was tested, each side of the sandwich samples was glued to a precast mortar beam $II$-$10$-$2.5$ ($50 \times 25 \times 76.75$ mm) (see Chapter 6 for the mix composition) using epoxy resin so that a sandwiched beam of a total length of 178 mm could be tested using the three-point bending set-up as shown in Figure 3.24. Note that the precast mortar beam $II$-$10$-$2.5$ was used to allow weaker geopolymeric mortars being tested, which was inspired by Trende and Büyükoztürk [3.74].

The interfacial three-point bending test on the rock/mortar sandwich specimens was conducted on an Instron 1000 machine at a loading rate of 0.1 mm/min under close-loop control. Failure loads were recorded and then divided by the cross-sectional area of the specimens ($50 \times 25 = 1250$ mm$^2$) to obtain the interfacial bonding strength. All the values collected were the averages of three separate tests. As the sandwich samples were difficult to prepare, the standard deviations of the interfacial bonding strength were rather large between
8.3 to 18.6 %, with the largest being associated with the weakest sample geopolymeric mortar.

### 3.3.3 Chemical Interactions between Aluminosilicate Solids and Gels

In a conventional chemical system, the chemical interactions between two different phases can be described by following the progressive change of the chemical bonds and/or the rate and extent of mass transfer of the reactants and/or the reaction products, which results in the formation of concentration gradients in the bulk phases, or across the interface. Consequently, the study of heterogeneous reactions inevitably entails the identification and the quantification of the chemical changes within the two bulk phases (and the interface if measurable) over a period of time. The measurable chemical changes may be in the form of chemical compositions and/or chemical bonds. Depending on the nature of the reacting systems, different analytical techniques can then be selected, which should consider the nature of the reaction(s) and the analyte(s), the machine capabilities/restraint(s) and the sampling methods available, which normally involves separation of individual phases for separate analyses.

From Section 2.2, it is clear that geopolymerisation is also a heterogeneous reaction process. It involves surface dissolution/precipitation, i.e. mass transfer across the solid/solution interface, and, hypothetically, nucleation and growth of colloidal particles in a solution, which then leads to the formation of aluminosilicate gels as the principal binding phase of geopolymers. Examination on the chemical interactions within a geopolymeric system, therefore, seems easy enough and straightforward. However, as observed by many investigators [3.21, 3.46, 3.58, 3.75, 3.76], conventional analytical procedures for the study of mass transfer across an interface are not applicable to ‘actual’ geopolymeric reacting system. This is because of the extremely high solid/solution ratio inherent to a geopolymeric system and the difficulty to separate the solid, the solution and the interface for separate analyses. As a result, nearly all studies conducted on the subject of chemical interactions between aluminosilicate solids and activating solutions, or aluminosilicate gels, concern only characterisation of the chemical bonds, before and after the geopolymerisation, without attempting to separate the different phases [3.21, 3.46, 3.75].
The difficulty of studying mass transfer processes in geopolymeric systems, however, could be reduced, theoretically, by building a reaction model, within which separation of the different phases would become possible, as was practised by Van Deventer and co-workers [3.58, 3.76, 3.77]. Obviously, the success of a reaction model would rely very heavily on its ‘closeness’ to reality. The results obtained as such can be seriously misleading if a wrong reaction model is applied to an actual reacting system. Unfortunately, the reaction models built so far in the geopolymer research community [3.58, 3.76, 3.77], despite providing excellent information towards the understanding and the quantification of the mass transfer processes between aluminosilicate solids and aqueous alkaline solutions, had all failed to incorporate the effects of soluble silicates in the activating solutions, which from Chapter 2, are vital towards the synthesis of mechanically strong and chemically stable geopolymeric binders and the related products.

In this thesis, a novel set of reaction models and an associated analytical procedure have been developed for the first time to incorporate the effects of soluble silicate addition in the various activating solutions. Both the identification and the quantification of mass transfer across the solid/solution interface, as well as the changes of chemical bonds within the dissolving solids, are within the capability of these reaction models, with the aid of the new analytical procedure. This reaction model has been shown to successfully describe a number of physical and chemical characteristics observed from the ‘real’ geopolymeric systems, which have been activated by solutions containing a wide range of alkali and/or soluble silicate concentrations, as well as those containing no soluble silicates at all. See Chapters 7 and 8 for the detailed accounts of the development and the applications of these reaction models. Furthermore, by adequately applying these reaction models, in situ study of geopolymerisation on real geopolymeric binders in real time is also possible, as will be presented in Chapter 9. The following is a detailed description of the new reaction models and the associated analytical procedure developed in this thesis.

3.3.3.1 The reaction models and the sampling technique

The reaction models developed in this thesis were inspired by the conventional leaching experiments from the minerals processing industry. In principle, solids in powder form were suspended in a well-mixed solution inside a batch reactor under carefully-monitored reaction conditions such as the type of the impeller used, the rotational speed of the impeller, the type
of the baffle installed inside the reactor, the solution temperature and the pressure inside the reactor. The novelty of these reaction models developed in this thesis lies mainly in the sampling technique and the analytical procedure especially for the systems containing high dosages of soluble silicates, which may precipitate out as gelatinous materials and prevent adequate solution analysis as noted by other investigators [3.78, 3.79].

In this thesis, all leaching experiments were conducted using the experimental set-up at 20 ± 0.5°C and atmospheric pressure. Before leaching had commenced, all solids were pre-dried at 105°C overnight to remove excessive adsorbed moistures. Polyethylene bottles and conical flasks were used for all solution preparations and leaching to avoid silicon contamination. Leaching solutions, or the activating solutions with or without soluble silicates, of the designated compositions were then prepared separately. See Chapters 7, 8, 9 and 10 for the individual requirements. According to Falcone [3.80], all the alkaline silicate solutions used throughout the entire leaching experiments of this thesis, with the designated soluble silicate concentrations (0 ≤ [SiO₂] ≤ 2.5 M), SiO₂/M₂O ratios (0 ≤ SiO₂/M₂O ≤ 1.0) and solution alkalinites (~0.6 ≤ [MOH] ≤ 10 M or pH ≥ 13.95), should contain predominantly monomeric silicates, and should attain equilibrium upon dilution quickly [3.81]. Hence, the leaching solution was sealed and stirred at ~90 rpm (revolutions per minute) and equilibrated to 20 ± 0.5°C for at least 2 hours prior to leaching. For each leaching experiment, 100 g of aluminosilicate solids were added to 1000 mL of the leaching solution. All leaching was run in parallel to minimise experimental errors for a specific investigation. During leaching, the reaction slurries were stirred at 20 ± 0.5°C with minimum agitation (150 rpm) to prevent sedimentation of the solids.

The sampling technique for separating the solids and the solutions from the reaction slurries is summarised in Figure 3.25. At the designated time intervals, 10 mL of the suspension was collected and centrifuged at low speed for 5 minutes to separate about 95% of the solids from the solution. These solids were then mixed with the solids obtained from the microfiltration step, and were subsequently washed with increments of 25 ml distilled/deionised water for a total of 10 times to remove the adsorbed alkalis. These ‘alkali-activated’ solids were retained for separate analysis.
According to Iler [3.82], Ray and Plaisted [3.83] and Otterstedt et al. [3.84], colloidal particles, which might have been formed in some of the supernatant solutions (activating solutions), should be less than 2 nm in diameter even in a highly concentrated solution of 5 M SiO$_2$ and SiO$_2$/M$_2$O > 2 at pH > 10. (The degree of soluble silicate polymerisation, or the size of the colloidal polysilicates, has been experimentally proven to increase with increasing SiO$_2$/M$_2$O ratio or decreasing solution alkalinity [3.81-84]) Hence a 0.2-µm Minisart$^\text{®}$ membrane filter from Sartorius AG Germany was suitable for removing the remainder of the undissolved aluminosilicate solids in the supernatant solutions and still allowing soluble silicates of monomeric, oligomeric and up to colloidal size polysilicates to pass through.

**Figure 3.25** The schematic drawing of the sampling procedure for separating the alkali-activated aluminosilicate solids from the activating solutions.
Because colloidal silicates in highly alkaline solutions are known to dissolve and reduce in size upon dilution [3.81], the filtrate was diluted to approximately 400 ppm Si (~14.2 mM), or to a pH of ~13.95, whichever had a smaller dilution factor. Hence, all the diluted solutions were expected to contain colloidal polysilicates of less than 2 nm in diameter, if present. The high solution alkalinity of the diluted filtrate (pH ≥ 13.95) should also be sufficient to ensure that the diluted solutions to be analysed ([SiO₂] = ~14.2 mM) are kept well below the instability region as presented in Figure 3.26. Consequently, no precipitation should be observed in these diluted solutions.

In this thesis, the diluted solution was allowed to equilibrate for 2 days in sealed polyethylene tubes before analysis. No precipitates or gelatinous materials were found in any of the diluted solutions even after two weeks, as expected. This means that all the elements leached from the aluminosilicate solids effectively remained in the solutions without precipitation before analysis. Note that the diluted solutions analysed in this thesis should include all soluble silicates of monomeric and oligomeric silicates and may also contain colloidal polysilicates. This thesis does not intend to differentiate the speciation of soluble silicates in the activating solutions.

![Figure 3.26](image)  
**Figure 3.26** Diagram showing pH and concentration of the various solutions studied in relationship to the instability region [3.85].
It is a well-known fact that pH determinations in highly alkaline solutions using glass electrodes may not always be accurate. The inaccuracy depends on the type of the electrode used as well as the alkali cations present in the solutions to be analysed. In this thesis, a glass electrode from Hanna Instruments Model HI 8424 was used. Corrections in pH measurements throughout the entire experiments were made by comparing the calculated pH of 0.6 M NaOH solution and 0.6 M KOH solution against the measured values from standard solutions made from analytical grade reagents (NaOH and KOH) and Milli-Q water (conductivity < 10^{-6} \text{ S cm}^{-1} \text{ at } 20^\circ\text{C}). The calculated pH of the 0.6 M NaOH (or KOH) solution is 13.78. The measured pH of the 0.6 M NaOH standard solution (without added soluble silicate) was 13.62, whereas it was 13.74 for the soluble silicate-free 0.6 M KOH standard solution. For each of the measurements obtained in this thesis, the corrected pH of the sodium solutions was obtained by adding 0.16 units to the measured values. Similarly, the corrected pH of the potassium solutions was obtained by adding 0.04 units to the measured values.

3.3.3.2 Solution analysis

As discussed above, the diluted activating solutions to be analysed should contain soluble silicates or colloidal polysilicates of less than 2 nm in diameter. From Section 3.1.2.6, any particulate suspensions carrying particles of less than 10 \mu m can be analysed using the technique of ICP-OES [3.55]. Therefore, ICP-OES, or other ICP-related spectroscopic techniques, is the ideal technique for the quantification of alkaline silicate solutions, as was also noticed by Hopp [3.56].

The accuracy of the solution elemental analysis described here relies not only on the ICP-OES itself but also on the preparation procedures of the solutions to be analysed, e.g. gradual dissolution of Al and Ca into the activating solutions as well as the subsequent solution dilutions. A pilot run was therefore designed to test whether the gradual dissolution of Al and Ca and sample dilution might affect the accuracy of the analysis. Also, for the sake of random testing, the final compositions of the standard solutions did not conform to any of the real systems applied in this thesis. The standard solutions were prepared as follows:

To make up the standard alkaline silicate solution, a calculated amount of the sodium silicate solution (Vitrol N(N40)) was dissolved in 800 mL of the 0.6 M NaOH stock solution in a 1 L
conical flask during vigorous agitation and then made up to 1000 mL. The pH was adjusted to 13.95 with vigorous stirring using the 15 M NaOH stock solution. The potassium silicate solution was prepared in the same way as the sodium silicate solution. A calculated amount of the potassium silicate solution (KASIL® 2236(K32)) was dissolved in 800 mL of the 0.6 M KOH stock solution and then made up to 1000 mL. Subsequently, the pH was adjusted to 13.95 using the 15 M KOH stock solution. The solutions were then stirred at ~90 rpm for 2 hours. The agitation was then changed to ~150 rpm, after which aluminium was added by increments of 110 μL from the 1 M AlCl₃·9H₂O stock solution and Ca was added by increments of 200 μL from the 4.5 M CaCl₂ stock solution every 15 minutes until the final concentrations of [Si] = 600 mM, [Al] = 3.52 mM and [Ca] = 6.30 mM were reached. As it was not certain whether the filtration process on the leached solutions might affect the overall accuracy of the analysis, the standard solutions were also filtered through a 0.2-μm Minisart® membrane filter (similar to the real runs) and then diluted (by calculation) to 15.0 mM Si, stirred overnight and left for 2 days before ICP-OES analysis. No precipitates were found before the analysis and the error was within 1% for each of the elements.

The ICP-OES, therefore, is a suitable and reliable technique for fast and highly accurate analysis on the alkaline silicate solutions.

3.3.3.3 Solid analysis

The analytical programme adopted for the characterisation of the reacted solids is similar to that of the solid raw materials in Section 3.1.2. Briefly, the changes of chemical bonds inside the solids through alkali-activation (or leaching with an activating solution), can be identified and cross-examined using XRD and FTIR analyses as demonstrated in Chapters 7 and 8. The results obtained can then be reconfirmed by surface topographical and compositional measurements on the reacted solids using SEM-EDS, as well as by the mass transfer measurement on the activating solution using ICP-OES as described in Section 3.3.3.2. An indirect quantification of the extent of chemical changes on the solids can also be provided utilising the infrared shift inherent to changes in the degree of polymerisation of the aluminosilicate solids such as Figures 3.7 and/or 3.9. See Chapter 9.


3.4 EXPERIMENTAL STRATEGIC PLAN

The central theme of this thesis – to examine the solid-gel interactions in geopolymers – has been split into two major areas in this chapter for the convenience of the experimental design. These include: (1) physical interaction, which describes the physical/mechanical bonding between solids and gels; and (2) chemical interaction, which involves mass transfer across the solid-gel interface and the associated chemical changes within the solid or the solution phases. Both the physical and the chemical interactions can then be further divided into ‘microscopic’ and ‘macroscopic’ interactions, which are distinguished by the particle sizes of the solids involved (Section 3.3.1).

The experimental programme for the examination of both the physical and the chemical interactions between aluminosilicate solids and gels, microscopically or macroscopically, can then be designed separately as shown in Section 3.3. With these analytical tools available, the next step is to decide ‘how much’ would have to be done to achieve meaningful and significant experimental results and conclusions, which should be relevant to all aspects of geopolymerisation. To achieve this, identification of the most critical experimental variables is vital for efficient experimental design.

At a designated reaction condition (i.e. temperature, pressure, humidity etc.), the possible experimental variables that can affect the three major phases of a geopolymeric binder, which include the aluminosilicate gel, the undissolved aluminosilicate solids and the ‘microscopic’ interface, are:

A. The aluminosilicate powder
   a. chemical composition
   b. crystallinity/mineralogy
   c. microstructure/porosity
   d. particle size

B. The activating solution
   e. solution alkalinity (M_2O/H_2O, or [MOH])
Similarly, the experimental variables that can affect the three major phases of a geopolymeric mortar or concrete, i.e. the geopolymeric binder, the aggregates and the ‘macroscopic’ interface, are:

A. The aggregate
   a. chemical composition
   b. mineralogy
   c. microstructure
   d. porosity/water absorption characteristics
   e. surface texture
   f. shape
   g. grading (particle size distribution)

   Aggregate reactivity

Physical interlocking with geopolymeric binder

B. The geopolymeric binder
   a. depends on the aluminosilicate powders and the activating solution used

Obviously, there are many variables affecting the geopolymeric systems especially when aggregates are included, apart from the possible inter-combinations of these variables. With consideration of the previous experimental findings described in Chapter 2, as well as the fact that the nature of microscopic, or macroscopic, chemical/physical interactions between solids and gels (or activating solutions) is a result of alkali-activation, the size of the experimental programme can be efficiently reduced by altering mainly the compositions of the activating solutions, i.e.:

   a. solution alkalinity (M₂O/H₂O, or [MOH]);
   b. SiO₂/M₂O ratio; and
   c. ionic species/electrolytes, through addition of common inorganic salts.

This thesis, therefore, aims to examine the interactions between aluminosilicate solids and gels by systematically changing the compositions of the activating solution while at the same time, limiting the number of solid raw materials to only Gladstone fly ash, Port Augusta fly
ash, HR1-grade kaolinite, albite, siliceous river sand, basalt and siltstone at 20 or 25°C (unless otherwise indicated) with a relative humidity of 50 ± 5 % under atmospheric pressure.

The effects associated with the compositional change of the activating solution will be examined by characterising the geopolymeric products produced, using the characterisation techniques described in Sections 3.2.4, 3.2.5 and 3.3.2. See Chapters 4, 5, and 6. This is then followed by building a ‘realistic’ reaction model to study the chemical interactions between aluminosilicate powders and activating solutions, as in Chapters 7, 8, 9 and 10, so that the experimental observations collected in Chapters 4, 5 and 6 can be mechanistically explained. Note that this thesis adopts the philosophy that the observed physical interactions between solids and gels are secondary effects caused by chemical interactions between solids and activating solutions.

3.5 REFERENCES


[3.63] Private communication with Ms. Natasha Wright, CSIRO (Commonwealth Scientific and Industrial Research Organisation), Clayton, Melbourne, Australia on April 10th, **2002**.


Early Age Properties of Geopolymeric Binders

Geopolymeric binders are inorganic polymers that consist of three major phases: (1) aluminosilicate gels that comprise of the newly formed aluminosilicate polymer and the included pore solution; (2) undissolved solids; and (3) the microscopic interface. These materials are synthesised by alkali-activating aluminosilicate powders with alkaline (silicate) solutions, or activating solutions. A geopolymeric binder, after all the ingredients are homogeneously mixed, will undergo a series of geopolymeric processes which transform the mouldable fluid-like paste to unmouldable rock-like solid as discussed in Chapter 3. This chapter is designed to characterise the early age properties of geopolymeric binders from the initial mixing to 7 days of curing. The nature of the activating solutions has been modified mainly by the introduction of common inorganic salts, which are both soluble or insoluble/partially soluble in water. As will be shown in this chapter, these inorganic salts can be used as reaction probes to yield important information on the subject of reaction mechanism(s) of geopolymerisation.

4.1 INTRODUCTION

One of the major chemical differences between mineral binders produced from geopolymerisation and Portland cement hydration, apart from the apparent differences of the starting solids used, which differ in their respective chemical compositions, mineralogy and microstructures, is the solution.
The aqueous solution used for Portland cement hydration is neutral water. Consequently, the pH of the Portland cement pore solution has been reported to start from ~7 to 12-13 with increasing extent of solid dissolution [4.1, 4.2]. After a series of solid hydrolysis/dissolution, mass transport and surface nucleation of the dissolved Ca and Si on the hydrolysed cement particles, a mixture of unhydrated (or undissolved) Portland cement particles, secondary precipitates such as portlandite and ettringite, as well as the various types of crystalline calcium silicate hydrate (CSH) crystals or amorphous CSH gels, is formed. Physically, the hydrated Portland cement paste is transformed from fluid-like paste to rock-like solid in 3-5 hours through the so-called setting reactions. See Chapter 2 for the detailed descriptions of Portland cement hydration chemistry.

On the other hand, a geopolymeric binder requires a strongly alkaline solution to ‘activate’ aluminosilicate solid hydrolysis/dissolution due to the relatively insoluble solids used for geopolymerisation as compared to Portland cement hydration [4.3-5]. To achieve the favourable solution composition for good physical and chemical properties of the hardened products, soluble silicates are often added to an alkaline solution to produce the activating solution highly concentrated in alkalis (MOH, where M = Na or K) and soluble silicates. These soluble silicates are prevented from extensive polymerisation and gellation by the initial high solution pH [4.6]. As soon as the pH starts to decrease from its original value of close to 14, or greater (immeasurable in the range of normal aqueous water chemistry), to a lower value due to hydrolysis on aluminosilicate solid, which consumes hydroxyl ions, polycondensation will take place at a very fast rate. This is because the pore solution inside the initial geopolymeric paste is already highly concentrated in soluble silicates. Extensive solid dissolution, therefore, is not required to reach the saturation/supersaturation state where soluble silicate would start polymerising to form (alumino)silicate precipitates or gels, which may involve the added solution silicates as well as the dissolved species from the solids. As a result, a geopolymeric system is normally characterised by a very fast setting time as compared to the Portland cement counterpart [4.7]. This can be an advantage or disadvantage, depending on the practical situation. The need to control the rate of setting for geopolymeric binders, and the related products, is obvious.

Hence, the majority of this chapter was dedicated to the study of the effects of activating solutions on the early paste strength developments and setting characteristics of geopolymeric binders. As inspired by the Portland cement industry [4.8], inorganic salts such as CaCl$_2$ were
added to the various activating solutions in an attempt to control the setting rate of aluminosilicate gels. The strength developments of early geopolymeric pastes before setting were characterised by yield stress measurements using a vane rheometer, while the setting times were determined using a modified Vicat needle. This is supplemented by the necessary characterisations on the physical/chemical properties of the inorganic salt-modified geopolymeric binders including compressive strength measurements, XRD and FTIR analyses up to 7 days of curing.

4.2 MATERIALS AND EXPERIMENTAL METHODS

4.2.1 Materials

In this chapter, the solid raw materials used for the geopolymeric binder syntheses included Gladstone fly ash (QCL, Queensland, Australia), Port Augusta fly ash (South Australia) and HR1-grade kaolinite (Commercial Minerals, Sydney, Australia). The solid compositions as determined by fusion analysis using a Siemens SRS3000 sequential x-ray fluorescence (XRF) spectrometer, are listed in Table 4.1. The chemicals used were inorganic salts of laboratory grade, including KCl, K$_2$CO$_3$, KNO$_3$, KOH, CaCl$_2$, Ca(OH)$_2$, CaCO$_3$, CaSO$_3$, CaO, MgCl$_2$·6H$_2$O, Mg(NO$_3$)$_2$·6H$_2$O and MgO. The sodium silicate solution (Vitrosol N(N40)$^{®}$, PQ Australia) was characterised by a molar ratio SiO$_2$/Na$_2$O = 3.32 and [SiO$_2$] = 6.63 moles/L (M).

4.2.2 Synthesis of Geopolymeric Binders

Four geopolymeric binder systems were used to study their early strength developments and setting characteristics. Each system differed from the others by its solid raw materials, solid/solution ratio and concentration of soluble silicates in the activating solution. The Control sample was activated with an activating solution without any inorganic salt contamination, which was used as the basis of comparison for examining the effects of inorganic salts on a particular geopolymeric binder system. See Table 4.2 for the
Table 4.1 The elemental compositions in mass percentages of the various minerals as determined by the method of XRF.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Port Augusta fly ash (wt%)</th>
<th>Gladstone fly ash (wt%)</th>
<th>HR1-Kaolinite (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>48.5</td>
<td>50.0</td>
<td>54.5</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>29.6</td>
<td>28.0</td>
<td>29.4</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>4.6</td>
<td>12.0</td>
<td>1.4</td>
</tr>
<tr>
<td>CaO</td>
<td>6.1</td>
<td>3.5</td>
<td>0.2</td>
</tr>
<tr>
<td>MgO</td>
<td>2.3</td>
<td>1.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Na₂O</td>
<td>3.7</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.9</td>
<td>0.7</td>
<td>0.2</td>
</tr>
<tr>
<td>TiO₂</td>
<td></td>
<td>1.7</td>
<td>2.8</td>
</tr>
<tr>
<td>Other minor oxides</td>
<td>4.3</td>
<td>0.6</td>
<td>0.2</td>
</tr>
<tr>
<td>Combustibles</td>
<td></td>
<td>2.0</td>
<td>11.0</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100.0</strong></td>
<td><strong>100.0</strong></td>
<td><strong>100.0</strong></td>
</tr>
</tbody>
</table>

Table 4.2 The compositions in terms of mass ratios of the various Controls.

<table>
<thead>
<tr>
<th></th>
<th>(Fly ash/ kaolinite) ratio</th>
<th>(Vitrosol N(N40))® sodium silicate solution / total solid) ratio</th>
<th>(15 M KOH solution / total solid) ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>System I</td>
<td>2.02</td>
<td>0.05</td>
<td>0.31</td>
</tr>
<tr>
<td>System II</td>
<td>9.00</td>
<td>0.18</td>
<td>0.28</td>
</tr>
<tr>
<td>System III</td>
<td>9.00</td>
<td>0.22</td>
<td>0.28</td>
</tr>
<tr>
<td>System IV</td>
<td>4.00</td>
<td>0.08</td>
<td>0.35</td>
</tr>
</tbody>
</table>

* Port Augusta fly ash was used.

# Gladstone fly ash was used.

compositions of the respective Control samples. All the other samples were named after the inorganic salts used for the contamination and are expressed in *italics* in the main text of this chapter. For example, when a sample was synthesised by using System II condition and the activating solution was contaminated by CaCl₂, the sample is named II-CaCl₂.
Table 4.3  The classification of the salts at 25°C [4.9,4.10].

<table>
<thead>
<tr>
<th>Water-soluble</th>
<th>Water-insoluble</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>Ca(OH)₂</td>
</tr>
<tr>
<td>K₂CO₃</td>
<td>CaCO₃</td>
</tr>
<tr>
<td>KNO₃</td>
<td>CaCl₂</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>CaO</td>
</tr>
<tr>
<td>Mg(NO₃)₂.6H₂O</td>
<td>MgCl₂.6H₂O</td>
</tr>
<tr>
<td>MgSO₃</td>
<td>MgO</td>
</tr>
</tbody>
</table>

The raw materials were prepared as follows: The solid starting raw materials of the designated ratios (Table 4.2) were mixed to homogeneity in a rotary mixer overnight before use. A stock solution of 15 M potassium hydroxide solution was prepared by dissolving KOH pellets in distilled/deionised water, and was allowed to cool to room temperature in sealed containers with stirring overnight. The activating solutions of the designated compositions (Table 4.2) were freshly prepared 2 minutes before mixing with the solids. The inorganic salts were dissolved or suspended in 20g of water as the inorganic salt transport medium, 5 minutes before their addition. As the hydration time for the salts was short, some of the less soluble salts were not allowed sufficient time to fully dissolve. Hence, the inorganic salts can be classified as in Table 4.3 according to their behaviour in aqueous solutions. This classification is very important to explain the effects of the various inorganic salts on the early strength developments of the geopolymeric pastes before setting, as will be discussed extensively later in this chapter.

The geopolymeric binders were synthesised as follows: The pre-mixed solids and the activating solutions of the designated solid/solution ratios (Table 4.2) were mixed in a mechanical mixer for 5 minutes to produce homogeneous pastes. Immediately, twenty grams of water were then added to the pastes and mixed for a further 5 minutes to produce the Control. Alternatively, aqueous solutions of water-soluble salts or suspension of water-insoluble salts (see above) were added to produce the contaminated geopolymeric binders. The various geopolymeric pastes were then transferred to alkali-resistant plastic containers, and cured under atmospheric pressure at 40 ± 2°C for 24 hours. Subsequently, the hardened binders were cured at room temperature of 20-25°C under atmospheric pressure and a relative humidity of 50 ± 5 % until testing.
4.2.3 Characterisation of Geopolymeric Binders

4.2.3.1 Physical/mechanical characterisation

The effects of activating solutions, with or without inorganic salt contamination, on the physical/mechanical characteristics of the various geopolymeric binders were studied by: (1) yield stress measurement to measure the early strength developments of the pastes before setting; (2) Vicat needle penetration to determine the setting times of the various binders; and (3) uniaxial compression to obtain the compressive strength of the hardened binders at 7 days.

4.2.3.2 Microstructural/chemical characterisation

Both XRD and FTIR were used to characterise the microstructures of the hardened pastes during the first 7 days. SEM-EDS was also performed for such a purpose. However as no significant topographical differences could be identified between the Control samples and the inorganic salt-contaminated counterparts within the first 7 days of curing, the results of SEM-EDS will not be presented in this chapter. See Chapter 5 for the long-term effects of the inorganic salt contamination on the nature of the geopolymeric binders.

4.3 EARLY AGE PROPERTIES OF GEOPOLYMERIC BINDERS

4.3.1 Setting

The results of the final setting time determination on the various geopolymeric systems, with and without the KCl, K₂CO₃ and KNO₃ contaminations, are included in Table 4.4.

From Table 4.4, the setting time of geopolymeric binders synthesised from two different solid starting raw materials was affected to varying extents under similar reaction conditions. For example, if Port Augusta fly ash was used, setting was accelerated with increasing fly ash/kaolinite ratio, sodium silicate solution/total solid ratio and decreasing 15 M KOH
Table 4.4 The effects of the anions on the final setting time of the various geopolymeric binders at 40°C.

<table>
<thead>
<tr>
<th>Dosage (moles)</th>
<th>KCl (minutes)</th>
<th>K₂CO₃ (minutes)</th>
<th>KNO₃ (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>62</td>
<td>62</td>
<td>62</td>
</tr>
<tr>
<td>0.02</td>
<td>84</td>
<td>70</td>
<td>69</td>
</tr>
<tr>
<td>0.04</td>
<td>124</td>
<td>79</td>
<td>83</td>
</tr>
<tr>
<td>0.08</td>
<td>153</td>
<td>88</td>
<td>95</td>
</tr>
<tr>
<td>0</td>
<td>48</td>
<td>48</td>
<td>48</td>
</tr>
<tr>
<td>0.02</td>
<td>47</td>
<td>46</td>
<td>45</td>
</tr>
<tr>
<td>0.04</td>
<td>49</td>
<td>46</td>
<td>48</td>
</tr>
<tr>
<td>0.08</td>
<td>44</td>
<td>47</td>
<td>48</td>
</tr>
<tr>
<td>0</td>
<td>67</td>
<td>67</td>
<td>67</td>
</tr>
<tr>
<td>0.02</td>
<td>67</td>
<td>67</td>
<td>67</td>
</tr>
<tr>
<td>0.04</td>
<td>65</td>
<td>65</td>
<td>66</td>
</tr>
<tr>
<td>0.08</td>
<td>67</td>
<td>69</td>
<td>67</td>
</tr>
<tr>
<td>0</td>
<td>34</td>
<td>34</td>
<td>34</td>
</tr>
<tr>
<td>0.02</td>
<td>51</td>
<td>46</td>
<td>37</td>
</tr>
<tr>
<td>0.04</td>
<td>65</td>
<td>52</td>
<td>49</td>
</tr>
<tr>
<td>0.08</td>
<td>84</td>
<td>52</td>
<td>59</td>
</tr>
</tbody>
</table>

solution/analytical ratio, i.e. by moving from Systems I to II (see Table 4.2). On the other hand, if Gladstone fly ash was used, setting was retarded by moving from Systems IV to III.

A common trend, however, could be identified if the geopolymeric binders were contaminated by the inorganic salts KCl, K₂CO₃ and KNO₃. According to Table 4.4, the final setting times of System II and System III geopolymeric binders, which contained high dosages of soluble silicates (see Table 4.2), were not affected by the inorganic salt contamination. Setting, however, was increasingly retarded by increasing dosages of the inorganic salts if an activating solution of a relatively low soluble silicate concentration was used as in System I and System IV. It therefore appears that the effects of inorganic salt contaminations on the setting characteristics of geopolymeric binders were dependent on the concentrations of soluble silicates added. This implies that the effects of inorganic salt contamination are
Figure 4.1  The effect of molar dosage on the setting time of (a) System I and (b) System III geopolymeric binders.

predictable regardless of the solid raw materials used. Modifying the solution chemistry of a geopolymeric system through inorganic salt addition could be a viable method for setting time control. As the initial activating solutions of Systems I to IV were already highly abundant in potassium cations, and the fact that the added potassium from the inorganic salts (KCl, K₂CO₃ and KNO₃) was less than 10 molar % of the total potassium contents in the solutions, the effects of the inorganic salts on the setting processes of geopolymeric binders should be largely attributed to their constituent anions.
When inorganic salts of divalent cations were used, the trends observed above were complicated by the fact that divalent alkaline earth cations, such as Ca$^{2+}$ and Mg$^{2+}$, should be highly insoluble in high pH environments \[4.10\]. When water-soluble salts of Ca and Mg were introduced to an activating solution in the form of aqueous solutions, it is expected that alkaline earth hydroxide precipitates such as Ca(OH)$_2$ and Mg(OH)$_2$ should be formed almost immediately upon contact with the alkaline aqueous solution. This should in turn cause set acceleration by providing heterogeneous nucleation templates for soluble silicate polymerisation (see Section 4.4 for the more detailed discussion), which had been experimentally proved in this work as shown in Figure 4.1, provided that the level of contamination was low.

However, when the contamination level was high, whether the effects were accelerating or retarding could be dependent on a number of factors including (1) the initial composition of the activating solution; (2) the nature of the starting solids; and (3) the nature of the contamination. This conclusion was drawn based on the experimental observations presented in Figure 4.1. For example, when the initial soluble silicate concentration was low (System I, which contained Port Augusta fly ash, see Figure 4.1 (a)), setting was retarded by CaCl$_2$ at high dosages. This trend, however, was not observed if water-insoluble salts such as Ca(OH)$_2$, CaO and CaSO$_3$ were used in System I, or if System III consisted of Gladstone fly ash was used (Figure 4.1 (b)). Another example lies in the fact that set acceleration as induced by water-insoluble salt contamination (Ca(OH)$_2$, CaO and CaCO$_3$) was found to reach its maximum value at the dosage of around 0.15 moles in System III. In System I, however, the maximum set acceleration appeared at a higher dosage than System III. Furthermore, between 0.04 moles and 0.1 moles of inorganic salt dosage, the final setting times of the System I geopolymeric binders were not affected by the dosages of the inorganic salts, except the ones containing CaO. The reason(s) for this observation can be partly explained by comparing the calcium contents of the Port Augusta and Gladstone fly ashes, which will be elaborated in Chapter 7.

Figure 4.2 is a radial plot not conventionally used for presenting scientific data. However, as demonstrated here, it can be a much easier tool than a tabulated form, as shown in Table 4.5, to study the trends of ionic contamination at the same contamination level. The *percentage change in setting time* is defined as:
Figure 4.2  The percentage change in setting time of alkali-activated cements caused by calcium and magnesium salts at the molar dosage of 0.08764 moles.

Table 4.5 The final setting time of the various geopolymeric binders at 40°C with an inorganic salt dosage of 0.08764 moles

<table>
<thead>
<tr>
<th></th>
<th>Control</th>
<th>CaCl₂</th>
<th>Ca(OH)₂</th>
<th>CaCO₃</th>
<th>CaO</th>
<th>MgCl₂</th>
<th>Mg(NO₃)₂</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>System I</td>
<td>62</td>
<td>56</td>
<td>58</td>
<td>---</td>
<td>40</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>System II</td>
<td>48</td>
<td>29</td>
<td>44</td>
<td>14</td>
<td>31</td>
<td>39</td>
<td>44</td>
<td>48</td>
</tr>
<tr>
<td>System III</td>
<td>67</td>
<td>43</td>
<td>64</td>
<td>30</td>
<td>49</td>
<td>67</td>
<td>65</td>
<td>67</td>
</tr>
<tr>
<td>System IV</td>
<td>34</td>
<td>22</td>
<td>31</td>
<td>7</td>
<td>25</td>
<td>30</td>
<td>27</td>
<td>31</td>
</tr>
</tbody>
</table>

Percentage change in setting time (\(\%\)) = \([\frac{(a-b) \times 100}{b}\] \hspace{1cm} (4.1)

where ‘a’ is the setting time of the inorganic salt-modified system and ‘b’ is the setting time of the Control. A more negative value of the percentage change in setting time means that the setting time has been reduced to a greater extent, as compared to the Control, through the use of an inorganic salt than a more positive value. A positive percentage change in setting time means setting has been retarded.
Using the Control samples as the reference points, Figure 4.2 describes the effects of the various inorganic salts on the setting times of the various geopolymeric binders. It is evident from the radial plot that all three systems (Systems II to IV) possessed similar curves and the distribution of results was in a systematic manner. This result is important as it allows predictions been made for a geopolymeric system that has never been tested. It also suggests that each of the inorganic salts examined may affect the setting processes through a certain set of reaction mechanisms.

In summary, setting was generally accelerated by calcium salts for all the geopolymeric systems examined at the molar dosage of 0.08764 moles. Magnesium salts, however, seemed to have little effect on the setting process(es). Potassium salts could be used as set retarders provided right combinations of the solid and the solution starting raw materials were used. The mechanism of setting in a geopolymeric system is extremely complicated. A large number of factors can contribute to setting, which will be further elaborated in Chapters 7 and 8. Precise setting time control using inorganic salts of double charged cations, or potassium salts, can remain essentially a trial-and-error process.

### 4.3.2 Before Setting

During the early stage(s) of geopolymerisation, the interparticle bonding strength within a freshly mixed geopolymeric paste is relatively weak because of the low degree of polymerisation of silicates and/or aluminosilicates in the solution phase. As a result, a paste can be deformed with ease during this period by applying only gentle external forces. This is the origin of the paste workability. A vane rheometer, hence, is an ideal technique to quantitatively measure the attractive forces inside the freshly mixed geopolymeric pastes, which simply involves inserting a vane-like rod into a solid-solution suspension to measure the rotational torque that is required to cause shear yielding [4.11].

As shown in Figure 4.3, the paste rheology of System II geopolymeric binder was clearly affected by the addition of the various salts. The results of yield stress measurement suggest that magnesium salts did affect the setting processes. This was difficult to see using the conventional penetration test as shown in Figure 4.2. A better insight can be established by
Figure 4.3  The yield stress developments of System II geopolymeric binders at an inorganic salt molar dosage of 0.08764 moles at 25°C.

Figure 4.4  The effects of Ca and Mg salts at a molar dosage of 0.08764 moles on the yield stress ratios of System II geopolymeric binders at 25°C.

comparing the actual yield stress results of Figure 4.3 with their yield stress ratios of Figure 4.4. A yield stress ratio was calculated by dividing the yield stress of an inorganic salt-contaminated sample at time t by its yield stress at t = 10 minutes.
From Figures 4.3 and 4.4, it was found that the samples containing Ca(OH)$_2$ and CaCO$_3$ had the same rate of change of yield stress (as indicated by the yield stress ratio), but the sample containing CaCO$_3$ had a higher yield stress at any given time. In other words, CaCO$_3$ had initiated the interparticle attractive forces within System II geopolymeric paste earlier than Ca(OH)$_2$. Once the interparticle attractive forces were initiated, the subsequent strength development was the same for both II-Ca(OH)$_2$ and II-CaCO$_3$. Other experimental observations that were learnt from Figures 4.3 and 4.4 include: (1) water-soluble magnesium salts of MgCl$_2$ and Mg(NO$_3$)$_2$ were found to give rise to the same yield stress characteristics (actual yield stress as well as yield stress ratio) at any given time; and (2) paste yield stresses for the samples containing oxides of calcium and magnesium were the same. Calcium chloride seemed to affect the paste strength in a different way from the water-insoluble counterparts II-Ca(OH)$_2$, II-CaCO$_3$ and II-CaO. However, it is anticipated that other water-soluble salts of calcium may give rise to the same yield stress curve as that of CaCl$_2$, probably due to the same reason as for MgCl$_2$ and Mg(NO$_3$)$_2$. A more detailed discussion on the results of the yield stress measurements will be presented in Section 4.4.

4.3.3 After Setting

4.3.3.1 Mechanical characteristics

The 7-days compressive strengths of System II and System III geopolymeric binders are presented in Figure 4.5. It can be seen that the inorganic salt contaminations used in this chapter did not cause any observable short-term detrimental effects. Some of the salts, such as CaCO$_3$ and CaO (Figure 4.5 (b)), even significantly increased the 7-days compressive strength of System III geopolymeric binder. As System II was synthesised using Port Augusta fly ash, which contained more CaO content than Gladstone fly ash (see Table 4.1), it seems the amount of calcium present, regardless of its initial source, in a geopolymeric reacting system is important in determining the nature of the aluminosilicate gels formed, which presumably controls the macroscopic strength (such as compressive strength) of a geopolymeric product. If the solid raw material is deficient in calcium, calcium salts of CaCO$_3$ and CaO can be introduced in the form of an aqueous suspension to improve the physical/mechanical properties of geopolymers. The mechanistic explanation for the effects of calcium in geopolymerisation will be presented in Chapter 11. The long-term impact of the inorganic salt contamination will be investigated in Chapter 5.
Figure 4.5 The 7-days compressive strengths of System II and System III geopolymeric binders containing (a) potassium salts (b) calcium salts and (c) magnesium salts.
4.3.3.2 Microstructural/chemical characteristics

FTIR and XRD techniques were used to characterise the microstructure of the various geopolymeric binders, with and without inorganic salt contamination. It was found that, within the first 7 days and by comparing with the Control samples, addition of the various inorganic salts did not cause any observable effects on the sample crystallinity in any of the systems examined. No new crystalline phase could be identified.

More information, however, can be gathered from the IR technique. The infrared spectra of the various Systems II and III geopolymeric binders were not affected significantly by the various inorganic salts except at the spectral region of 1500-1350 cm\(^{-1}\), which are demonstrated in Figure 4.6. The peaks at 1463 cm\(^{-1}\) could be attributed to carbonates in solution form, which might be in close association with Na\(^+\) or K\(^+\) cations [4.12]. Hence, it appears that carbonation of all the geopolymeric binders was serious initially, but later disappeared upon ageing as little or no carbonation could be observed on the samples at 28 days old. This observation, however, is in contradiction to what has been observed in the Portland cement systems, where carbonation should become more serious with age [4.1, 4.13]. As alkali cations (Na\(^+\) and K\(^+\)) are required to charge-balance the negatively charged and fourth coordinated aluminium (Al\(^{IV}\)) inside the newly formed aluminosilicate gel [4.3, 4.4, 4.12], the ‘free’ alkali contents of a geopolymeric system should become increasingly less with age due to the continuous solid dissolution and gel formation. Consequently, carbonation should become less serious in a geopolymeric system at a more mature age, if assuming that free alkalis in the pore solution are responsible for absorbing atmospheric CO\(_2\). Furthermore, examination of the degree of carbonation using an IR technique can be very useful in fast and on-line investigation on the extent of geopolymerisation of a geopolymeric product, or identification of whether an activating solution is ‘too’ alkali concentrated, as was also observed by Barbosa et al. [4.12]. In this case, nearly all the alkalis originally present in the System III activating solution had been consumed through geopolymerisation by the end of 28 days. It is important to point out here that the addition of carbonates did not change the spectra significantly due to its small quantity as compared to the atmospheric carbonation.

Apart from carbonation, the nitrate-containing samples (II-Mg(NO\(_3\))\(_2\), III-KNO\(_3\) and III-Mg(NO\(_3\))\(_2\)) were also found to display significant changes on the FTIR spectra collected as
Figure 4.6 The FTIR spectra of III-Control at 1 day and 28 days and III-KNO$_3$ at 7 days.

Figure 4.7 The IR bands attributable to NO$_3$ molecular vibrations in geopolymeric binders III-KNO$_3$ and III-Mg(NO$_3$)$_2$ at 7-days and in pure KNO$_3$ and Mg(NO$_3$)$_2$·6H$_2$O solids.
shown in Figure 4.6. A new IR band at 1385 cm$^{-1}$ could be identified in all the nitrate-contaminated geopolymeric binders, which was also present in the pure KNO$_3$ and Mg(NO$_3$)$_2$.6H$_2$O chemical reagents. See Figure 4.7. As IR is highly sensitive to the local chemical environments of a molecule, the spectral band of nitrates in aqueous solution can be expected to be narrower in solution than in solid due to the less molecular interaction in the solution. Hence, according to Figure 4.7, it is likely that nitrate anions could be soluble in the pore solution of geopolymeric binders II-Mg(NO$_3$)$_2$, III-KNO$_3$ and III-Mg(NO$_3$)$_2$. From Figure 4.6, the 1385 cm$^{-1}$ IR band, though of much less intensity than the nitrate-contaminated samples, was also evident in all the other geopolymeric binders investigated as well as in the unreacted Port Augusta and Gladstone fly ashes. This suggests that the solid raw materials could already be contaminated with nitrates before use.

4.4 MECHANISTIC CONSIDERATIONS ON THE EFFECTS OF INORGANIC SALT CONTAMINATION

Before solid dissolution has started, the solution phase of a geopolymeric system can be regarded as consisting of only alkali cations, soluble silicate anions, hydroxyl anions and water molecules. When an aqueous solution of a salt of Group II metal cation, such as Ca$^{2+}$ or Mg$^{2+}$, is added to such a system, it can be expected that the local ‘free’ hydroxyl anions in the vicinity of the divalent metal cations should be removed almost immediately from the solution phase to form the metal hydroxide precipitates (Ca(OH)$_2$ or Mg(OH)$_2$) [4.6, 4.9, 4.10]. This should induce a sudden pH drop around the newly formed metal hydroxide precipitates. The interface between the metal hydroxide precipitates and the alkaline silicate solution, hence, can be depleted in hydroxyl anions (which are vital in preventing soluble silicate polymerisation [4.6]) and subsequently triggers polymerisation and gellation of the silicate species at the metal hydroxide precipitate surfaces as reported by Iler [4.6]. Therefore, the introduction of aqueous calcium or magnesium salt solution to geopolymeric systems can be expected to produce many heterogeneous nucleation templates (the metal hydroxide precipitates) inside the solution phase of a geopolymeric system, which promote silicate/aluminosilicate gellation growth through a heterogeneous nucleation mechanism. Without such a salt addition, extensive solid dissolution, which simultaneously consumes
OH\(^-\) and M\(^+\) (M = Na or K), and releases Al\(^{3+}\) and Si\(^{4+}\), will be required to reach the state of supersaturation whereby soluble silicate will start polymerising to generate attractive forces inside the geopolymeric paste. Consequently, the systems contaminated by aqueous calcium or magnesium salt solutions should be expected to demonstrate shorter setting times than the systems without such contaminations.

The results obtained from this chapter can be used to prove, or disprove, the above postulate by utilising the fact that the rate of gel formation through a heterogeneous nucleation mechanism should be highly dependent on the nature of the nucleation templates present [4.14-17]. If the templates are different, the gellation rate observed should also be different. Note that the rate of gel formation is assumed to be proportional to the macroscopic paste strength measured through yield stress determination and Vicat needle penetration, since aluminosilicate gel is the principal binding phase of a geopolymeric system [4.3-5, 4.7, 4.12].

From Table 4.5, Figures 4.1 and 4.2, the various calcium and magnesium salt contaminations were found to have caused varying degrees of set acceleration to the various geopolymeric binders. In general, the magnesium salts had exerted little effect on the binder setting characteristics measured by the modified Vicat needle, while the calcium salts were more effective in achieving set acceleration. This observation seems to overturn the heterogeneous nucleation theory as postulated above. However, by examining the yield stress characteristics of the various geopolymeric pastes before setting, see Figures 4.3 and 4.4, it is clear that magnesium salts (MgCl\(_2\)-6H\(_2\)O, Mg(NO\(_3\))\(_2\)-6H\(_2\)O and MgO) did initiate an earlier interparticle strength development within the early paste as compared to II-Control, which conforms to the above heterogeneous nucleation postulate. This is despite the fact that the rate of yield stress development of the magnesium salt-contaminated pastes was found to drop off since its initiation, which could be used to explain why magnesium salts did not appear to affect setting. The penetration test using a Vicat needle, therefore, is a less favourable technique to study the early paste strength and its development as this technique can lead to incorrect conclusions.

As MgCl\(_2\)-6H\(_2\)O and Mg(NO\(_3\))\(_2\)-6H\(_2\)O were both soluble in water, these salts should be dissociated very quickly in water to release the respective divalent Mg\(^{2+}\) cations and monovalent Cl\(^-\) or NO\(_3\)^- anions. When these aqueous solutions were added to the fresh
geopolymeric pastes, the Mg$^{2+}$ cations should be immediately converted to form magnesium hydroxides due to their high affinity towards hydroxyl ions for complexation reactions [4.10]. These Mg hydroxides should be chemically the same regardless of the origins. Because the same molar dosage was used, both of these salts should generate the same amount of magnesium hydroxides and released the same amount of anions to the paste solutions. From Table 4.4, the anions Cl$^{-}$ and NO$_3^-$ (through the additions of KCl and KNO$_3$) were found to cause minimal effects on the speed of setting if the initial activating solution was highly concentrated in soluble silicates as in System II. See Section 4.3.1. Hence the anions can be regarded as spectator ions under the conditions of System II, as far as setting was concerned. Because the same amount of Mg hydroxides was formed, the yield stress developments for both II-MgCl$_2$ and II-Mg(NO$_3$)$_2$ pastes should be expected to be the same, which had been experimentally confirmed by the yield stress experiment as shown in Figures 4.3 and 4.4. A heterogeneous mechanism, hence, is satisfactory to explain the early paste strength initiation of II-MgCl$_2$ and II-Mg(NO$_3$)$_2$ as compared to II-Control (Figure 4.3).

The heterogeneous nucleation mechanism postulated above can be used to explain a number of experimental observations encountered in this chapter. These are:

1. Both calcium and magnesium oxides are expected to hydrolyse in water to form the respective hydroxides. The fact that the paste yield stress developments of II-Ca(OH)$_2$ and II-CaO were different suggests that, by applying the heterogeneous nucleation model, CaO was not completely hydrolysed in water due to the very short contact time employed in this investigation.

2. Because the affinity of Ca for water molecules was higher than that of Mg [18], the extents of hydration for both salts should be different given the same hydrolysis time and the same chemical dosage used. If the heterogeneous nucleation mechanism suggested above was true, one should expect that the paste strength developments of both II-CaO and II-MgO should be different. However, the results in Figures 4.3 and 4.4 showed that these samples had demonstrated exactly the same paste yield stress characteristics. This was unexpected because the hydrolysed products of the oxides were chemically different. The most probable explanation is that hydration spheres were formed at the surfaces of the hydrolysing oxides. To form these hydration spheres, water molecules and hydroxyl ions should be taken away from the bulk.
alkaline silicate solution, which lowered the local solution pH, or increased the local silicate concentration beyond saturation level. As a result, silicate polymerisation outside the oxide hydration spheres was triggered in the same way as that of the heterogeneous nucleation observed in the water-soluble salt-contaminated systems as discussed above. These hydration spheres masked the chemical differences between the Ca and Mg cations and thus gave rise to the same nucleation effects as in Figures 4.3 and 4.4. When these hydration spheres were eventually broken down, differences towards the binder strength development should be experienced as shown in Figure 4.2.

3. The reason why yield stress developments of the Ca(OH)$_2$-containing sample and the CaCl$_2$-containing sample were different can once again be explained from the heterogeneous nucleation point of view. When aqueous solution of CaCl$_2$ was added to the alkaline paste solution, Ca(OH)$_2$ was produced by taking in hydroxyl ions from the surrounding solution. This caused gellation of the soluble silicates as discussed above. For the Ca(OH)$_2$-containing sample, however, Ca(OH)$_2$ was already present and was insoluble in high pH environment. Hence the mechanism for the heterogeneous nucleation of the Ca(OH)$_2$-containing paste was different from that of the CaCl$_2$-containing paste. The increase of gellation rate thus should be of purely a collision-type for the Ca(OH)$_2$-containing sample. The same can be expected for the highly insoluble CaCO$_3$ as well. The reason why CaCO$_3$ promoted gellation at a much earlier age than any of the salts is still unknown and deserves to be further investigated.

### 4.5 CONCLUSIONS

The early age properties, within the first 7 days, of a number of geopolymeric binders have been studied through the use of yield stress measurement to characterise the early paste strength development before setting; a Vicat needle penetration was used to determine the final setting time; an uniaxial compression was used to obtain the 7-says compressive strengths; XRD analysis was conducted to examine the change in sample crystallinity; and
FTIR spectroscopy was used to determine the chemical changes within the geopolymeric binders.

From the above experimental programme, it can be concluded that:

1. Anions of inorganic salts can affect the early paste strength developments and setting times of geopolymeric binders if the initial activating solutions are relative low in soluble silicate concentrations. The effects of anions on geopolymerisation will be further investigated in Chapter 8.

2. Inorganic salts of Group II metal cations, such as Ca$^{2+}$ and Mg$^{2+}$, accelerate early geopolymeric paste strength developments through a heterogeneous nucleation mechanism whereby silicate and/or aluminosilicate gels nucleate and grow from these nucleation templates. Depending on the nature or how these templates are formed, the rates of gellation are affected differently.

3. The compressive strength of an early geopolymeric binder can be improved through the addition of calcium-containing salts, which can be both soluble or insoluble in water, if the solid raw materials are deficient in the calcium oxide contents, as was also suggested by other investigators [4.18, 4.19]. The role of Ca in geopolymerisation will be further investigated in Chapters 7 and 8.

4. Carbonation of geopolymeric products is closely associated with the ‘free’ alkali content of the pore solution within a geopolymeric binder. With increasing extent of geopolymerisation to produce more aluminosilicate gels, increasing amounts of the alkalis are fixed in the solid gels for charge compensation on the negatively charged and fourth coordinated Al$^{IV}$. Theoretically, a geopolymeric binder without free alkali content can be achieved through good activating solution mix design, as in III-Control, which was also observed by Barbosa et al. [4.12].
4.6 REFERENCES


CHAPTER 5

Properties of Matured Geopolymeric Binders

— This chapter is based on the publication: The Effects of Inorganic Salt Contamination on the Strength and Durability of Geopolymers, Coll. Surf. A. 2002, 211, 115-126.

Long-term stability is one of the most critical material properties for any construction materials. Obviously, an investigation on the chemical stability and durability of geopolymeric binders, and the related products, is of paramount importance. This chapter, hence, aims to investigate the long-term effects of activating solutions on the properties of geopolymeric binders. The mechanism of gel deterioration process(es) in geopolymeric binders will also be suggested based on the experimental results presented in this chapter, which used some of the inorganic salts from Chapter 4 as the reaction probes. The long-term stability of geopolymeric mortars and concretes will be presented in Chapter 6.

5.1 INTRODUCTION

Geopolymeric binders are mineral binders produced from alkali-activating aluminosilicate powders with activating solutions, which may or may not contain soluble silicates. In principle, any reactive aluminosilicates such as natural clays, rock-forming minerals and industrial aluminosilicate wastes can all be used to produce physically attractive products via alkali activation at room or elevated temperatures [5.1]. While the synthesis methods and product mechanical properties at a designated time have been widely studied, little attention has been paid to follow the structural change of the hardened products especially after 3 months of curing. This is partly because geopolymeric binders, and the related products, are highly heterogeneous and amorphous [5.2-4], as well as the fact that inadequate analytical technique(s) have often been applied for such a study.
The most common microstructural characterisation techniques for composite materials to date may include infrared vibration (IR), x-ray diffraction (XRD), nuclear magnetic resonance (NMR), electron microscopy, and pore characterisation techniques such as inert gas adsorption or mercury intrusion. While gas adsorption and electron microscopy have been successfully applied to characterise the microstructure of geopolymeric binders [5.5, 5.6], these techniques may not be ideal for studying material chemical stability and durability because they do not reveal the nature of chemical bonds within such materials. Characterising the change of pore size distribution or sample topography, hence, is insufficient to understand the actual solid transformation processes inside a mineral binder, which are the origins of the micro/macrostructural change inherent to gel hardening (strength gain), or deterioration.

On the other hand, data collected using analytical techniques that are extremely sensitive to local chemical environments are difficult to interpret. This is because amorphous materials with high degrees of heterogeneity, such as geopolymeric binders, lack short-range as well as long-range structural order. It is not unusual to acquire spectra of low signal to noise ratios and limited numbers of well-resolved spectral peaks due to spectral broadening in these materials. As a result, spectral interpretation can be extremely complicated with little fruitful results. Solid state NMR is particularly difficult to use in this regard. The nature of Al$^{3+}$ substitution in silicate tetrahedral sites within aluminosilicate gels further complicates the problem: Al$^{3+}$ and Si$^{4+}$ have been known to share nearly the same x-ray scattering factor [5.7], which renders XRD indistinguishable to microstructures of aluminosilicate materials of varying degrees of Al$^{3+}$ network substitutions. This is so especially when the materials under study are amorphous as in the case of geopolymeric binders.

As discussed in Section 3.1.2.4, Fourier-transform infrared spectroscopy (FTIR) is renowned for its sensitivity to structures of short-range structural order [5.7, 5.8]. Hence, the signal to noise ratio of the acquired FTIR spectra in general is good even for structures of low crystallinity. In particular, the inherent response of an IR spectrum to structures of the same chemical composition but varying degrees of structural order, or to structures of varying chemical compositions, can be greatly exploited for the study of chemical bonds as well as the characterisation of the microstructures on heterogeneous amorphous materials. See Section 3.1.2.4. This leaves FTIR as probably the most appropriate technique for studying structural
evolution of amorphous aluminosilicates of high heterogeneity. As will be shown below, by comparing the contours (number of IR bands, positions, widths, intensities and shapes) of the IR spectra between samples, together with the help from XRD and SEM-EDS analyses, information such as aluminosilicate gel crystallisation and/or precipitation during ageing can be identified within a particular geopolymeric binder, which has never been achieved before.

In this chapter, two very different geopolymer binder systems were synthesised by activating the same Gladstone fly ash/HR1-kaolinite mixture (fly ash/kaolinite = 9) with two different activating solutions of the same soluble silicate dosage but very different alkali (MOH, M = Na and K) concentrations. This ensures that the only non-fixed process variable was the level of alkalinity in the activating solutions. System III geopolymeric binders from Chapter 4 were used in this chapter to compare with the more alkali-concentrated System V binders. Mixing water, with or without the dissolved or suspended chloride or carbonate salts, was then added to the freshly prepared pastes in the same manner as that of Chapter 4. The effects of the inorganic salt-contamination on product ultimate strengths and durability will be characterised and discussed as below. Note that ‘durability’ is defined as the sample age when substantial reduction in strength from the ultimate value (5 %) is observed. See Figure 5.1 for the graphical illustration of the definition of ‘durability’. A sample that never reaches its ultimate strength is said to have a durability of infinity.
5.2 MATERIALS AND EXPERIMENTAL METHODS

5.2.1 Materials

Gladstone fly ash and HR1-grade kaolinite were used as the solid raw materials. The inorganic salts used were of laboratory grade, including KCl, K\(_2\)CO\(_3\), KOH, CaCl\(_2\), CaCO\(_3\), Ca(OH)\(_2\), MgCl\(_2\).6H\(_2\)O, MgCO\(_3\) and Mg(OH)\(_2\). Vitrosol N(N40)\(^\circledR\) sodium silicate solution was used to prepare the activating solutions.

5.2.2 Synthesis of Geopolymeric Binders

The methods of geopolymeric binder syntheses and the inorganic salt contaminations in this chapter are the same as that of Chapter 4. See Section 4.2.2. The starting solid raw material employed for both Systems III and V geopolymeric binder syntheses is a mixture of Gladstone fly ash and HR1-grade kaolinite at a mass (fly ash/kaolinite) ratio of 9. Samples are labelled using the same system as that of Chapter 4, for the sake of continuity throughout the thesis. For example, a sample activated with System V activating solution with CaCl\(_2\) contamination is called V-CaCl\(_2\). The compositions of the two Control samples are presented in Table 5.1.

For all the inorganic salt-contaminated binders, a common chemical dosage was used at 0.08 moles per 450 g of Gladstone fly ash. All samples were cured at 20-25°C and a relative humidity of 45-55 % until testing.

<table>
<thead>
<tr>
<th></th>
<th>System III</th>
<th>System V</th>
</tr>
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<tbody>
<tr>
<td>Gladstone fly ash</td>
<td>450 g</td>
<td>450 g</td>
</tr>
<tr>
<td>HR1-grade kaolinite</td>
<td>50 g</td>
<td>50 g</td>
</tr>
<tr>
<td>Vitrosol N(N40)(^\circledR) sodium silicate solution</td>
<td>110 g</td>
<td>110 g</td>
</tr>
<tr>
<td>Potassium hydroxide solution</td>
<td>120 *</td>
<td>120 *</td>
</tr>
</tbody>
</table>

* 15 M KOH solution was used.

** 20 M KOH solution was used.
5.2.3 Characterisation of Geopolymeric Binders

5.2.3.1 Mechanical characterisation

Uniaxial compression was used to obtain the compressive strengths of the geopolymeric binders from 7 days up to 9 months. See Section 3.2.4.3 for the detailed testing method.

5.2.3.2 Microstructural/chemical characterisation

XRD, FTIR and SEM-EDS were employed to characterise the microstructures of the hardened geopolymeric binders from 7 days up to 9 months. FTIR was further used to identify the chemical changes that were associated with solid-state transformation processes within the hardened geopolymeric binders, with and without inorganic salt contaminations. The FTIR spectra were baseline corrected as shown in Figure 5.2. See Section 3.1.2 for the detailed testing methods. Some of the pulverised samples were thermal treated in an oven at 105°C for 24 hours to study the dehydration and thermal stability of the geopolymeric binders.

![FTIR Spectra](image)

**Figure 5.2** The FTIR spectra of (a) the solid starting mixture (fly ash/kaolin = 9) and (b) III-Control at the age of 9-months. The arrows indicate where baseline corrections were made.
5.3 MATURE AGE PROPERTIES OF GEOPOLYMERIC BINDERS

5.3.1 Compressive Strength and Durability

The results of the uniaxial compressive strength determination on the various geopolymeric binders, with and without inorganic salt contamination, are presented in Table 5.2. It can be seen that the ultimate strength of III-Control is clearly higher than V-Control.

From Table 5.2, it was also observed that the mechanical performances of the two geopolymeric binder systems were affected to varying degrees by the various inorganic salt contaminations. Briefly, the hydroxides (Ca(OH)$_2$ and Mg(OH)$_2$) were found to exert no negative effects on the strength and durability of the two geopolymeric systems. In fact, these hydroxides had accelerated the strength development of System V binder. On the other hand, chloride salts, such as KCl, CaCl$_2$ and MgCl$_2$, were found to increase the early strengths of System III binder. These chloride salts, however, had also been observed to cause an earlier product deterioration on System III binder. Typically, the durability of System III chloride-contaminated binders was ~1 month. III-KCl was the worst performer as far as the strength and the durability was concerned. It reached a top of 44 MPa in 7 days but at the end of this investigation (9 months), the strength was a massive 20 MPa lower (~45 % reduction). The same chloride salts (KCl, CaCl$_2$ and MgCl$_2$), however, were not deleterious to System V binder. In fact, the ultimate strengths of the System V chloride-contaminated binders were only slightly lower than V-Control. Furthermore, increased product ultimate strengths without any apparent adverse effects could be achieved for both of the geopolymeric binder systems if the binders were contaminated by the carbonate salts, K$_2$CO$_3$, CaCO$_3$ and MgCO$_3$, during syntheses.

The significant differences between the two geopolymeric systems as observed above, with and without inorganic salt contaminations, suggest that the chemical processes involved in the two systems were immensely different. These, presumably, were caused by the different alkali contents of the activating solutions. As solid-state transformations of heterogeneous amorphous aluminosilicate gels were extremely difficult to follow, a two-step investigation
Table 5.2 (a) The compressive strengths of System III geopolymeric binders

<table>
<thead>
<tr>
<th></th>
<th>Control</th>
<th>KCl</th>
<th>K$_2$CO$_3$</th>
<th>CaCl$_2$</th>
<th>CaCO$_3$</th>
<th>Ca(OH)$_2$</th>
<th>MgCl$_2$</th>
<th>MgCO$_3$</th>
<th>Mg(OH)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>27.4</td>
<td>44.7</td>
<td>39.8</td>
<td>31.4</td>
<td>25.4</td>
<td>25.8</td>
<td>28.4</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>21</td>
<td>38.4</td>
<td>33.3</td>
<td>47.4</td>
<td>37.9</td>
<td>37.0</td>
<td>41.9</td>
<td>29.7</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>90</td>
<td>52.3</td>
<td>29.0</td>
<td>57.2</td>
<td>23.2</td>
<td>63.0</td>
<td>49.3</td>
<td>13.4</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>180</td>
<td>62.3</td>
<td>25.4</td>
<td>65.5</td>
<td>19.3</td>
<td>68.1</td>
<td>55.8</td>
<td>12.1</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>270</td>
<td>65.6</td>
<td>24.9</td>
<td>65.7</td>
<td>18.4</td>
<td>70.0</td>
<td>60.7</td>
<td>12.2</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

Table 5.2 (b) The compressive strengths of System V geopolymeric binders

<table>
<thead>
<tr>
<th></th>
<th>Control</th>
<th>KCl</th>
<th>K$_2$CO$_3$</th>
<th>CaCl$_2$</th>
<th>CaCO$_3$</th>
<th>Ca(OH)$_2$</th>
<th>MgCl$_2$</th>
<th>MgCO$_3$</th>
<th>Mg(OH)$_2$</th>
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<td>12.1</td>
<td>14.5</td>
<td>16.7</td>
<td>18.5</td>
<td>17.9</td>
<td>21.3</td>
</tr>
<tr>
<td>21</td>
<td>22.9</td>
<td>31.7</td>
<td>27.3</td>
<td>22.1</td>
<td>25.0</td>
<td>31.7</td>
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<td>90</td>
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<td>32.8</td>
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<td>39.2</td>
</tr>
<tr>
<td>180</td>
<td>40.3</td>
<td>33.1</td>
<td>38.9</td>
<td>40.3</td>
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<td>47.8</td>
<td>45.2</td>
<td>58.9</td>
<td>43.2</td>
</tr>
<tr>
<td>270</td>
<td>44.1</td>
<td>33.9</td>
<td>45.3</td>
<td>43.2</td>
<td>56.3</td>
<td>51.6</td>
<td>44.2</td>
<td>68.3</td>
<td>45.6</td>
</tr>
</tbody>
</table>

was conducted to understand these processes. Firstly, the major microstructural and chemical changes within the geopolymeric binders were monitored by FTIR, XRD and SEM-EDS. The ‘transformed’ products were then identified accordingly. The information gathered from these microstructural/chemical characterisations should provide valuable insight on how the
aluminosilicate gels were transformed, with and without the inorganic salt contaminations, as will be discussed in Section 5.4.

5.3.2 Sample Crystallinity

From the XRD analyses, it was found that kaolinite was the only major crystalline phase within the starting solid mixture to dissolve significantly in System III binders. All the other crystalline phases remained largely alkali-resistant in System III condition even after 9 months. The 28-day XRD diffractograms of III-Control is shown in Figure 3.17. Note that III-Control was activated with an activating solution (by calculation) of 6.85 M MOH (Na/K = 0.2) and 3.26 M Soluble silicates.

System V binders, on the other hand, were characterised by the complete disappearance of the kaolinite peaks at, for example, d-spacing = 3.570 and 7.142 Å. Extensive dissolution, or loss of crystallinity, of other crystalline phases, such as α-quartz (d-spacing = 3.340 Å), mullite (d-spacing = 3.393 and 3.424 Å) and calcite (d-spacing = 3.029 Å), was also observed as the XRD intensity of their respective characteristic peaks was found to decrease substantially as compared to the starting solid mixture. During the 9-month investigation, it was found that most of the crystalline phase dissolution was completed within the first 7 days of curing in System V binders. This was in clear contrast to the slow and gradual dissolution in System III binders. The dissolution characteristics described here were not unexpected as the activating solution used for System V synthesis was far more alkali-concentrated than System III activating solution.

When the inorganic salts were added, it was found that the crystalline phase dissolution characteristics in the two geopolymeric binder systems were not affected to any significant extent by the inorganic salts as compared to the respective Controls. A new crystalline phase as indicated at d-spacing = 3.011 Å was, however, detected in both of the geopolymeric binder systems contaminated by the chloride salts. See Figure 5.3. This new phase (NP) was found to exist exclusively in the binders contaminated by the chloride salts KCl, CaCl₂ and MgCl₂. Useful information can be further acquired by considering the rate of NP crystallisation: Crystallisation of NP was slow in System III, which required an incubation time of ~6 months before confident identification could be made. On the other hand, the time
Figure 5.3  The XRD diffractograms of the various geopolymeric binders at 9 months. The dotted lines indicate the Ca$_2$SiO$_3$Cl$_2$ crystalline phase, which shows the 2 strongest lines at d-spacing = 3.01 and 3.34 Å.

needed to detect NP was only 21 days in System V. It therefore appears that higher activating solution alkalinity could accelerate the chloride-induced crystallisation processes within a geopolymeric binder.

Finally, the carbonate salts (K$_2$CO$_3$, CaCO$_3$ and MgCO$_3$) and the calcium and magnesium hydroxides appeared to have little effects on the sample crystallinity in both of the geopolymeric binder systems throughout the present investigation.

5.3.3 Infrared Vibrational Characteristics

FTIR spectra of the starting solid mixture (Gladstone fly ash/HR1- kaolinite = 9) and a typical geopolymeric binder are shown in Figure 5.2. By referring to numerous previous studies, the
major vibrational bands from the fly ash/kaolinite mixture can be assigned, which are summarised in Table 3.3. The solid phase transformation within geopolymeric binders was evidenced by, for example, the decrease of the various kaolinite characteristic bands particularly at 914 and 793 cm\(^{-1}\). See also Figure 3.18. Note that the geopolymeric binder shown in Figure 3.18 is the same as \textit{III-Control}. In any case, atmospheric carbonation, which was characteristic at the infrared spectral region 1570-1410 cm\(^{-1}\) [15], was present in all the samples at any sample age. The extent of carbonation, however, was found to decrease with time for all the samples examined in this chapter, indicating that the free alkalis originally present in the geopolymeric binders were consumed by increasing extent of geopolymerisation. See Section 4.3.3.2 for the detailed discussion on the role of free alkalis with atmospheric carbonation inside geopolymeric binders.

The fundamental structural differences between the two \textit{Controls} are demonstrated in Figure 5.4. At 9-months old, they were similar in their respective IR characteristics – both showed the same number of spectral bands and the band positions were exactly the same. However, there were still some fundamental differences between these two binders:

(a) The spectral region at 1380-810 cm\(^{-1}\) of \textit{III-Control} was broader than \textit{V-Control}. This suggests that \textit{System V} was likely to produce more homogeneous geopolymers as a result of a greater silicate structural reorganisation involving the solid starting materials. By comparing the results of the XRD analysis (see Section 5.3.2) and the FTIR analysis, the broader IR band in \textit{III-Control} could be attributed to the less kaolinite dissolution experienced in \textit{III-Control}, as evidenced by the stronger 1104 cm\(^{-1}\) and 914 cm\(^{-1}\) shoulders characteristic of kaolinite crystallites, than \textit{V-Control};

(b) The Si-O bending vibration band at \(\sim 465\) cm\(^{-1}\) was wider in \textit{III-Control} than \textit{V-Control} due to the existence of the strong band at 435 cm\(^{-1}\), which is attributable to the undissolved kaolinite (Table 3.3);

(c) The spectral region at 810-400 cm\(^{-1}\) was stronger in intensity in \textit{III-Control} than \textit{V-Control}; and
Figure 5.4  The FTIR spectra of III-Control and V-Control at 9-months before baseline corrections.

(d) The structure of V-Control included more molecular water (1640 cm$^{-1}$, see Table 3.3), which might be due to the greater alkali content in the pore solution and inhibited water evaporation [5.10].

From Table 5.1, the compressive strengths of the geopolymeric binders were clearly affected by the inorganic salt contaminations. Since the macroscopic strength of an aluminosilicate gel is generally believed to be a function of the nature of its microstructure, as well as the nature of the chemical bonds that constitute the gel [5.2-6], it is therefore expected that the microscopic/chemical characteristics of the inorganic salt-contaminated binders should also differ from those of the Controls accordingly.

Microstructural analysis of these amorphous gels is difficult, as XRD virtually provides no information. Moreover, FTIR without spectral manipulation offers little help in resolving the differences (not shown). After baseline corrections as shown in Figure 5.2, FTIR spectra
Figure 5.5  The 9-months baseline corrected FTIR spectra of (a) before thermal treatment, and (b) after thermal treatment at 105°C for 24 hours. x = III-Control, y = III-CaCO₃, z = III-CaCl₂.

could be used to show the delicate structural evolutions, as well as the fundamental structural deviations of the inorganic salt-contaminated geopolymeric binders from the Controls. See Figure 5.5.
The baseline-corrected FTIR spectra of III-Control, III-CaCl_2 and III-CaCO_3 at 9-months are included in Figure 5.5 (a). It is obvious that the intensity of the spectral region 810-400 cm\(^{-1}\) of III-CaCl\(_2\) was significantly stronger than that of III-Control and III-CaCO_3. This spectral difference could be reduced if the samples were thermal treated at 105°C for 24 hours. From Figure 5.5 (b), the vibrational characteristics of III-Control and III-CaCO_3 were not affected by the thermal treatment at all. However, the intensity of the 810-400 cm\(^{-1}\) spectral region was much reduced in III-CaCl\(_2\) after the thermal treatment. This suggests that whatever was causing the spectral difference between III-CaCl\(_2\) and III-Control, or III-CaCO_3, at 810-400 cm\(^{-1}\) was thermally unstable. Note that the moisture contents as shown at ~1640 cm\(^{-1}\) [5.10] of III-Control and III-CaCl\(_2\) were about the same before and after the thermal treatment. Moisture interference, hence, was unlikely to cause the spectral difference in this region. Therefore, it appears that there was a ‘hidden’ band(s) lying underneath the 810-400 cm\(^{-1}\) region in the unheated III-CaCl\(_2\) sample. This ‘hidden’ band(s), denoted as HB, could be attributed to a separate phase, which could be precipitate(s) in nature and was (were) not network-bonded to the bulk aluminosilicate gel of the geopolymeric binder, if assuming thermal transformation of IR bands is a result of unstable phase(s).

The results obtained from thermal treating III-Control, III-CaCl\(_2\) and III-CaCO\(_3\) as above suggest that the IR spectral region at 810-400 cm\(^{-1}\) can be used to follow the structural evolutions of the various System III geopolymeric binders. As the number and the position of the resolvable IR vibrational bands were found to remain unaffected before and after the thermal treatment, spectral integration on the 810-400 cm\(^{-1}\) region could be very useful in determining whether precipitation of the HB phase could exist in a particular geopolymeric binder system. On top of this, spectral integration was also performed on the 3700-1700 cm\(^{-1}\) spectral region to yield semi-quantitative information on the water/hydroxyl contents of the various System III geopolymeric binders.

The progressive infrared vibrational changes of all the System III geopolymeric binders at 810-400 cm\(^{-1}\) are summarised in Figure 5.6. As the vibrational spectra were found to be similar with one to another at the early stages (before 28 days), the initial structures of the System III geopolymeric binders, with and without inorganic salt contaminations, could be similar in nature. The subsequent structural evolution of the various binders, however, was
Figure 5.6 The relative integrated areas of the 810-400 cm\(^{-1}\) FTIR spectral region for System III geopolymeric binders before thermal treatment. The relative integrated area was calculated by dividing the integrated area of the spectral region of interest by the integrated area of the T-O-Si stretching vibration region 1380-810 cm\(^{-1}\).

greatly affected by the inorganic salt contaminations. The chloride-affected geopolymeric binders (III-KCl, III-CaCl\(_2\) and III-MgCl\(_2\)) were found to deviate greatly from the rest of the binders with a significantly stronger 810-400 cm\(^{-1}\) spectral region. This structural deviation could start as early as 1 month after the geopolymers were made. Apart from HB, the occurrence of the 719 cm\(^{-1}\) IR band was also observed in the System III geopolymeric binders contaminated with the various chloride salts after 1 month, but not others. See Figure 5.5. The assignments of these two spectral bands will be dealt with in Section 5.4. At this stage, it is useful to know that HB, NP and the 719 cm\(^{-1}\) IR band were exclusive to only the chloride-contaminated binders under System III reaction condition.

Contaminations on System III geopolymeric binder by calcium and magnesium hydroxides were found to cause little structural deviations as compared to III-Control, whereas
carbonates (K$_2$CO$_3$ and CaCO$_3$) were effective in reducing the molecular water and/or hydroxyl contents within the binders. See Figure 5.7.

From Table 5.3, a stronger 810-400 cm$^{-1}$ spectral region as compared to that of III-Control was observed for all of the System V geopolymeric binders synthesised, with and without inorganic salt contamination. A ‘hidden’ band (HB’), which was thermally unstable at 105°C for 24 hours (Table 5.3), again could be attributed to the increased intensity within the spectral region 810-400 cm$^{-1}$. It is important to note that HB’ was common in all the System V binders. Chloride contamination did not cause any increase in intensity of this spectral region. This is despite the fact that water evaporation was less in the chloride-contaminated cinders (V-KCl, V-CaCl$_2$ and V-MgCl$_2$) whereas the carbonates (K$_2$CO$_3$, CaCO$_3$ and MgCO$_3$) were effective to reduce the water and/or hydroxyl contents in the binders.
Table 5.3 The relative integrated areas of the IR spectral regions before and after thermal treating pulverised geopolymeric binders at 9-months at 105°C for 24 hours

<table>
<thead>
<tr>
<th>System</th>
<th>Spectral region (cm⁻¹)</th>
<th>Control</th>
<th>CaCl₂</th>
<th>CaCO₃</th>
<th>Ca(OH)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before</td>
<td>810-400</td>
<td>0.25</td>
<td>0.53</td>
<td>0.23</td>
<td>0.28</td>
</tr>
<tr>
<td>heating</td>
<td>3700-2700</td>
<td>2.97</td>
<td>3.80</td>
<td>2.40</td>
<td>2.75</td>
</tr>
<tr>
<td>After</td>
<td>810-400</td>
<td>0.23</td>
<td>0.32</td>
<td>0.19</td>
<td>0.21</td>
</tr>
<tr>
<td>heating</td>
<td>3700-2700</td>
<td>1.07</td>
<td>1.41</td>
<td>0.87</td>
<td>0.89</td>
</tr>
</tbody>
</table>

5.3.4 Microscopic Morphology

The SEM micrograph of III-CaCl₂ at 9-months is shown in Figure 5.8. It was found that the structure of the chloride-contaminated binder was clearly divided into two regions.

The right-hand side of Figure 5.8 shows the normal geopolymeric binder, which according to SEM-EDS analysis, contained traces of chlorine presumably from the added inorganic salt. Although the chloride-affected gel was found to resemble closely the III-Control gel (see Figure 3.16. Note that the geopolymeric binder shown in Figure 3.16 is the same as III-Control), the chloride-affected gel, including those in III-KCl and III-MgCl₂, was found to contain more precipitates, which were clearly not bonded to the aluminosilicate gel binding phase. These precipitates were exclusive to only the chloride-contaminated gels (III-KCl, III-CaCl₂ and III-MgCl₂), which can be expected to cause structural discontinuity within the aluminosilicate gel and consequently lowered the compressive strengths of the chloride-affected binders as shown in Table 5.2 (a). As the precipitates were only observed in the chloride-contaminated gels after 90 days, which corresponds to the initiation of the product deteriorations observed from the compressive strength measurements (Table 5.2 (a)), it
Figure 5.8  The BSE-SEM micrograph of III-CaCl$_2$ at 9-months. The white dotted circles indicate where the SEM-EDS analyses were performed.

appears that the occurrence of these precipitates could be responsible for the decrease of durability of the chloride-contaminated System III binders III-KCl, III-CaCl$_2$ and III-MgCl$_2$. This aspect will be further discussed in Section 5.4. Note also that no such precipitates were found in any of the other System III binders.

At the left-hand side of Figure 5.8, on the other hand, a structure of greater brightness under BSE-SEM with less gel voids, which are usually caused by the dissolved fly ash particles, was again exclusive to the chloride-contaminated binders (III-KCl, III-CaCl$_2$ and III-MgCl$_2$) after 90 days. No such structure could be identified in any of the other System III binders at any sample age. The results of SEM-EDS on this chloride-infected region, or CR, at 9-months are presented in Table 5.4. CR was clearly abundant in potassium and chlorine.

Precipitation, in contrast to System II geopolymeric binders, was common in all the System V binders at all ages. See Figure 5.9. Similar to III-KCl, III-CaCl$_2$ and III-MgCl$_2$, the aluminosilicate gel structural continuity of all System V binders was adversely affected by these precipitates. Consequently, lower compressive strengths were observed in all System V binders as compared to the System III counterparts except for the chloride-contaminated binders III-KCl, III-CaCl$_2$ and III-MgCl$_2$. This is despite the fact that the System V activating solution was more alkali-concentrated than that of System III. As indicated by the XRD and
Figure 5.9  The BSE-SEM micrograph of V-Control at 21-days. The white dotted circle indicates where the SEM-EDS analysis was performed.

Table 5.4  The results of the SEM-EDS analyses

<table>
<thead>
<tr>
<th>Element</th>
<th>Gel in III-CaCl₂</th>
<th>CR in III-CaCl₂</th>
<th>Fly ash in V-Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>39.95</td>
<td>25.41</td>
<td>37.98</td>
</tr>
<tr>
<td>Al</td>
<td>10.70</td>
<td>5.22</td>
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<tr>
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<td>8.06</td>
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<tr>
<td>Ca</td>
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</tr>
<tr>
<td>Mg</td>
<td>0.18</td>
<td>-0.03</td>
<td>0.09</td>
</tr>
<tr>
<td>Na</td>
<td>1.54</td>
<td>0.25</td>
<td>1.46</td>
</tr>
<tr>
<td>K</td>
<td>11.72</td>
<td>26.35</td>
<td>14.14</td>
</tr>
<tr>
<td>Cl</td>
<td>2.89</td>
<td>27.55</td>
<td>0.25</td>
</tr>
</tbody>
</table>

FTIR analyses, fly ash dissolution in System V was quite extensive. The larger fly ash particles, which were insoluble in System III binders, were dissolved and replaced by the precipitates shown at the top right-hand corner of Figure 5.9 marked with a white dotted circle. The SEM-EDS analysis in Table 5.4 shows that the composition of the reacted fly ash particle was very similar to the surrounding gel, which was potassium aluminosilicate(s) with minor impurities such as Na.
5.4 MECHANISM OF GEL DETERIORATION PROCESSES IN GEOPOLYMERIC BINDERS

The combined results from the XRD, FTIR and SEM-EDS analyses above suggest that the chloride salts (KCl, CaCl₂ and MgCl₂) could induce crystallisation and/or precipitation within a geopolymeric system. A new crystalline phase NP was found in both of the geopolymer systems investigated (Systems III and V), which was exclusive to only the chloride-contaminated geopolymeric binders. However, the incubation time for NP was much shorter in System V than System III. The fact that NP, HB and CR were only detected in the chloride-contaminated System III binders may intuitively suggest that these phases could belong to the same phase. This, however, is not the case after careful considerations on the analytical capabilities of the techniques employed.

As CR was shown to mainly consist of potassium and chlorine according to the SEM-EDS analysis presented in Table 5.4, whose chemical bonds are infrared inactive in the mid-infrared range [5.7, 5.11], it is unlikely that CR could cause the significant spectral change at the 810-400 cm⁻¹ IR spectral region as shown in Figure 5.5 (a), which was otherwise assigned to HB in Section 5.3.3. Hence, HB and CR should be attributed to two different phases. The fact that HB’ existed in all the System V binders (see Section 5.3.3) further suggests that HB’ is not the same as NP since HB’ was not exclusive to the chloride-contaminated System V binders. The chloride salts thus may cause crystallisation on some certain phases which incorporate chlorine atoms in the structures to produce the NP crystalline phase exclusive only to the chloride-contaminated binders.

The absolute identification of NP is still not possible without rigorous phase separation operations. Nevertheless, the most likely suspect for NP is calcium silicate chloride (Ca₂SiO₃Cl₂) with the 2 strongest XRD bands at d-spacing = 3.01 and 3.34 Å, which was found to match the XRD patterns of the chloride-contaminated binders. See Figure 5.3. As Ca₂SiO₃Cl₂, or chlorinated dicalcium silicate, is likely to exist as a ring structure with the characteristic IR bands located at 780-500 cm⁻¹ [5.20], the 719 cm⁻¹ IR band observed in the chloride-contaminated System III binders, as well as in the chloride-contaminated System V binders (not shown), could be assigned to Ca₂SiO₃Cl₂. As will be shown in Chapter 6, this chloride-induced crystallisation can be very useful for the investigation of the macroscopic...
interface between siliceous aggregates and geopolymeric binders. See also Chapter 8 for the possible identity and the formation mechanism of the chloride-induced crystallisation.

Sinkó et al. [5.12] had previously conducted a structural analysis on aluminosilicate gels of the same Al/Si ratio but different preparation methods using combined FTIR, NMR and SAXS (small angle x-ray spectroscopy) techniques. They showed that if the Al was not incorporated into the parent silica gel through network substitution, in other words, the parent silica gel was ‘network modified’ by Al, its infrared spectrum was characterised by a stronger 800-400 cm⁻¹ spectral region as compared to the aluminosilicate gel in which Al was bonded through network substitution. This Al network-modified aluminosilicate gel was found to consist of mainly ‘isolated’ units of Al⁶⁺O₆ with minor amount of Al⁴⁺O₄ [5.12-14], which is typical of neso-, cyclo- and ino-aluminosilicates [5.7, 5.13] (see also Section 3.1.2.4) and may be precipitates in nature. Consequently, the overall spectrum appeared to be a combination of two separate phases – pure silica gel and, in Sinkó et al.’s case [5.12], aluminium salt of nitrate (Al(NO₃)₃.9H₂O). The assumption that there was a ‘hidden’ band located at the 810-400 cm⁻¹ spectral region attributable to a separate phase HB in III-CaCl₂ at 9-months (Figure 5.5), and HB’ in all of the System V binders (Table 5.5), is therefore valid. A separate experiment had shown that the intensity of these hidden bands, HB and HB’, could be greatly reduced if the pulverised samples were washed in distilled water for 6 hours. This further strengthens the argument that HB and HB’ could exist in the aluminosilicate gels within geopolymeric binders as separate phases, which could be aluminosilicate precipitates that were readily removable by water leaching.

From Figure 5.7 and Table 5.3, the water and/or hydroxyl contents of the chloride-contaminated System III binders (III-KCl, III-CaCl₂ and III-MgCl₂), and all of the System V binders investigated in this chapter, were significantly greater than that of III-Control. It seems that the greater water contents in these binders might have caused the formation of the HB and the HB’ phases. According to Takata et al. [5.15], the mobility of Na⁺ ions in sodium silicate glasses was found to increase with increasing dissolved water content within the silicate structure (the molecular water physically bound to surface silanols –Si-OH). A greater basicity was thus induced not only to the non-bridging oxygens (NBO) but also to the bridging oxygens as well, which labilised/weakened the T-O-Si bonds (T = Si and Al) within the silicate network. Consequently, the chance of hydrolytic attack on the silicate structure is
increased by the increased dissolved water content that facilitates ion-exchange reactions through the following simplified reactions [5.16]:

\[
\begin{align*}
\equiv \text{Si-O}^+ \text{Na}^+ + \text{HOH} & \rightarrow \equiv \text{Si-OH} + \text{Na}^+ + \text{OH}^- \\
\equiv \text{Si-O-Si} & + \text{OH}^- \rightarrow \equiv \text{Si-OH} + \equiv \text{Si-O}^- \\
\equiv \text{Si-O}^- + \text{HOH} & \rightarrow \equiv \text{Si-OH} + \text{OH}^- 
\end{align*}
\]

The phenomena of increased hydrolytic attack, or glass corrosion, on alkali silicate glasses through ion-exchange reactions, which exchanged the network modifying Na\(^+\) for H\(^+\), were also confirmed by Clark et al. [5.17] and Tomozawa et al. [5.18].

According to Rahier et al. [5.19] as well as the work conducted in this thesis, see Chapter 9, the structure and the chemistry of the hardened geopolymeric binders activated by activating solutions of SiO\(_2\)/M\(_2\)O > ~0.2 (M = Na and K) are similar to those of the conventional alkali silicate/aluminosilicate glasses. As Systems III and V geopolymeric binders were both activated with activating solutions of SiO\(_2\)/M\(_2\)O > 0.2 (SiO\(_2\)/M\(_2\)O = ~0.48 for System III and ~0.39 for System V), the chloride-induced gel deterioration processes observed in III-KCl, III-CaCl\(_2\) and III-MgCl\(_2\) (Table 5.2 (a)) could therefore be attributed to the relatively high dissolved water contents of the chloride-contaminated binders as compared to other System III binders (Table 5.3 and Figure 5.7). Furthermore, the deterioration products, such as silicate and/or aluminosilicate precipitates, could also be assigned to HB, which was only observed in the chloride-contaminated System III binders. From the same reasoning, it is also possible that HB' in System V geopolymeric binders might be silicate and/or aluminosilicate precipitates produced as a result of hydrolytic attacks initiated by the ion-exchange process of eq (5.1-3) due to the high dissolved water content in the gel structure, which is inherent to a system activated with high solution alkalinity [5.21].

Though not presented in this thesis, \(^{29}\text{Si}\) and \(^{27}\text{Al}\) magic-angle-spinning (MAS) NMR conducted as a separate study did not reveal nearly as clear a result as the IR analyses presented in this chapter. Structural heterogeneity and low crystallinity of geopolymeric binders had caused significant peak broadening in the NMR spectra collected, which masked the capability of such technique to detect any structural differences in the geopolymeric binders before and after product deterioration. A future experiment should be designed to
understand the role of the dissolved water, and the maximum dissolved water content allowable in the aluminosilicate gels of geopolymeric binders.

### 5.5 CONCLUSIONS

The combined results of the experimental programme employed in this chapter, which involves mechanical and microstructural/chemical characterisation, have been shown to provide valuable and novel explanation on the gel deterioration processes within geopolymeric binders.

If a geopolymeric binder was synthesised by activating aluminosilicate powders with an activating solution over-saturated with alkalis, such as *System V*, gel deterioration could start at a very early sample age to produce aluminosilicate precipitates of little interparticle strengths. This then rendered the binder a low ultimate strength. From the various experimental observations and from the alkali silicate glass literature, the most likely gel deterioration mechanism in this geopolymeric binder is a hydroxyl-promoted hydrolytic attack on the silicate/aluminosilicate bridging oxygens, which was initiated by ion-exchange of the network modifiers such as Na$^+$ and K$^+$ for H$^+$ of the surface silanols due to excessive dissolved water content inside the geopolymerised aluminosilicate gel. In other words, the aluminosilicate gel was phase separated by the excessive free hydroxyl present. The possibility of phase separation within a geopolymeric gel matrix will be further investigated in Chapter 9.

The experimental results presented in this chapter also suggest that inorganic salt contamination during processing was not detrimental to the resultant geopolymeric binder provided that chloride salts were not present. The effects of chloride-contamination could be two-fold. Firstly, it promoted aluminosilicate gel deterioration possibly through water-initiated hydrolytic attack on the gel, giving rise to aluminosilicate precipitates and lowered the binder durability. The processes involved here could be similar to those experienced in the alkali over-saturated system as mentioned above. Secondly, crystallisation of possibly
Ca$_2$SiO$_3$Cl$_2$ was also present in the chloride-contaminated binders, which will be further investigated in Chapter 8.

5.6 REFERENCES


[5.6] Yip, C. K.; Van Deventer, J. S. J. Effect of Granulated Blast Furnace Slag on Geopolymerisation, in CD-ROM Proceedings of the 6th World Congress of Chemical Engineering, Melbourne, Australia, **2001**.


As discussed in Chapter 2, addition of natural aggregates such as crushed stones to a Portland cement binder is a cost effective method to improve the material properties such as compressive strength and fracture toughness. Systematic research on the effects of aggregate addition on the material properties of geopolymers, however, is still lacking in the current geopolymer literature. Hence, this chapter is dedicated to study the effects of both fine and coarse aggregate additions on one of the most important properties of geopolymeric products – compressive strength. In addition, the macroscopic interface between natural aggregates and geopolymeric binders will be investigated both microstructurally as well as mechanically in this chapter. The formation mechanism of the macroscopic interface will be presented in Chapter 10.

6.1 INTRODUCTION

Over the last decade, much research has been conducted on the chemical, mechanical and microstructural aspects of geopolymers [6.1-4]. Little attention, however, has been paid to study the interactions between mineral aggregates and geopolymeric binders. As the macroscopic interface (ITZ) in an ordinary Portland cement (OPC) system is the weakest region of the whole mortar/concrete structure (see Section 2.1.6 for a more detailed discussion on the nature and the formation mechanism of ITZ as well as the failure mechanism), it is not surprising that the lack of current understanding on the nature and the properties of the
macroscopic interface within geopolymeric mortars/concretes is one of the major drawbacks for their practical applications.

This chapter, therefore, is aimed to microstructurally and mechanically characterise the macroscopic interface within geopolymeric mortars/concretes, using the experimental program presented in Section 3.3.2. Furthermore, the inter-relationships between the overall mechanical strength of geopolymeric mortars/concretes and the macroscopic interface will also be examined. This is achieved by fixing the solid starting material used for the geopolymeric binder synthesis (Gladstone fly ash/KR1-kaolinite = 9) while systematically modifying the solution alkalinity, soluble silicate concentration and inorganic salt contamination of the activating solution. The natural aggregates used in this chapter include siliceous sand, basalt and siltstone.

In Chapters 4 and 5, solution alkalinity and solution contamination by inorganic salts have been shown to cause significant variations on the material properties of geopolymeric binders. Inorganic salts of chlorides were particularly effective in causing aluminosilicate gel precipitation and crystallisation (Chapter 5). Though unfavourable in practical situations, the chloride-induced precipitation and crystallisation can be very a useful tool for the study of the macroscopic interface in geopolymeric systems, as will be presented below.

### 6.2 MATERIALS AND EXPERIMENTAL METHODS

#### 6.2.1 Materials

Gladstone fly ash and HR1-grade kaolinite were used as the solid raw materials for geopolymeric binder synthesis. Laboratory-grade reagents (NaOH, KOH, KCl and K$_2$CO$_3$) were obtained from Ajax Chemicals Australia. Vitrosol N(N40)$^\circledR$ sodium silicate solution and distilled/deionised water were used to prepare the activating solutions. Siliceous sand, basalt and siltstone were used as the fine and coarse aggregates for geopolymeric mortar and concrete syntheses.
6.2.2 Synthesis of Geopolymeric Products

The methods of geopolymeric binder syntheses and the inorganic salt contaminations in this chapter are the same as those of Chapters 4 and 5. See Sections 4.2.2 and 5.2.2. Briefly, the starting solid raw material employed in this chapter was a mixture of Gladstone fly ash and HR1-grade kaolinite at a mass (fly ash/kaolinite) ratio of 9 for all the geopolymeric binder syntheses. Geopolymeric mortars were prepared by adding 2 parts (by weight) of sand to 1 part (by weight) of the geopolymeric binders. One part (by weight) of coarse aggregates was then added to 1 part (by weight) of the mortars to produce geopolymeric concretes. See Sections 3.2.2 and 3.2.3 for the more detailed synthesis methods for geopolymeric mortars and concretes. The compositions of the geopolymeric binders, mortars and concretes are summarised in Table 6.1.

Note that the sample labelling system employed in this chapter is slightly different from the rest of the thesis due to the obvious complexity of the geopolymeric products produced. In this chapter, System I-5-2.5 denotes the geopolymeric binder which was synthesised by activating the fly ash/kaolin mixture with an activating solution of 5 M hydroxyl (OH) and 2.5 M soluble silicates. System II-10-2.5 denotes the geopolymeric mortar that was synthesised by adding the required amount of sand to the binder I-10-2.5. System III-10-2.5-B is the geopolymeric concrete produced by adding basalt (B) coarse aggregates to mortar II-10-2.5. The geopolymeric products were cured at 40 ± 3°C for 24 hours. The samples were then demoulded and cured at 20 ± 3°C and a relative humidity of 50 ± 5% under atmospheric pressure until testing.

The sandwich specimens for the macroscopic interfacial bonding strength determination using the method of interfacial three-point bending were prepared in accordance with Section 3.3.2.1. When the II-5-2.5 mortar was glued to basalt (B), the resultant sandwich specimen was named B&II-5-2.5. Similarly, if siltstone (S) was used, the specimen was named S&II-5-2.5.
Table 6.1  The calculated mass compositions of the geopolymeric products

<table>
<thead>
<tr>
<th>System a, b, c</th>
<th>Activating Solution d</th>
<th>Aggregate e</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[OH]₀ (M)</td>
<td>[SiO₂]₀ (M)</td>
</tr>
<tr>
<td>I-5-0</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>I-5-0.5</td>
<td>5</td>
<td>0.5</td>
</tr>
<tr>
<td>I-5-1</td>
<td>5</td>
<td>1.0</td>
</tr>
<tr>
<td>I-5-2.5</td>
<td>5</td>
<td>2.5</td>
</tr>
<tr>
<td>I-5-2.5-Cl</td>
<td>5</td>
<td>2.5</td>
</tr>
<tr>
<td>I-5-2.5-CO₂</td>
<td>5</td>
<td>2.5</td>
</tr>
<tr>
<td>I-10-0</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>I-10-0.5</td>
<td>10</td>
<td>0.5</td>
</tr>
<tr>
<td>I-10-1</td>
<td>10</td>
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</tr>
<tr>
<td>I-10-2.5</td>
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<td>2.5</td>
</tr>
<tr>
<td>I-10-2.5-Cl</td>
<td>10</td>
<td>2.5</td>
</tr>
<tr>
<td>I-10-2.5-CO₂</td>
<td>10</td>
<td>2.5</td>
</tr>
<tr>
<td>II-5-0</td>
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<td>0</td>
</tr>
<tr>
<td>II-5-0.5</td>
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<tr>
<td>II-5-1</td>
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<td>1.0</td>
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<td>0</td>
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</tr>
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</tr>
<tr>
<td>II-10-2.5</td>
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<td>2.5</td>
</tr>
<tr>
<td>III-5-2.5-Cl-B</td>
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<td>2.5</td>
</tr>
<tr>
<td>III-5-2.5-CO₂-B</td>
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<td>2.5</td>
</tr>
<tr>
<td>III-5-2.5-S</td>
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<td>2.5</td>
</tr>
<tr>
<td>III-5-2.5-Cl-S</td>
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<td>2.5</td>
</tr>
<tr>
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<td>2.5</td>
</tr>
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<td>III-10-2.5-S</td>
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</tr>
<tr>
<td>III-10-2.5-CO₂-S</td>
<td>10</td>
<td>2.5</td>
</tr>
</tbody>
</table>

a I = binder; mass (solid/solution) ratio, excluding aggregates, is 2; mass (fly ash/kaolin) ratio is 9.
b II = mortar; mass (binder/sand) ratio is 0.5.
c III = concrete; mass (mortar/coarse aggregate) ratio is 1.
d The overall molar (Na/K) ratio is 0.2.
e B = basalt, S = siltstone, and T = siliceous sand.
6.2.3 Characterisation of Geopolymeric Products

6.2.3.1 Mechanical characterisation

Uniaxial compression was used to obtain the compressive strengths of the geopolymeric binders from 7 days up to 90 days. See Section 3.2.4.3 for the detailed testing method. An interfacial three-point bending test (see Section 3.3.2.1) was performed on the rock aggregate-mortar specimens to obtain the macroscopic interfacial bonding strengths.

6.2.3.2 Microstructural characterisation

SEM-EDS was employed to characterise the microstructures of the hardened geopolymeric products from 7 days up to 9 months. The rock aggregate-mortar/binder sandwich samples were cut cross-sectionally, lightly polished and carbon-coated before micrographs were taken. The micrographs of the geopolymeric binders were taken on freshly fractured samples.

6.3 GENERAL CHARACTERISTICS

6.3.1 Salt-Free Systems

6.3.1.1 Mechanical characteristics

The results of the compressive strength tests on the various geopolymeric binders, mortars and concretes are summarised in Table 6.2. From Table 6.2, it was found that when the soluble silicate dosage in the activating solution ([SiO$_2$]$_0$) was below 2.5 M, the resultant salt-free geopolymeric binders and mortars were mechanically weak regardless of the solution alkalinity ([OH$^-$_]$_0$). On the other hand, the product compressive strength was found to increase with increasing solution alkalinity at [SiO$_2$]$_0$ = 2.5 M. From these observations, it is clear that the product mechanical performance of geopolymeric binders and mortars is a function of both the solution alkalinity and the soluble silicate dosage of the activating solution, which is consistent with the existing literature [6.1, 6.5, 6.6].
Table 6.2 The compressive strengths of the geopolymeric products

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Compressive Strength (MPa)</th>
<th>7 days</th>
<th>28 days</th>
<th>90 days</th>
</tr>
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<tbody>
<tr>
<td>I-5-0</td>
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<td>6.4</td>
<td></td>
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<tr>
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<td>7.0</td>
<td>6.4</td>
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<tr>
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<td>25.3</td>
<td>21.2</td>
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<td>34.5</td>
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<td>50.7</td>
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<td></td>
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</tbody>
</table>

*a* Values too low to register.

*b* Not tested.
Figure 6.1 The compressive strengths of the salt-free binders (I) versus the mortars (II) for the geopolymeric systems at two alkali concentrations ([OH\(^-\)] = 5 and 10 M) for 0, 0.5, 1.0 and 2.5 M of soluble silicates added.

Figure 6.1 shows that when a 5 M OH\(^-\) activating solution was used, addition of siliceous sand to a salt-free geopolymeric binder was detrimental to the overall product mechanical performance irrespective of the soluble silicate dosage used. This result is surprising as the compressive strength of the OPC systems is normally increased through the addition of aggregates [6,7]. On the other hand, if 10 M OH\(^-\) activating solutions were used, the geopolymeric mortars were stronger than their binder counterparts for all the soluble silicate dosages investigated. If assuming the differences between the 5 M OH\(^-\) and 10 M OH\(^-\) geopolymeric systems were due to the differences in the interfacial bonding capacity between the fine aggregates and the binders, it is possible that the alkali concentration in the activating solution could determine whether an aluminosilicate gel produced by alkali-activating aluminosilicate solids (fly ash and kaolin) is likely to bind to natural aggregates. This aspect will be further discussed in Section 6.4.
The inter-relationships between the geopolymeric mortar and the concrete counterpart synthesised from the same geopolymeric binder are presented in Figure 6.2. It was found that the compressive strengths of geopolymeric mortars were approximately the same as those of the concretes, irrespective of the solution alkalinitities used. Again, this observation is inconsistent with the OPC systems where OPC concretes are normally stronger than the mortar counterparts [6.7]. It is therefore obvious that the chemical and/or physical interactions between mineral binders and siliceous aggregates in geopolymeric systems are tremendously different as compared to the OPC systems. Figure 6.2 further shows that the geochemical nature, such as mineralogy, porosity and water absorptivity etc. (see Section 3.4), of the coarse aggregates (basalt or siltstone) appeared to have little effects on the overall geopolymeric concrete compressive strength. This is consistent with the previous experience on the normal OPC concretes [6.7]. In high performance concretes (see Section 2.1.6 for the

**Figure 6.2** The time evolution of compressive strengths of the salt-free binders (I), the mortars (II) and the concretes (III) for the geopolymeric systems at two alkali concentrations ([OH]₀ = 5 and 10 M).
Table 6.3 The interfacial bonding strength of the rock & geopolymeric mortar sandwich specimens at 28 days

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Interfacial Bonding Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B&amp;II-5-0</td>
<td>0.435</td>
</tr>
<tr>
<td>B&amp;II-5-2.5</td>
<td>0.428</td>
</tr>
<tr>
<td>S&amp;II-5-0</td>
<td>0.411</td>
</tr>
<tr>
<td>S&amp;II-5-2.5</td>
<td>1.273</td>
</tr>
<tr>
<td>B&amp;II-10-0</td>
<td>0.565</td>
</tr>
<tr>
<td>B&amp;II-10-0.5</td>
<td>0.579</td>
</tr>
<tr>
<td>B&amp;II-10-1</td>
<td>1.112</td>
</tr>
<tr>
<td>B&amp;II-10-2.5</td>
<td>1.048</td>
</tr>
<tr>
<td>B&amp;II-10-2.5-CI</td>
<td>1.056</td>
</tr>
<tr>
<td>B&amp;II-10-2.5-CO₃</td>
<td>0.565</td>
</tr>
<tr>
<td>S&amp;II-10-0</td>
<td>0.405</td>
</tr>
<tr>
<td>S&amp;II-10-0.5</td>
<td>1.048</td>
</tr>
<tr>
<td>S&amp;II-10-1</td>
<td>1.056</td>
</tr>
<tr>
<td>S&amp;II-10-2.5-CI</td>
<td>0.565</td>
</tr>
<tr>
<td>S&amp;II-10-2.5-CO₃</td>
<td>1.056</td>
</tr>
</tbody>
</table>

brief discussion of the synthesis methods), however, the geochemical properties and surface roughness of the coarse aggregates have been known to significantly affect the overall mechanical performance of concrete including compressive strength, flexural strength and fracture toughness [6.8-10].

From Table 6.2 and Figures 6.1 and 6.2, it seems that an activating solution of both high solution alkalinity and soluble silicate dosages is an absolute necessity to produce mechanically strong geopolymeric mortars and concretes that are stronger than the constituent binders. From Table 6.3, similar conclusions can also be drawn from the three-point bending experiments on the aggregate & salt-free mortar sandwich specimens.

When the activating solution was low in solution alkalinity and/or soluble silicate concentration, the interfacial bonding strengths between the rock slices (basalt and siltstone) and the corresponding salt-free geopolymeric mortars were also low. Furthermore, it seems that the basalt always yielded a slightly stronger interfacial bonding strength than the siltstone. This difference, however, was too small to cause significant differences in the respective concrete compressive strengths as shown in Table 6.2 and Figure 6.2.
Figure 6.3 The binder (I) compressive strength versus mortar (II) compressive strength (f'_c) and macroscopic interfacial bonding strength (f'_i) for the salt-free geopolymeric systems activated at 5 M OH⁻ at 28 days.

Trende and Büyüköztürk [6.10], using similar specimen dimensions as this work but with a Mode I four-point bending set-up, showed that the 7-days interfacial bonding strength between a smooth granite aggregate slice and a high-strength cement mortar (81.1 MPa in 7 days) was 0.503 MPa. The interfacial bonding strength obtained as such is only ~40 % of the 28-days interfacial bonding strength of the B&II-10-2.5 sandwich specimen of this work (1.273 MPa, Mode I three-point bending), whose mortar (II-10-2.5) compressive strength at 28 days was only 48.2 MPa (Table 6.2), which was ~60 % of Trende and Büyüköztürk’s [6.10]. Although direct comparison of the present work with that of Trende and Büyüköztürk [6.10] should be conducted with caution due to the obvious differences in the experimental set-up, sample age, rock types, and maybe the aggregate surface roughness as well, it nevertheless appears that the geopolymeric binders activated with high concentrations of alkalis and soluble silicates were effective to produce very strong macroscopic interfaces between natural siliceous rocks and geopolymeric mortars.
Figure 6.4 The binder (I) compressive strength versus concrete (III) compressive strength ($f'_{c}$) and macroscopic interfacial bonding strength ($f'_{i}$) for the salt-free geopolymeric systems activated at 10 M OH$^{-}$ at 28 days.

Furthermore, the results of the experimental programme described above (Tables 6.2 and 6.3 and Figures 6.1 and 6.2) suggest that a strong geopolymeric binder may not necessarily give rise to a strong mortar, concrete and/or the macroscopic interface. For example, although the 28-days compressive strength (Table 6.2) of binder I-5-2.5 (36.6 MPa) was significantly higher than that of I-10-1 (10.8 MPa), the macroscopic interfacial bonding strengths of the corresponding sandwich specimens S&II-5-2.5 (0.428 MPa) and S&II-10-1 (0.405 MPa) were similar (Table 6.3); on the other hand, the 28-days compressive strength of the corresponding mortar II-5-2.5 (15.6 MPa) was lower than that of II-10-1 (26.6 MPa). From this observation, it appears that there was no direct relationship between the strengths of geopolymeric binders, mortars, concretes and/or the macroscopic interface. If, however, the data were plotted separately as shown in Figures 6.3 ($[\text{OH}^-]_0 = 5$ M) and 6.4 ($[\text{OH}^-]_0 = 10$ M), it was found that a stronger salt-free binder was always associated with a stronger macroscopic interface as well as a stronger mortar (Figure 6.3), or concrete (Figure 6.4).
6.3.1.2 Microstructural characteristics

The SEM images taken on the polished siltstone and the polished rock & salt-free mortar sandwich specimens are shown in Figures 6.5 to 6.12. At $[\text{OH}^-]_0 = 10 \text{ M}$ and $[\text{SiO}_2]_0 = 0 \text{ M}$, the macroscopic interface between the siltstone aggregate and the geopolymeric binder I-10-0 appears to be very porous (Figure 6.6). When the soluble silicate dosage was increased from 0 to 2.5 M at the same solution alkalinity (Figures 6.6 to 6.10), it can be seen that the salt-free binder near the interface gradually became denser with increasing soluble silicate dosage. This observation agrees well with the macroscopic interfacial bonding strengths presented in Table 6.3. The greater the soluble silicate dosage at a certain solution alkalinity, the denser was the aggregate & binder macroscopic interface, and hence the greater was the macroscopic interfacial bonding strength.

By comparing the BSE-SEM images of the sandwich specimens to those of the bulk reference binders (not shown), which were prepared separately under the same experimental conditions as those of the sandwich specimens, it was found that the morphologies of all the macroscopic interfaces shown in Figures 6.6 to 6.12 resembled those of the reference binders. A similar conclusion could also be drawn from the systems using basalt as the rock slice (not shown). In conclusion, it appears that the topographical characteristics of the macroscopic interface in salt-free geopolymeric systems are similar to those of the bulk geopolymeric binder, in agreement with other observations on alkali-activated systems [6.11-13]. This is in stark contrast to what has been observed in the normal OPC systems (see Section 2.1.6).

The results of the elemental composition analyses provided by SEM-EDS on the various phases in the rock & mortar sandwich specimens are summarised in Table 6.4. The various rock phases were crudely assigned based on the respective elemental compositions and from the optical microscopy (not shown). From Table 6.4, it is clear that the mica/clay as shown in Figure 6.6 (not differentiable using the current techniques. However, from the results obtained in Chapter 10, it is most likely to be clay) had acquired significant amounts of Na from the nearby alkaline pore solution. (The unreacted mica/clay contained only 0.24 % of Na and 0.32 % of K, whereas the mica/clay in Figure 6.7 contained 12.56 % of Na and 0.88 % of K.) By comparing the SEM images of the sandwich specimen (Figure 6.6) with the fresh rock
Figure 6.5  The BSE-SEM image of the mica/clay region (F) of the fresh siltstone (S).

Figure 6.6  The BSE-SEM image of the sandwich specimen S&II-10-0. F = mica/clay, I = binder I-10-0 and II = mortar II-10-0. The block arrows indicate where SEM-EDS analyses were taken.
Figure 6.7  The BSE-SEM image of the sandwich specimen S&II-10-0. Q = quartz, I = binder I-10-0 and II = mortar II-10-0. The block arrows indicate where SEM-EDS analyses were taken.

Figure 6.8  The BSE-SEM image of the sandwich specimen S&II-10-0.5. Q = quartz, I = binder I-10-0.5 and II = mortar II-10-0.5. The block arrows indicate where SEM-EDS analyses were taken.
Figure 6.9  The BSE-SEM image of the sandwich specimen S&II-10-1. Q = quartz, I = binder I-10-1 and II = mortar II-10-1. The block arrows indicate where SEM-EDS analyses were taken.

Figure 6.10  The BSE-SEM image of the sandwich specimen S&II-10-2.5. Q = quartz, I = binder I-10-2.5, II = mortar II-10-2.5 and T = sand. The block arrows indicate where SEM-EDS analyses were taken.
Figure 6.11  The BSE-SEM image of the sandwich specimen S&II-10-2.5. F = mica/clay, I = binder I-10-2.5 and II = mortar II-10-2.5.

Figure 6.12  The SEM image of the sandwich specimen S&II-5-2.5. Q = quartz, I = binder I-5-2.5 and II = mortar II-5-2.5 and T = sand. The block arrows indicate where SEM-EDS analyses were taken.
Table 6.4 The SEM-EDS analysis of the siltstone & mortar sandwich specimens at 28 days

<table>
<thead>
<tr>
<th>Element</th>
<th>Figure 6.6 S &amp; II-10-0</th>
<th>Figure 6.7 S &amp; II-10-0</th>
<th>Figure 6.8 S &amp; II-10-0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F (^{a}) (%)</td>
<td>Binder (%)</td>
<td>Q (^{b}) (%)</td>
</tr>
<tr>
<td>O</td>
<td>48.79 46.81 53.91</td>
<td>Before After</td>
<td>48.20 48.08 55.33</td>
</tr>
<tr>
<td>Si</td>
<td>36.98 29.45 14.17</td>
<td>50.35 50.60 4.33</td>
<td>0.00 0.00 2.08</td>
</tr>
<tr>
<td>Al</td>
<td>11.05 8.60 5.08</td>
<td>0.00 0.00 2.08</td>
<td>0.00 0.00 2.08</td>
</tr>
<tr>
<td>Fe</td>
<td>0.55 0.63 1.93</td>
<td>0.35 0.45 2.41</td>
<td>0.02 0.00 7.77</td>
</tr>
<tr>
<td>Ca</td>
<td>0.80 0.42 3.90</td>
<td>0.00 0.00 0.03</td>
<td>0.00 0.00 0.00</td>
</tr>
<tr>
<td>Mg</td>
<td>0.71 0.00 0.11</td>
<td>0.00 0.00 0.07</td>
<td>0.00 0.00 0.00</td>
</tr>
<tr>
<td>Na</td>
<td>0.24 12.56 0.18</td>
<td>0.00 0.00 0.00</td>
<td>0.00 0.00 0.00</td>
</tr>
<tr>
<td>K</td>
<td>0.32 0.88 19.34</td>
<td>0.42 0.41 25.72</td>
<td>0.42 --- 24.47</td>
</tr>
<tr>
<td>Ti</td>
<td>0.08 0.09 0.61</td>
<td>0.00 0.01 0.29</td>
<td>0.00 --- 0.50</td>
</tr>
<tr>
<td>P</td>
<td>0.30 0.43 0.40</td>
<td>0.00 0.00 1.75</td>
<td>0.00 --- 0.48</td>
</tr>
<tr>
<td>S</td>
<td>0.14 0.04 0.17</td>
<td>0.00 0.00 0.00</td>
<td>0.00 --- 0.00</td>
</tr>
<tr>
<td>Cl</td>
<td>0.04 0.09 0.20</td>
<td>0.00 0.00 0.00</td>
<td>0.00 --- 0.00</td>
</tr>
<tr>
<td>Total</td>
<td>100.00 100.00 100.00</td>
<td>100.00 100.00 100.00</td>
<td>100.00 --- 100.00</td>
</tr>
</tbody>
</table>

Table 6.4 (continued) The SEM-EDS analysis of the siltstone & mortar sandwich specimens at 28 days

<table>
<thead>
<tr>
<th>Element</th>
<th>Figure 6.9 S &amp; II-10-1</th>
<th>Figure 6.10 S &amp; II-10-2.5</th>
<th>Figure 6.12 S &amp; II-5-2.5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Q (^{b}) (%)</td>
<td>Binder (%)</td>
<td>Q (^{b}) (%)</td>
</tr>
<tr>
<td>O</td>
<td>48.50 48.02 54.19</td>
<td>Before After</td>
<td>50.05 48.49 19.66</td>
</tr>
<tr>
<td>Si</td>
<td>50.05 50.43 10.97</td>
<td>0.00 0.00 10.59</td>
<td>0.00 0.00 10.90</td>
</tr>
<tr>
<td>Al</td>
<td>0.00 0.00 8.00</td>
<td>0.35 0.29 1.04</td>
<td>0.00 0.00 0.11</td>
</tr>
<tr>
<td>Fe</td>
<td>0.35 0.08 2.71</td>
<td>0.02 0.11 2.22</td>
<td>0.00 0.00 3.13</td>
</tr>
<tr>
<td>Ca</td>
<td>0.02 0.17 2.51</td>
<td>0.00 0.00 0.04</td>
<td>0.00 0.00 0.10</td>
</tr>
<tr>
<td>Mg</td>
<td>0.00 0.00 0.04</td>
<td>0.00 0.00 0.00</td>
<td>0.00 0.00 0.00</td>
</tr>
<tr>
<td>Na</td>
<td>0.00 0.06 3.58</td>
<td>0.00 1.63 3.10</td>
<td>0.00 0.00 3.13</td>
</tr>
<tr>
<td>K</td>
<td>0.42 0.47 16.27</td>
<td>0.42 0.73 12.44</td>
<td>0.42 0.18 12.58</td>
</tr>
<tr>
<td>Ti</td>
<td>0.00 0.05 0.60</td>
<td>0.00 0.00 0.00</td>
<td>0.00 0.00 0.41</td>
</tr>
<tr>
<td>P</td>
<td>0.66 0.66 0.30</td>
<td>0.00 0.00 0.00</td>
<td>0.00 0.00 0.41</td>
</tr>
<tr>
<td>S</td>
<td>0.00 0.06 0.26</td>
<td>0.00 0.00 0.23</td>
<td>0.00 0.00 0.70</td>
</tr>
<tr>
<td>Cl</td>
<td>0.00 0.00 0.57</td>
<td>0.00 0.06 0.21</td>
<td>0.00 0.04 0.13</td>
</tr>
<tr>
<td>Total</td>
<td>100.00 100.00 100.00</td>
<td>100.00 100.00 100.00</td>
<td>100.00 100.00 100.00</td>
</tr>
</tbody>
</table>

\(^{a}\) F = mica/clay (not differentiated).
\(^{b}\) Q = quartz.
\(^{c}\) Not tested.
\(^{d}\) Values are averages of 5 different analyses on 5 separate locations. The standard deviation of the mica/clay was 5.3 to 15.6 % and 2.3 to 3.7 % for the quartz depending on the element.
(Figure 6.5), together with the SEM-EDS analysis, it is clear that the mica/clay phase had been corroded by the alkalis in the nearby pore solution if an activating solution was without soluble silicates \( ([\text{OH}^-]_0 = 10 \text{ M} \) and \( [\text{SiO}_2]_0 = 0 \text{ M} \)). On the other hand, alkali corrosion on the rock aggregate was not observed if soluble silicates of high concentration were used as shown in Figure 6.11 \( ([\text{OH}^-]_0 = 10 \text{ M} \) and \( [\text{SiO}_2]_0 = 2.5 \text{ M} \)). In any case, quartz was found to show no signs of structural deterioration even when no soluble silicates were used. See Figures 6.7 to 6.10. SEM-EDS analysis (Table 6.4) also showed that quartz had acquired little alkalis from the activating solutions. It therefore appears that alkali corrosion on siliceous aggregates was phase specific, as was also found in Chapter 10.

### 6.3.2 Inorganic Salt-Contaminated Systems

#### 6.3.2.1 Mechanical characteristics

In Chapter 5, it was found that addition of inorganic salts to the activating solutions was effective in causing structural variations to the geopolymeric binders, which then affected the binder compressive strengths. This observation is confirmed again in this chapter: The addition of inorganic salts, such as \( \text{KCl} \) and \( \text{K}_2\text{CO}_3 \), to the activating solutions containing 2.5 M soluble silicates was found to cause significant differences to the compressive strengths of the resultant binders, mortars and concretes. See Table 6.2. At 5 M \( \text{OH}^- \), the chloride was found to accelerate the early strength development of the binder \( I-5-2.5 \), which yielded an ultimate strength of 31.2 MPa in 7 days. The chloride contaminated binder \( (I-5-2.5-\text{Cl}) \) then became weaker with time, indicating that the aluminosilicate gel deterioration had initiated between the sample age of 7 days to 28 days. The carbonate, on the other hand, was found to exert no adverse effects on the product performance at any solution alkalinity or soluble silicate dosage. Furthermore, if a solution of 10 M \( \text{OH}^- \) and 2.5 M soluble silicates was used, addition of both the chloride and the carbonate salts seems to exert no apparent effects on the binder compressive strength. In short, the observations made on the various geopolymeric binders in this chapter were found to agree well with those as shown in Chapter 5.

As will be shown in Chapter 9, the activating solution containing 10 M of \( \text{OH}^- \) and 2.5 M of soluble silicates was far more efficient in producing the principal binding phase of geopolymeric systems, i.e. the aluminosilicate gel, than the activating solution containing 5 M of \( \text{OH}^- \) and 2.5 M of soluble silicates. This is probably why the 10 M \( \text{OH}^- \) and 2.5 M soluble
silicates activated geopolymeric binder (I-10-2.5) seems to be unaffected by the 0.32 M chloride contamination, whereas the effect was quite noticeable in I-5-2.5. See Table 6.2.

When siliceous aggregates were used, the chloride-induced aluminosilicate gel deterioration appears to have little effect on the mortar and the concrete compressive strengths when the geopolymeric products were activated with an activating solution of 5 M OH⁻ and 2.5 M soluble silicates. See Table 6.2. This is despite the fact that significant structural weakening was observed in the constituent binder I-5-2.5-Cl as mentioned above. As the salt-free mortar (II-5-2.5) and the concretes (III-5-2.5-B and III-5-2.5-S) were already significantly weaker than the constituent binder (I-5-2.5), it is possible that the structural weakening effects of chloride-contamination were masked by the strength weakening effects of aggregate addition to I-5-2.5 binder due to insufficient amount of binding phase that was produced from the I-5-2.5 activating solution. See Chapter 9.

On the other hand, if a solution of 10 M OH⁻ and 2.5 M soluble silicates was used, it was found that the chloride-contaminated mortar (II-10-2.5-Cl) and concretes (III-10-2.5-Cl-B and III-10-2.5-Cl-S) were significantly weaker than the salt-free (II-10-2.5, III-10-2.5-B and III-10-2.5-S) and the carbonate-contaminated counterparts (II-10-2.5-CO₃, III-10-2.5-CO₃-B and III-10-2.5-CO₃-S). This could be explained by performing SEM-EDS microstructural characterisation on the aggregate & geopolymeric binder sandwich specimens, as will be presented in the next section.

6.3.2.2 Microstructural characteristics

From Chapter 5, chloride-induced aluminosilicate gel precipitation and crystallisation have been attributed to the gel deterioration observed in the chloride-contaminated geopolymeric binders. The SEM micrographs in Figures 6.13 to 6.15, reconfirm again that, regardless of solution alkalinity ([OH⁻]₀ = 5 M and 10 M), potassium-rich aluminosilicates of crystalline appearances, whose elemental compositions are presented in Table 6.5, were indeed present in the chloride-contaminated geopolymeric systems activated with significant soluble silicate dosages. See also Chapter 8 for the chloride-induced crystallisation of aluminosilicates. As shown in Figures 6.14 and 6.15 and Table 6.5, two crystalline phases were present in the
Figure 6.13  The SEM image of the sandwich specimen S&II-5-2.5-Cl.

Figure 6.14  The SEM image of the sandwich specimen B&II-10-2.5-Cl.
Table 6.5 The SEM-EDS analysis of the chloride-induced potassium aluminosilicate crystals from the siltstone & mortar sandwich specimens at 28 days

<table>
<thead>
<tr>
<th>Element</th>
<th>Figure 6.13</th>
<th>Figure 6.14</th>
<th>Figure 6.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>64.05</td>
<td>62.48</td>
<td>66.74</td>
</tr>
<tr>
<td>Si</td>
<td>11.61</td>
<td>5.18</td>
<td>11.65</td>
</tr>
<tr>
<td>Al</td>
<td>4.06</td>
<td>1.32</td>
<td>4.59</td>
</tr>
<tr>
<td>Fe</td>
<td>1.13</td>
<td>2.88</td>
<td>1.04</td>
</tr>
<tr>
<td>Ca</td>
<td>1.36</td>
<td>0.20</td>
<td>1.22</td>
</tr>
<tr>
<td>Mg</td>
<td>0.31</td>
<td>4.36</td>
<td>0.11</td>
</tr>
<tr>
<td>Na</td>
<td>2.16</td>
<td>0.31</td>
<td>1.11</td>
</tr>
<tr>
<td>K</td>
<td>13.43</td>
<td>22.41</td>
<td>12.44</td>
</tr>
<tr>
<td>Ti</td>
<td>0.00</td>
<td>0.00</td>
<td>-0.06</td>
</tr>
<tr>
<td>P</td>
<td>0.69</td>
<td>0.21</td>
<td>0.66</td>
</tr>
<tr>
<td>S</td>
<td>0.30</td>
<td>0.47</td>
<td>0.23</td>
</tr>
<tr>
<td>Cl</td>
<td>0.90</td>
<td>0.18</td>
<td>0.21</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

a SEM-EDS was conducted at the white dotted circles as shown in Figures 14, 15 and 16.

chloride-contaminated samples, whose crystal morphology and composition were probably determined by the relative proportions of the elements such as Si, Al, Na and K within the gel before crystallisation.
These chloride-induced crystals were found to mainly concentrate at the aggregate (basalt, siltstone and siliceous sand) surfaces. Very few were found in the bulk binders. This chloride-induced and aggregate-facilitated aluminosilicate crystallisation is probably why debonding occurred between the aggregates and the chloride-contaminated mortars. See Table 6.3. The interfacial bonding strengths between the basalt (0.579 MPa) and the siltstone (0.565 MPa) and \( II-10-2.5-Cl \) mortar were thus significantly lower than the salt-free systems (1.273 MPa and 1.048 MPa respectively). Consequently, a weak mortar strength (\( II-10-2.5-Cl \)) as well as weak concrete strengths (\( III-10-2.5-Cl-B \) and \( III-10-2.5-Cl-S \)) were observed due to chloride-contamination (Table 6.2). Carbonate (\( K_2CO_3 \))-contamination, on the other hand, seems to exert no effects on the nature of the aluminosilicate gel formed, nor the macroscopic interfacial bonding strength between aggregates and geopolymeric binders. Hence, the strengths of the mortar and the concretes were not adversely affected by carbonate contamination irrespective of the activation solutions used.

### 6.4 THE MACROSCOPIC INTERFACE IN GEOPOLYMERIC MORTARS & CONCRETES

Of all the major ITZ models developed for the OPC systems [6.14-16], it is fair to say that they all originated from a single fact, that at the beginning of the hydration, the region close to the aggregates has on average less cement grains and is rather filled with water. Ions including Ca, Si, Al, Na, K, S and others have to diffuse from the cement grains, or from the aggregate, to this water-rich region so that the formation of the ITZ is possible. Therefore, it is generally believed that the greater concentrations of portlandite and ettringite, and the less concentration of calcium silicate hydrate (CSH) of the OPC ITZ as compared to the bulk OPC binder, is a result of the differential diffusivity of, for example, Ca to Si [6.14-16]. As Ca is more ‘mobile’ than Si, Ca is allowed to diffuse further into the water-rich regions of a hydrated OPC system. Consequently, the OPC ITZ has been observed to be more concentrated in Ca (in the form of portlandite, or calcium hydroxide crystallite) than Si (in the form of calcium silicate hydrate crystallite or gel).
The origin of the mobility of Ca in a hydrated OPC system can be understood by considering the OPC hydration chemistry:

During early OPC hydration, a large amount of Ca is dissolved and subsequently released from the OPC grains into the surrounding solution [6.17]. This in turn increases the solution pH until supersaturation with respect to Ca(OH)$_2$ is reached. The Ca then starts to precipitate out and crystallise as portlandite crystallite (CH) in the solution and away from the hydrating OPC grains [6.18]. This CH then acts as a buffer to ensure that the system is always saturated with respect to Ca(OH)$_2$ and consequently limits the solubility of Si [6.19]. In other words, the mobility and diffusivity of Si in a hydrated OPC system are limited by the local chemical environment saturated with CH. According to Breton et al. [6.20], this is what accounts for the high porosity and high CH content of the OPC ITZ. Similarly, CH is often found in the voids and/or (micro)cracks within OPC concretes. See Section 2.1.

The high porosity of the ITZ is generally believed as one of the reasons why OPC concretes often fail at the aggregate-binder interface. Improving the ITZ properties, therefore, is important in achieving high mechanical performance of concrete structures especially in high performance concretes. See Section 2.1.6. For those that achieved major improvements in increasing the macroscopic interfacial bonding strengths [6.21, 6.22], the ITZ was reported to exhibit a lower Ca/Si ratio as well as a lower porosity than the normal OPC systems. That is, the CH crystallite content was much reduced while the CSH content was increased. According to Kjellsen et al. [6.21], an ITZ with no measurable or observable difference to the bulk OPC binder could be obtained if the water/solid ratio was reduced to 0.25 in conjunction with 10% silica fume replacement. A similar result was also reported in high-volume fly ash concretes [6.23]. In these systems, the “excessive” Ca (those that are not participating directly in the CSH formation) was consumed by the pozzolanic reactions with the silica fume grains (or fly ash) to form more CSH [6.24-26]. Consequently, the Ca/Si ratio of the OPC ITZ was lowered through the addition of pozzolans. The ITZ was thus densified and strengthened/toughened through the addition of pozzolans that produced ‘additional’ CSH from pozzolanic reactions. This implies that a true two phase system consisting of just the aggregates and the binder could exist if excessive Ca and water were removed or avoided in hydrated Portland cement systems.
In geopolymeric systems, Na,K-modified aluminosilicate gel is the principal binding phase that provides interparticle bonding and hence the macroscopic strength [6.1-6]. As the aluminosilicate gel network has the capacity to incorporate calcium [6.1, 6.19], calcium-substituted/modified aluminosilicate can also co-exist with the original Na,K-modified aluminosilicate gel, if there is a calcium source present. Furthermore, if a high-calcium aluminosilicate solid, such as blast furnace slag, is used, CSH phase similar to what has been found in the OPC systems has also been reported to in the geopolymeric systems [6.12, 6.13, 6.27].

In this thesis, low calcium-content fly ash (ASTM Class F classification) and HR1-grade kaolinite, which was also low in calcium, were used as the solid raw materials for the geopolymer synthesis. As Ca was incorporated in the aluminosilicate gel network, the pore solution was not saturated with Ca(OH)$_2$. Indeed, no CH crystals could be identified in any of the various geopolymeric products anywhere throughout this investigation.

As shown in Figures 6.6 and 6.7, when an activating solution containing no soluble silicates was used, the salt-free geopolymeric binder I-10-0 was found to consist of two major phases. A region of discrete spherical particles (Figure 6.6) of potassium aluminosilicate(s) (see Table 6.4), which appeared to possess little interparticle bondings, was observed near the mica/clay (F) region of the siltstone aggregate. On the other hand, elongated, potassium-rich and silicon (and aluminium)-depleted secondary products (Table 6.4) were identified near the quartz region of the siltstone aggregate. The elongated potassium secondary products (Figure 6.7) were also found in the voids away from the aggregate & binder interface – an indication that the system was over-saturated with potassium (hydroxide). These two phases coexisted near the aggregate & binder interface as well as in the bulk binder phase, which could be attributed to the high apparent porosity of the macroscopic interface of S&II-10-0. As a result, the macroscopic interfacial bonding strength (Table 6.3) was weak between natural siliceous aggregates (basalt and siltstone) and II-10-0 mortar. The high porosity of I-10-0 could also contribute to the weak compressive strengths observed in I-10-0, II-10-0, III-10-0-B and III-10-0-S as shown in Table 6.2.

According to the SEM micrographs shown in Figures 6.8 to 6.11, increasing soluble silicate dosage in the activating solution at a solution alkalinity of [OH$^-\]_0 = 10 M was found to be very effective in reducing the formation of the elongated potassium secondary products. The
addition of soluble silicates, hence, was effective in removing the ‘free’ alkalis within the geopolymeric reacting system, and consequently reduced the state of over-saturation of potassium (hydroxide) in geopolymeric systems. In effect, this is similar to adding pozzolans (such as silica fume and fly ash) to reduce the CH contents in Portland cement systems as discussed above. According to Figures 6.8 to 6.12, addition of soluble silicates to activating solutions was also effective in decreasing the discrete spherical aluminosilicate content of Figure 6.6. In fact, when 2.5 M of soluble silicates were used at a solution alkalinity of both 5 and 10 M OH⁻, no loose particles were identified within all the geopolymeric products produced (binders, mortars and concretes). This excellent interfacial cohesion even existed between the aggregates and the salt-free binders I-5-2.5 and I-10-2.5 (Table 6.3 and Figures 6.10 to 6.12). As a result, improvements in the binder, the mortar and the concrete compressive strengths as well as the macroscopic interfacial bonding strengths could be achieved with increasing soluble silicate dosage at both 5 and 10 M OH⁻ as shown in Tables 6.2 and 6.3. See Chapters 7 to 9 for the explanation of the effects of soluble silicates in promoting the extent of geopolymerisation, which reduces free alkali content of the alkali-activating systems.

From the above, it seems that the interpartic le bonding within the salt-free geopolymeric systems was solely provided by the added soluble silicates. This is true if only one solution alkalinity is considered. If, however, the results of the systems activated by 10 M OH⁻ and 2.5 M soluble silicates were compared with those of 5 M OH⁻ at the same soluble silicate dosage, different conclusions could be reached. From Tables 6.2 and 6.3, the binder, the mortar, the concrete as well as the interfacial bonding strengths produced from the 10 M OH⁻ activating solution were all significantly greater than those of the 5 M OH⁻ counterparts at the same soluble silicate dosage (2.5 M). If the macroscopic strengths of geopolymeric products are largely controlled by the interparticle bondings within the binder matrix as well as the macroscopic interface, then the 10 M OH⁻ activating solution can be understood to provide more of the binding phase than that of the 5 M OH⁻ solution. This aspect will be further investigated in Chapter 9. Nevertheless, the experimental results collected in this chapter are sufficient to suggest that the macroscopic strengths of the various geopolymeric products are functions of both the added soluble silicates as well as the solution alkalinitities.

When a chloride salt (KCl) was added to the activating solution containing 10 M OH⁻ and 2.5 M soluble silicates, potassium-rich aluminosilicate crystals were found at the aggregate
surfaces as shown in Figures 6.14 and 6.15 and Table 6.5. Although the chloride-contaminated binder strength at 28 days ($I-10-2.5-Cl$, 40.9 MPa) was close to that of the salt-free binder ($I-10-2.5$, 41.6 MPa), it was apparent that the interfacial bonding strength (Table 6.3) was significantly decreased due to the chloride-induced gel deterioration. The fact that the chloride-contaminated mortar ($II-10-2.5-Cl$) and concretes ($III-10-2.5-Cl-B$ and $III-10-2.5-Cl-S$) were also significantly weaker than the salt-free systems suggests that, within these geopolymeric systems, the interfacial bonding strength may be the critical factor in determining the overall mortar and/or concrete strengths.

6.5 CONCLUSIONS

By systematically changing the solution alkalinity, soluble silicate dosage and inorganic salt contamination of the activating solution, it was found that there was no ‘clear’ macroscopic interface in the salt-free geopolymeric mortars and concretes. The interface was found to resemble that of the bulk geopolymeric binder, which is in stark contrast to the OPC systems.

It was also found that the effects of soluble silicate addition were two-fold. At first, soluble silicates were effective in reducing alkali saturation in the geopolymeric mortar/concrete pore solutions even when the solution alkalinity was extremely high. Secondly, soluble silicates were found to provide/promote greater interparticle bondings within the geopolymeric binders (the microscopic interface, see Section 3.3.1), as well as at the aggregate/binder macroscopic interface, which consequently rendered the geopolymeric products, including binders, mortars and concretes, greater macroscopic strengths as compared to the systems activated without soluble silicates.

If the macroscopic interfacial bonding between aggregates and geopolymeric binder activated with high dosages of soluble silicates was interrupted by, for example, KCl-induced gel crystallisation, the overall mortar and concrete strengths were shown to significantly weaken as compared to the salt-free systems. From this observation, it is proposed that the macroscopic interfacial bonding between siliceous aggregates and geopolymeric binders is
critical in determining the overall mechanical strengths of the geopolymeric mortars and concretes. See Chapter 10 for the formation mechanisms of the macroscopic interface.

6.6 REFERENCES


As discussed in Chapter 3, the research philosophy employed in this thesis suggests that the physical/mechanical bonding that exists in a geopolymeric system is a secondary by-product of the chemical interactions between aluminosilicate solids and activating solutions. Consequently, it is proposed that understanding the chemical interactions within a geopolymeric system is vital for its process optimisation. As has also been discussed in Chapter 3, sampling of the geopolymeric (aluminosilicate) gel, which is essential for direct chemical measurements on any chemical systems, is restricted by the extremely high physical strength as well as the high solid/solution ratio, which according to Chapter 4, could set in less than 1 hour under normal conditions. As a result, a ‘realistic’ reaction model is required for such a study.

This chapter uses Gladstone fly ash as the solid raw material as a case study for the development of the realistic reaction model as well as the associated analytical programme. As will be shown in this chapter, as well as in Chapters 8, 9 and 10, this reaction model and the associated analytical programme are suitable for the study of the chemical interactions between various different silicate/aluminosilicate solids and activating solutions of any solution alkalinitities, soluble silicate dosages and inorganic salt contaminations. The results obtained as such are very successful to explain the observed physical/mechanical interactions within the various geopolymeric systems as presented in Chapters 4, 5 and 6. This aspect will be further discussed in Chapters 8, 9 and 10.
7.1 INTRODUCTION

Coal fly ash, such as Gladstone fly ash, has been known for many years to dissolve very quickly when brought into contact with water at ambient temperature and pressure. The dissolved species, however, were found to precipitate out almost immediately on top of the primary phases as secondary deposits of lower solubility. Further dissolution of the primary phases was then retarded or inhibited because the mass fluxes of ions and water became diffusion-controlled across this secondary layer [7.1]. To ‘activate’ the fly ash for numerous industrially important applications such as zeolite synthesis [7.2-4] and geopolymeric binder production [7.5-7], strongly alkaline aqueous solution is often used to increase the rate of the dissolution processes. This is the origin of alkali-activation or geopolymerisation processes employed to ‘activate’ the reactivity of the relatively unreactive fly ash for mineral binder synthesis (as compared to the tricalcium silicate used for Portland cement binder synthesis, see Section 2.1).

From Chapters 4, 5 and 6, activating solutions of high soluble silicate concentrations are required to produce geopolymeric products such as mineral binders, mortars and concretes with desired mechanical properties. It is however well known in geochemistry that excessive soluble silicates, typically more than $10^{-2.8}$ to $10^{-3.5}$ M SiO$_2$ depending on the solution pH, at the alkaline pH regime can inhibit silicate (kaolinite) dissolution [7.8]. This apparently contradicts the observations made in Chapters 3, 4, 5 and 6, as well as in numerous other investigations on geopolymerisation [7.5-7]: Geopolymeric binder is an inorganic polymer of undissolved aluminosilicate particles embedded in a newly formed and mainly amorphous aluminosilicate gel of significant Al substitution and Ca modification within the gel network [7.5, 7.9]. This significant Al network substitution and Ca network modification on the structural backbone of the aluminosilicate gel has to be a result of significant solid dissolution, as the activating solution does not contain any soluble aluminates or dissolved calcium. Understanding the role of soluble silicates in the processes of chemical interactions between aluminosilicate solids and alkaline aqueous solutions, no doubt, is vital towards the understanding of the overall geopolymerisation processes.

In this chapter, a ‘realistic’ reaction model and a novel analytical procedure were developed for the first time to, at first, study the chemical interactions between glassy aluminosilicates using Gladstone fly ash as a case study and various activating solutions with and without...
soluble silicates. Secondly, the implication of the observed chemical interactions between the fly ash and the various activating solutions to geopolymer synthesis and process optimisation will also be discussed.

7.2 MATERIALS AND EXPERIMENTAL METHODS

7.2.1 Materials

Gladstone fly ash, KASIL® 2236(K32) potassium silicate solution, Vitrosol N(N40)® sodium silicate solution and laboratory-grade reagents (NaOH and KOH) were used to study the chemical interactions between a typical glassy aluminosilicate (see Chapter 9 for the glassy nature of the Gladstone fly ash) and the various activating solutions of varying soluble silicate dosages. Distilled/deionised water was used for all solution preparations and dilutions.

7.2.2 Leaching Experiments

The reaction model used for the study of the chemical interactions between the fly ash and the activating solutions was inspired by the conventional leaching experiments from the minerals processing industry. See Section 3.3.3.1 for the detailed accounts of the reaction model as well as the sampling techniques. In short, activating solutions of the designated compositions (see Table 7.1) were prepared at pH = ~13.95 and allowed to equilibrate to 20 ± 0.5°C. The solution pH of ~13.95 was chosen due to the fact that during leaching, rapid determination of the solution pH was required to see if leaching would induce significant changes to the concentration of hydroxyl ions in the solution. (If the solution was too alkali concentrated, tedious titration will have to be employed for accurate measurements of the hydroxyl concentration.) At the same time, it was necessary to ensure that high alkalinity was used in the leaching solution so that the synthesis conditions of geopolymers (see Section 7.2.3.2) could be simulated. The fly ash was then added to the activating solutions at a solid/solution of 0.1 to make up the leaching slurries at 20 ± 0.5°C. At a designated time, the reacted solids were separated from the solutions using the sampling techniques described in Section 3.3.3.1.
Table 7.1 The calculated molar compositions of the activating solutions

<table>
<thead>
<tr>
<th>System</th>
<th>M</th>
<th>[SiO$_2$] (mM)</th>
<th>SiO$_2$/M$_2$O ($R_m$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Na</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td>B</td>
<td>Na</td>
<td>14.24</td>
<td>0.0237</td>
</tr>
<tr>
<td>C</td>
<td>Na</td>
<td>28.48</td>
<td>0.0475</td>
</tr>
<tr>
<td>D</td>
<td>Na</td>
<td>42.72</td>
<td>0.0712</td>
</tr>
<tr>
<td>E</td>
<td>Na</td>
<td>71.20</td>
<td>0.119</td>
</tr>
<tr>
<td>F</td>
<td>Na</td>
<td>213.60</td>
<td>0.356</td>
</tr>
<tr>
<td>G</td>
<td>Na</td>
<td>427.60</td>
<td>0.712</td>
</tr>
<tr>
<td>H</td>
<td>Na</td>
<td>569.60</td>
<td>0.949</td>
</tr>
<tr>
<td>I</td>
<td>K</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td>J</td>
<td>K</td>
<td>14.24</td>
<td>0.0237</td>
</tr>
<tr>
<td>K</td>
<td>K</td>
<td>28.48</td>
<td>0.0475</td>
</tr>
<tr>
<td>L</td>
<td>K</td>
<td>42.72</td>
<td>0.0712</td>
</tr>
<tr>
<td>M</td>
<td>K</td>
<td>71.20</td>
<td>0.119</td>
</tr>
<tr>
<td>N</td>
<td>K</td>
<td>213.60</td>
<td>0.356</td>
</tr>
<tr>
<td>O</td>
<td>K</td>
<td>427.60</td>
<td>0.712</td>
</tr>
<tr>
<td>P</td>
<td>K</td>
<td>569.60</td>
<td>0.949</td>
</tr>
</tbody>
</table>

7.2.2.1 Solution analysis

The rate and extent of mass transfer across the ‘microscopic’ interface between the fly ash and the activating solutions were measured by analysing the reacted solutions from the reaction model using inductively-coupled plasma equipped with optical emission spectrometer (ICP-OES). See Section 3.3.3.2 for the detailed analytical methods. In addition, solution pH of the activating solutions was monitored continuously throughout the leaching experiments using a glass electrode from Hanna Instruments Model HI 8424, which was corrected for aqueous alkaline solutions using the procedure described in Section 3.3.3.1.
7.2.2.2 Solid analysis

X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS) were used to characterise the unreacted and the reacted solids microstructurally. See Section 3.3.3.3 for the detailed analytical methods. Note that secondary electron (SE)-SEM images were taken on gold-coated samples whereas carbon-coated samples were scanned under backscattered electron (BSE) detection. SEM-EDS analyses were only conducted on the carbon-coated samples.

7.2.3 Geopolymeric Binder and Silica Gel Syntheses and Characterisation

7.2.3.1 Silica gel synthesis

Silica gel Gel-I was prepared by drying the KASIL\textsuperscript{®} 2236(K32) potassium silicate solution at 60°C for 72 hours. Gel-II was prepared from the reacted System P activating solution (Table 7.1) after 8 hours of leaching, which was subsequently dried at 60°C for 72 hours.

7.2.3.2 Geopolymeric binder synthesis

The geopolymeric binder System VI was synthesised as follows: Potassium silicate solution (\(\text{SiO}_2/\text{K}_2\text{O} = Rm = 1.5, [\text{SiO}_2] = 5 \text{ M}\)) was prepared using calculated amounts of distilled H\(_2\)O, KOH and potassium silicate solution (KASIL\textsuperscript{®} 2236(K32)) and was allowed to cool to room temperature overnight. After placing 450 g of the fly ash in a mixing bowl, 230 g of the activating solution was added. The contents of the mixing bowl were mixed in a mechanical mixer for 5 minutes to produce homogeneous pastes. The pastes were then transferred to plastic containers, which were alkali resistant, and cured at 40°C under atmospheric pressure for 7 days before analysis. The System VI geopolymeric binder had a compressive strength of 20 MPa after 7 days.
7.2.3.3 Characterisation

The IR spectra and SEM-EDS topographic analyses of the silica gels and the geopolymeric binders were taken using the same procedures as in Section 7.2.2.2.

7.3 MASS TRANSFER BETWEEN GLASSY ALUMINOSILICATES AND ACTIVATING SOLUTIONS

7.3.1 Without Soluble Silicates

As an experimental observation, it was found that the solution pH of all the activating solutions, with and without added soluble silicates, was found to remain very stable throughout the entire leaching experiments at 13.93-13.98 even without any additional buffer. At such a high pH regime, Bronsted acid-base reactions between surface silanol/aluminol groups of silicate/ aluminosilicate minerals and the alkaline aqueous solutions have been known to proceed at a very fast rate. As a result, complete deprotonation of the surface groups can be achieved even before the surface T-O-Si (T = Si and Al) bonds are hydrolysed to induce the so-called mineral dissolution [7.10, 7.11]. Consequently, the interfacial solvent structure and properties between silicate/aluminosilicate minerals and alkaline aqueous solutions are modified by the charge-balancing cations, which subsequently affect the frequency of successful bond rupture and rate of mineral dissolution [7.11, 7.12]. As Na has a higher charge density and smaller ionic radius than K, it can be expected that OH\(^-\) should have a higher accessibility to the surface T-O-Si bonds underneath the \(-\text{Si-O}^+\text{Na}^+\) surface than the \(-\text{Si-O}^-\text{K}^+\) surface. In other words, the rate and extent of aluminosilicate dissolution should be higher in the sodium than in potassium alkaline aqueous solutions.

Figure 7.1 shows the dissolution profiles of Gladstone fly ash in activating solution initially free of soluble silicates. The Na-system (System A) was found to exhibit a higher initial Si dissolution rate as well as a slightly higher extent of Si dissolution at the 168\(^{th}\) hour of leaching, than the K counterpart (System I). This is in agreement with the above expectation as well as with the experimental observations from Xu and Van Deventer [7.13].
Figure 7.1 The effects of alkali cations on the dissolution profiles of Al, Si, Ca and Mg of Gladstone fly ash as a function of time in (a) System A, Na-activating solution, and (b) System I, K-activating solution.

Also from Figure 7.1, it was found that Ca and Si were the first two elements to dissolve in both System A (Na-activating solution) and I (K-activating solution). By the end of the second
hour of leaching, their concentrations in the solution phase were about the same. The level of Ca in the reacted activating solutions then subsequently dropped off while Si continued to dissolve. This observation suggests that Ca was precipitating out to form secondary precipitates as was also observed by Fraay et al. [7.14]. See also Section 7.4.3 for the topographic evidence of these Ca-rich secondary precipitates, which could inhibit further fly ash dissolution. As a result, only about 1.3% of Al and 0.6% of Si were dissolved from the fly ash after 168 hours of leaching in both System A and I.

On the other hand, Al was only detected after 6 hours of leaching and Mg was not detected at all throughout the entire investigation. See Figure 7.1. The preferential leaching of Si than Al at the initial stages of Gladstone fly ash dissolution was also observed when other aluminosilicates such as kaolinite and albite were leached in aqueous alkaline solutions. See Chapter 10. According to \textit{ab initio} quantum-mechanic calculation [7.15], Al-O-Si bonds of an aluminosilicate should be relatively weak as compared to Si-O-Si bonds. Aluminium was thus expected to dissolve more preferentially than Si especially at the early stages. This trend, however, was not observed in the present study, possibly because the Si–O bonds of the surface silanol groups (≡Si–OH) are preferentially polarised and weakened over the surface aluminol groups (≡Al–OH) due to the greater electronegativity of Si than Al [7.16]. See Chapter 10 for a more detailed discussion on this subject.

In conclusion, the results obtained in this chapter using activating solutions initially free of soluble silicates were found to agree well with the current literature [7.1, 7.11-14].

7.3.2 With Soluble Silicates

From Figures 7.2 and 7.3 and Table 7.2, it is clear that the fly ash dissolution/reprecipitation characteristics in the activating solutions containing added soluble silicates (Systems B to H and Systems I to P) were significantly different from those observed without added soluble silicates (System A and I). In any case, addition of soluble silicates to the initial activating solutions was found to initiate earlier Al dissolution than the ones without added soluble silicates. Furthermore, the sodium systems (Systems A to H) and the potassium systems (Systems I to P) were found to share similar trends in terms of their dissolution and
Figure 7.2  The effects of soluble silicate dosage on the dissolution profiles of Systems A to H as a function of time for (a) aluminium, (b) silicon and (c) calcium. \([\text{Al}] = \text{concentration of Al in the solution at time } t. \ [\text{Al}]_0 = \text{concentration of Al in the initial activating solution. Same notations for Si and Ca.}
Figure 7.3  The effects of soluble silicate dosage on the dissolution profiles of Systems I to J as a function of time for (a) aluminium, (b) silicon and (c) calcium. $[\text{Al}] = \text{concentration of Al in the solution at time t}$. $[\text{Al}]_0 = \text{concentration of Al in the initial activating solution}$. Same notations for Si and Ca.
Table 7.2 The maximum apparent dissolution observed from Gladstone fly ash in the various activating solutions at 20°C

<table>
<thead>
<tr>
<th>System</th>
<th>Al (mM)</th>
<th>Si (mM)</th>
<th>Ca (mM)</th>
<th>Mg (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>7.0 (168)</td>
<td>4.6 (168)</td>
<td>1.1 (2)</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>9.1 (168)</td>
<td>--- b</td>
<td>0.2 (168)</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>7.3 (168)</td>
<td>--- b</td>
<td>0.2 (168)</td>
<td>0</td>
</tr>
<tr>
<td>D</td>
<td>1.7 (168)</td>
<td>--- b</td>
<td>0.1 (168)</td>
<td>0</td>
</tr>
<tr>
<td>E</td>
<td>0.6 (97)</td>
<td>--- b</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F</td>
<td>1.1 (26)</td>
<td>0.7 (26)</td>
<td>2.3 (26)</td>
<td>0</td>
</tr>
<tr>
<td>G</td>
<td>2.3 (10)</td>
<td>20.5 (10)</td>
<td>15.8 (10)</td>
<td>0</td>
</tr>
<tr>
<td>H</td>
<td>3.5 (8)</td>
<td>154.9 (8)</td>
<td>30.2 (8)</td>
<td>0</td>
</tr>
<tr>
<td>I</td>
<td>6.9 (168)</td>
<td>4.5 (168)</td>
<td>0.8 (2)</td>
<td>0</td>
</tr>
<tr>
<td>J</td>
<td>9.6 (168)</td>
<td>--- b</td>
<td>0.1 (24)</td>
<td>0</td>
</tr>
<tr>
<td>K</td>
<td>7.7 (168)</td>
<td>--- b</td>
<td>0.1 (48)</td>
<td>0</td>
</tr>
<tr>
<td>L</td>
<td>2.2 (168)</td>
<td>--- b</td>
<td>0.1 (168)</td>
<td>0</td>
</tr>
<tr>
<td>M</td>
<td>0.9 (168)</td>
<td>--- b</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>N</td>
<td>0.9 (48)</td>
<td>6.05 (8)</td>
<td>3.8 (8)</td>
<td>0</td>
</tr>
<tr>
<td>O</td>
<td>1.9 (48)</td>
<td>16.8 (8)</td>
<td>11.1 (8)</td>
<td>0</td>
</tr>
<tr>
<td>P</td>
<td>3.7 (8)</td>
<td>167.3 (8)</td>
<td>23.3 (8)</td>
<td>0</td>
</tr>
</tbody>
</table>

Theoretical max. dissolution: 548.7  832.3  62.1  32.8

* The parentheses denote the time of leaching in hours when the value of the maximum apparent dissolution was taken.

b Only precipitation was observed.

precipitation characteristics for all the elements analysed, which included Al, Si, Ca and Mg (Figures 7.2 and 7.3). It was also observed that the sodium systems (Systems A to H) induced somewhat greater initial dissolution rates than the potassium counterparts (Systems I to P) at the same soluble silicate dosage.

If the soluble silicate dosage was less or equal to 28.48 mM (0 < [Si]₀ ≤ 28.48 mM, Systems B, C and System J, K), it was found that the maximum apparent Ca dissolution observed in
these systems was much lower than the systems initially free of soluble silicates ([Si]₀ = 0 mM, System A and I). See Table 7.2 and Figures 7.2 (c) and 7.3 (c). Note that the ‘apparent dissolution’ measures the amount of the dissolved species as detected by the ICP-OES analysis described in Section 7.2.2.1. Thus, those that were precipitated out or gelled out as precipitates or gels were not accounted for in the apparent dissolution presented in Figures 7.2 and 7.3 as well as in Table 7.2.

From Figures 7.2 (a) and 7.3 (a), at [Si]₀ ≤ 28.48 mM, both the rate and the extent of the apparent Al dissolution in Systems B and C (J and K) were increased as compared to those from System A (I) ([Si]₀ = 0 mM). In particular, when an activating solution containing [Si]₀ = 14.24 mM (System B (J)) was used, it was found that there was an initial Si precipitation stage involving mainly the added soluble silicates ([Si] – [Si]₀ was negative), which was then followed by a net Si dissolution stage ([Si] – [Si]₀ was positive). This suggests that the apparent fly ash dissolution was a result of the competition between mineral dissolution and precipitation processes. The initial Si precipitation stage at 0 < [Si]₀ ≤ 28.48 mM (Systems B, C and Systems J, K), however, was found to exert no effects on the Al dissolution profile. Furthermore, the solubility of Ca in Systems B, C and Systems J, K was lowered in the presence of the added soluble silicates at the dosage of 0 < [Si]₀ ≤ 28.48 mM.

When leaching solutions of 28.48 ≤ [Si]₀ < 213.60 mM (Systems C, D, E and K, L, M) were used, it was found that the maximum apparent Ca dissolution was again much lower in these systems than Systems A and I. See Table 7.2 and Figures 7.2 (c) and 7.3 (c). It was also found that the rate and the extent of the apparent Al dissolution were also reduced with increasing soluble silicate dosage from [Si]₀ = 28.48 to 71.20 mM (Systems C, D, E and K, L, M. See Figures 7.2 (a) and 7.3 (a). Furthermore, no apparent Si dissolution of the fly ash was detected in these systems (i.e. [Si] – [Si]₀ < 0, see Figures 7.2 (b) and 7.3 (b)). From these observations, it is likely that Al, Si and Ca could precipitate out as Ca-modified aluminosilicate phase(s) on top of the fly ash particles. These aluminosilicate precipitates may also contain other alkali cations such as Na or K from the activating solutions – a phenomenon known as polysialation according to Phair and Van Deventer [7.17]. These polysialates (Na,K,Ca-modified aluminosilicates) could be attributed to the limited fly ash dissolution observed in Systems C, D, E and K, L, M. See Section 7.4.3 for the topographical evidence for these polysialate precipitates.
When more than 213.60 mM of soluble silicates were added to the initial activating solution (Systems G, H and O, P), the fly ash dissolution/reprecipitation characteristics were found to deviate even more from those observed in Systems A and I. See Figures 7.2 and 7.3. After the initial rapid precipitation of the added soluble silicates, there followed a clear yet greatly enhanced net dissolution of Al, Si and Ca, which was again followed by the apparent precipitation of the dissolved species as well as the added soluble silicates. In any case, no apparent Mg dissolution was detected at all. As a general trend for the systems of $[\text{Si}]_0 \geq 213.60$ mM (Systems F, G, H and N, O, P), the greater the soluble silicate dosage, the greater was the extraction of Al, Si and Ca before their ultimate precipitation. The percentage of the maximum apparent Ca dissolution was as high as ~49 % for System H whereas it was 0.64 % for Al and 18.61 % for Si. When compared to the soluble silicate-free system (System A), it was found that both the maximum apparent dissolutions of Si and Ca were about 30 times greater in System H than in System A. The percentage of maximum apparent dissolution was obtained as $\frac{100 \times \text{(maximum apparent dissolution in mM)}}{\text{(theoretical maximum dissolution in mM)}}$.

In conclusion, addition of soluble silicates to the activating solutions was found to cause significant alterations to the mass transfer characteristics (dissolution and (re)precipitation) of the fly ash in the Na or K activating solutions. Increasing soluble silicate dosage to more than ~200 mM could promote greater structural breakdown of the primary phases in the fly ash at a fixed pH. To elucidate this point, solid microstructural characterisation techniques such as XRD, FTIR and SEM-EDS were applied to the reacted solids as below.

### 7.4 Evidence of Chemical Interactions from the Reacted Solids

#### 7.4.1 Change of Crystallinity by XRD

From Figure 7.4, it was found that, within the time frame of the present investigation, no new crystalline phase was formed as a result of the leaching experiments. In addition, the crystalline peak intensities of all the major crystalline phases within Gladstone fly ash, such
Figure 7.4 The XRD diffractograms collected using Cu Kα radiation ($\lambda_{\text{Cu Kα}} = 1.54184$ Å). a = unreacted Gladstone fly ash; b = fly ash reacted under System H for 168 hours; c = fly ash reacted under System P for 168 hours; d = System VI geopolymer after 168 hours. Q = α-quartz. M = mullite.

as quartz (Q) and mullite (M), were found to remain unaffected throughout the leaching experiments. As XRD is only sensitive to crystalline phases within a material, the results in Figure 7.4 suggest that quartz and mullite were unreactive in the activating solutions employed in this chapter, with and without soluble silicates. This is consistent with the observations made on the real geopolymeric binders as in Chapter 5 or the System VI geopolymeric binder of this chapter. Furthermore, the polysialate precipitates that have been proposed in the last section could be amorphous in nature, or the amount of crystalline precipitates was too small to be detected by the XRD technique (typical detection limit is ~5%).

7.4.2 Change of Chemical Bonds by FTIR

As was observed in Chapters 4 and 5, FTIR is a better technique to characterise a heterogeneous amorphous material such as geopolymeric binders or fly ash. This is because FTIR is highly sensible to structures of short-range orders. See Chapters 3 and 5.
Figure 7.5 The FTIR spectra of Gladstone fly ash reacted under (a) *System A* to *H* and (b) *System I* to *P*. Each spectrum was taken when maximum apparent Si dissolution was observed from the leaching experiments. Gdf = unreacted Gladstone fly ash. A = fly ash treated under *System A*. Same notations for B to *P*.

Furthermore, it can also generate valuable information such as the relative degree of polymerisation of a silicate/aluminosilicate network, as discussed in Section 3.1.2.4. As Gladstone fly ash was found to interact extensively with the activating solutions containing more than \(~200\) mM of soluble silicates (*Systems A* to *E* and *I* to *M*, Section 7.3.2), it is expected that the FTIR spectra of these reacted fly ashes should also differ considerably from that of the unreacted fly ash.
The IR spectra of the unreacted Gladstone fly ash and the various reacted fly ashes, which were taken when the maximum apparent Si dissolutions were observed, are presented in Figure 7.5. The very broad band (~1200-950 cm\(^{-1}\)) at the T-O-Si (T = Al and Si) stretching vibration region is due to the multi-phase nature of Gladstone fly ash. The strong bands at 1165 cm\(^{-1}\), 1080 cm\(^{-1}\), which existed as spectral shoulders, and the medium band at 798 cm\(^{-1}\) are attributable to \(\alpha\)-quartz [7.18, 7.19]. The strong band at 561 cm\(^{-1}\) and the shoulders at 1138 cm\(^{-1}\) and 620 cm\(^{-1}\) are indicative of mullite [7.18, 7.19]. According to Vempati et al. [7.19], amorphous aluminosilicate phase is likely to cause IR vibration at around 1080-1070 cm\(^{-1}\), since similar band positions can be observed for natural and glassy aluminosilicate materials. Thus, the 1074 cm\(^{-1}\) band was assigned to the amorphous aluminosilicate phase(s). See also Chapter 9 for further justification on this spectral assignment. The broad band located at 650-500 cm\(^{-1}\) is also indicative of silicate and aluminosilicate glasses, which possess long-range structural order in the form of rings of tetrahedra or octahedra [7.20-22].

From Figure 7.5, if the soluble silicate dosage was less than 200 mM (Systems A to E and I to M), the IR spectra of the reacted fly ash were not very different from that of the unreacted fly ash. However, when the fly ash was reacted under Systems H and P for 8 hours, it was found that the T-O-Si stretching vibration band maximum originally located at 1074 cm\(^{-1}\) had been shifted to the lower frequency field by more than 20 cm\(^{-1}\). This is indicative of significant depolymerisation of the silicate/aluminosilicate networks [7.23-25]. See also Section 3.1.2.4.

Also from Figure 7.5, it was found that the broad band at 561 cm\(^{-1}\) and the spectral shoulder at 620 cm\(^{-1}\) attributable to mullite [7.18, 7.19], or glassy aluminosilicates of rings of tetrahedra or octahedra [7.20-22], had become significantly weaker after 8 hours of leaching in Systems H and P. As mullite dissolution was insignificant according to the XRD analysis (Figure 7.4), it is more likely that the intensity reduction over this spectral region was due to the depolymerisation of the aluminosilicate glassy phase(s) within Gladstone fly ash, which lost its long-range structural order due to its chemical interactions with the Systems H and P activating solutions. The new IR bands at 1045 cm\(^{-1}\) for the System H-reacted solid and 1053 cm\(^{-1}\) for the System P-reacted solids, hence, could be attributed to the depolymerisation or structural reorganisation of the glassy aluminosilicate phase(s) originally located at 1074 cm\(^{-1}\). See Chapter 9 for the IR frequency shift of the 1074 cm\(^{-1}\) band in relation to the extent
of alkali-activation on the fly ash. In short, the greater the soluble silicate dosage above a concentration threshold of ~200 mM at a constant solution alkalinity, the greater was the degree of depolymerisation of the fly ash glassy phase, hence the greater the extent of chemical interactions between glassy aluminosilicates and activating solutions.

7.4.3 Change of Surface Topography and Compositions by SEM-EDS

The SEM images of the unreacted and the reacted fly ash under secondary electron (SE) detection are shown in Figures 7.6 to 7.11. These SE-SEM images clearly demonstrate the surface topographical differences between the unreacted fly ash and the fly ash reacted in the various activating solutions, with and without added soluble silicates.

When the fly ash was reacted in a soluble silicate-free activating solution (System A, Figure 7.7), some secondary precipitates of relatively low density were found to randomly scatter on top of the reacted fly ash particles after 168 hours of leaching. These secondary precipitates were not observed if backscattered electron detection (BSE) was used for imaging. Due to the incomplete coverage of the secondary precipitate layer, some of the primary phases were still in direct contact with the leaching solution, allowing further dissolution to take place. The reduction of the exposed interfacial area, however, should be responsible for the decrease in the primary dissolution rate with time as shown in Figure 7.2. A similar surface topography was also observed on the System B-reacted fly ash after 168 hours of leaching ([Si]₀ = 14.24 mM, Figure 7.8).

When a greater dosage of soluble silicate was used (28.48 mM (Systems C and K), 42.72 mM (Systems D and L) and 71.20 mM (Systems E and M)) (see for example Figure 7.9) it was found that the reacted fly ash particles were covered by layers of high-density secondary precipitates. The surface topography of these reacted solids resembled that of the polysialate products as described by Phair and Van Deventer [18]. See Figures 2.9 and 2.10. Furthermore, the surface coverage of the secondary precipitates was higher in these systems than Systems A and B, which is consistent with the ICP-OES solution analysis: Lower apparent dissolutions were observed in Systems C, D and K, L than Systems A and B (see Figures 7.2 and 7.3 and Table 7.2).
Figure 7.6  The SE-SEM micrographs of unreacted Gladstone fly ash.

Figure 7.7  The SE-SEM micrographs of the System A-reacted Gladstone fly ash after 168 hours of leaching.
Figure 7.8    The SE-SEM micrographs of the System B-reacted Gladstone fly ash after 168 hours of leaching.

Figure 7.9    The SE-SEM micrographs of the System C-reacted Gladstone fly ash after 168 hours of leaching.
Figure 7.10  The SE-SEM micrographs of the *System H*-reacted Gladstone fly ash after 168 hours of leaching.

Figure 7.11  The SE-SEM micrographs of the *System P*-reacted Gladstone fly ash after 168 hours of leaching.
Figure 7.12  The BSE-SEM micrographs of the System P-reacted Gladstone fly ash after 168 hours of leaching. The dotted circle indicates the areas (as an example) of where the 15 EDS analyses were taken.

Figure 7.13  The BSE-SEM micrographs of the System VI geopolymeric binder after 168 hours of curing at 40°C. The dotted circle indicates the areas (as an example) of where the 15 EDS analyses were taken.
Table 7.3 The results of the SEM-EDS analyses on the unreacted Gladstone fly ash, the reacted fly ash under the various conditions (System I and P after 168 hours), and the geopolymer after 168 hours of curing at 40°C

<table>
<thead>
<tr>
<th>Element</th>
<th>Unreacted</th>
<th>System I-reacted</th>
<th>System P-reacted</th>
<th>Geopolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>55.97 ± 2.09</td>
<td>50.78 ± 3.13</td>
<td>61.96 ± 2.95</td>
<td>37.12 ± 5.21</td>
</tr>
<tr>
<td>Al</td>
<td>20.30 ± 1.99</td>
<td>19.85 ± 1.15</td>
<td>3.22 ± 0.11</td>
<td>8.25 ± 1.19</td>
</tr>
<tr>
<td>Si</td>
<td>22.28 ± 1.87</td>
<td>21.50 ± 1.73</td>
<td>21.48 ± 1.38</td>
<td>26.94 ± 1.54</td>
</tr>
<tr>
<td>Ca</td>
<td>0.80 ± 0.52</td>
<td>0.56 ± 0.32</td>
<td>6.41 ± 0.94</td>
<td>10.05 ± 1.03</td>
</tr>
<tr>
<td>Na</td>
<td>0.04 ± 0.05</td>
<td>0.27 ± 0.07</td>
<td>0 ± 0.03</td>
<td>1.14 ± 0.18</td>
</tr>
<tr>
<td>K</td>
<td>0.35 ± 0.06</td>
<td>0.53 ± 0.10</td>
<td>4.97 ± 0.55</td>
<td>12.02 ± 2.13</td>
</tr>
</tbody>
</table>

* Values shown are averages of 15 analyses from 15 different locations. The ± values represent the standard deviations.

When soluble silicate of even higher dosage was used (213.60 mM (Systems F and N), 427.20 mM (Systems G and O) and 569.60 mM (Systems H and P)), it was found that the larger fly ash particles appeared to be covered by scales of secondary precipitates resembling polysialates as described above. On the other hand, the smaller fly ash particles were almost completely transformed into some secondary products as observed in Systems H (Figure 7.10) and P (Figure 7.11) after 168 hours of leaching. Figures 7.10 and 7.11 further compare the morphological differences between the reacted solids using Na and K activating solutions at a common soluble silicate dosage of 569.60 mM. The potassium silicate-reacted secondary gel-like products (System P) were clearly more edgy and flaky than the sodium silicate-reacted products (System H), which were found to resemble more closely to polysialates than gels. The microstructure of the secondary products of the alkali-activating processes using activating solutions of high dosages of soluble silicates, therefore, appeared to be cation-dependent. The implication of this observation to the overall mechanical strength of ‘real’ geopolymeric binders will be discussed in Section 7.5.

The results of the SEM-EDS analyses on the unreacted fly ash and the solids reacted under Systems I and P are presented in Table 7.3. It was found that the surface topographical compositions of the unreacted fly ash particles were similar to those of the System I-reacted particles. See Table 7.3. This suggests that the activating solution initially free of soluble
silicates at pH ~13.95 did not cause significant fly ash dissolution. In other words, the extent of chemical interactions between the fly ash and the soluble silicate-free activating solution was insignificant at pH = ~13.95 in the absence of significant amount of soluble silicates ([Si]₀ ≤ ~200 mM). On the other hand, the flaky gel-like secondary products of System P were found to consist of much less Al but much more Ca and K than the unreacted fly ash. (Note that the values included in Table 7.3 were the average of 15 analyses from 15 different flaky secondary products. The dotted circle shown in Figure 7.12 was only a demonstration of what the flaky structure meant and where the SEM-EDS was conducted.) The results obtained from SEM-EDS analyses (Table 7.3), thus, agree well with those obtained from the ICP-OES solution analyses and the infrared solid analyses: Activating solutions of high soluble silicate dosages can promote greater extents of chemical interactions between the fly ash glassy phases and the various activating solutions. The flaky gel-like structure of System P, hence, is a result of significant Al, Si and Ca dissolution, followed by the subsequent gellation of the dissolved fly ash and the added soluble silicates. The fact that the flaky gel-like structure of System P contained much less Al than the unreacted fly ash could be a result of the polysialate formation on the larger fly ash particles that consumes significant amounts of the dissolved Al.

### 7.5 GEOPOLYMERISATION IN PRESENCE OF SOLUBLE SILICATES

As was discussed in Section 2.2.3.2 and Chapters 5 and 6, addition of high concentrations of soluble silicates to the various activating solutions is one of the most critical reaction conditions for the synthesis of high mechanical strength geopolymeric products. The experimental results obtained in this chapter by monitoring (1) the mass transfer of the dissolved species across the microscopic interface (see Section 3.3 for the definition) through the use of ICP-OES solution analyses, and (2) the microstructures of the unreacted and the reacted solids from the leaching slurries, through the use of XRD, FTIR and SEM-EDS, suggest that addition of soluble silicates over a concentration threshold of ~200 mM at pH = ~13.95 at 20°C is very effective in enhancing the chemical interactions between the glassy phase(s) of the fly ash and the activating solutions. The enhanced glassy phase
dissolution and the subsequent precipitation/gellation of the dissolved species then led to the formation of two major classes of secondary products: polysialate precipitates or aluminosilicate gels. The SEM images presented in Figures 7.10 and 7.11 indicate that the Na-activating solutions (e.g. System H) are more likely to produce polysialate-like secondary precipitates, whereas K-activating solutions (e.g. System P) should promote the formation of aluminosilicate gels. The above experimental observations and classification are consistent with the existing literature on geopolymer technology, soluble silicate chemistry and zeolite synthesis:

1. According to Xu and Van Deventer [7.13] and Van Jaarsveld and Van Deventer [7.26], the geopolymeric binders synthesised from activating aluminosilicate powders with Na-activating solutions of high soluble silicate dosages were weaker than the K-counterparts at exactly the same reaction conditions except the alkali cations used. From Figures 7.10 and 7.11 of this work, the aluminosilicate gel produced from the K-activating solution seems to possess a higher interparticle strength than that of the polysialate products from the Na-activating solution. Indeed, a separate experiment conducted on the filter cakes (20 x 20 cm cube) of the reacted fly ash showed that the K-reacted solids (System P) was ~1.7 times stronger in compressive strength than the Na counterpart (System H).

2. From the soluble silicate and zeolite chemistry [7.27-46], it is widely proposed that K\(^+\) has a greater ability to promote the formation of larger oligomeric silicates possibly because of its greater ionic radius than Na\(^+\) [7.16]. Hence, the K-activating solutions employed in this work (e.g. System P) are expected to contain a greater portion of larger oligomeric silicates than the Na counterparts (e.g. System H). As larger oligomeric silicates, or polysilicates, are known to promote gellation rather than precipitation [7.32, 7.46], the above hypothesis, which states that K-activating solution favours the formation of aluminosilicate gel than polysialate precipitates, are justified.

Figure 7.14 shows the IR spectra of the System VI geopolymeric binder, silica gels Gel-I, Gel-II, the reacted fly ash after 168 hours of leaching under System P, and the unreacted Gladstone fly ash (Gdf). Note that all these products were originated from pure potassium
silicate solutions. As shown in Figure 7.14, System VI geopolymeric condition employed in this chapter did not cause complete dissolution of all the phases in Gdf as evidenced by the existence of the 1080 cm$^{-1}$ band of α-quartz and the 620 cm$^{-1}$ and 560 cm$^{-1}$ bands of mullite in the geopolymeric binder. The XRD analysis also confirmed this finding (Figure 7.4). The dissolution and structural reorganisation on the glassy phases of Gdf in the geopolymeric binder, however, were significant: The 650-500 cm$^{-1}$ band attributable to glassy aluminosilicates containing ring structures had almost completely disappeared. Furthermore, the T-O-Si stretching vibration band of the glassy phase of Gdf originally located at 1074 cm$^{-1}$ was found to shift to 1013 cm$^{-1}$ after geopolymerisation. (See Chapter 9 for further
discussion on the subject of IR frequency shift of glassy aluminosilicates with the extent of geopolymerisation.) This new 1013 cm\(^{-1}\) band could be assigned to the gel phase similar to Gel-II (1010 cm\(^{-1}\), gelled by drying the reacted activating solution of System P after 8 hours of leaching, i.e. at the maximum apparent Si dissolution, see Table 7.2). The weak 778 cm\(^{-1}\) band of System VI geopolymeric binder further indicates that there is very little contribution from the gel phase similar to Gel-I (gelled by drying potassium silicate solution of \(R_m = 3.50\), SiO\(_2\) = 5.30 M at 60°C). The binding phase of geopolymers, therefore, could originate from solutions similar in composition to the System P reacted activating solution after 8 hours of leaching. This is consistent with the SEM & EDS observations: The flaky gel structure in System P (Figure 7.12) was morphologically similar to the gel phase of System VI geopolymeric binder (Figure 7.13). The results of the SEM-EDS analyses in Table 7.3 further indicate that both of these gels were silicates with substantial network substitutions of Al and network modifications of Ca and M (M = Na or K). The higher concentration of Si in the flaky gel of System VI geopolymeric binder is probably a result of the higher soluble silicate dosage used for its synthesis. As SEM-EDS analysis is a highly localised technique and fly ash is a highly heterogeneous mixture, the higher Ca concentration of the geopolymeric flaky gel could be attributed to the initially higher CaO content near the region of SEM-EDS analysis.

As the constitution of soluble silicates in aqueous solution is highly dependent on the soluble silicate concentration, the impurities present (such as Al and Ca) and the \(R_m\) ratio at a given pH [7.27-42], the infrared spectral differences of Gel-I, Gel-II and the geopolymeric binding phase (Figure 7.14) can be a result of the differences of soluble silicate speciation and distribution before gellation. Furthermore, it is possible that polysilicates or colloidal silicates, which can form as a result of changing \(R_m\) ratio with time in the solutions of high soluble silicate dosages such as Systems H and P, can adsorb the dissolved Ca and Al, and in effect, stabilises the Ca and Al in the solution phase, as was experimentally proved by numerous investigators [7.35, 7.42-46]. These Ca and Al-containing polysilicates then coagulate and polymerise to produce the final amorphous silicate gels with network substitutions of Al and network modifications of Ca and M (Na or K). This aspect will be further discussed in Chapter 11. Without the presence of higher oligomeric polysilicates, which only occurs at high \(R_m\) ratios or at high soluble silicate dosages at a given pH, it was found that the apparent mass transfer processes between the fly ash and the activating solutions were very limited due to the formation of the interfacial polysialate precipitates,
which subsequently inhibited further solid dissolution. This interfacial polysialate formation could be attributed to the fact that Ca is known to significantly reduce the solubility of silicates or aluminosilicates through the formation of calcium silicate hydrate or aluminium-substituted calcium silicate hydrate [7.10]. This postulate will be further tested in Chapter 8.

7.6 CONCLUSIONS

Soluble silicates were found to significantly alter the microscopic chemical interactions between the glassy aluminosilicates and the activating solutions of pH ~13.95 at 20°C with a solid/solution ratio of 0.1. When low soluble silicate concentration was used, aluminosilicate dissolution was inhibited by secondary precipitation on the surfaces of the reacted fly ash particles, which might be scattered precipitates or films of polysialates, depending on the soluble silicate dosage. On the other hand, significant structural alteration on the glassy contents of the fly ash was observed if the solids were reacted with high concentrations of soluble silicates. The greatly enhanced aluminosilicate dissolution in such conditions was followed by the subsequent gellation of the dissolved species. This could be responsible for the formation of a gel phase similar in morphology as well as elemental compositions as a typical geopolymeric gel. From these experimental observations, the mechanism of geopolymerisation in soluble silicate-rich activating solutions can be similar to those observed in the soluble silicate-rich leaching experiment. On the other hand, weak geopolymeric products should be formed if the activating solutions were deficient in soluble silicates, as was observed in Chapters 5 and 6. Thus, the leaching experiment employed in this chapter, together with the associated analytical procedure, is a well-justified ‘realistic’ reaction model suitable for the study of geopolymerisation under alkaline aqueous solutions of varying soluble silicate dosages.
7.7 REFERENCES


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209
Anionic-Contaminated Chemical Interactions Between Glassy Aluminosilicates and Activating Solutions


In Chapter 4, divalent alkaline earth cations such as Ca\(^{2+}\) and Mg\(^{2+}\) were found to accelerate early geopolymerisation before setting through a heterogeneous mechanism. The mechanism of anion-affected geopolymerisation, however, was less clear. In Chapter 4, it was found that setting of Systems I and IV geopolymeric binders was retarded by anions of Cl\(^{-}\), CO\(_3^{2-}\) and NO\(_3^{-}\). In Chapter 5, it was observed that the long-term product stability of geopolymeric binders using Systems III and V as a case study was adversely affected by Cl\(^{-}\). In particular, it was proposed that the chloride anion had caused aluminosilicate gel precipitation and crystallisation, which was responsible for the decreased product durability of the chloride-affected geopolymeric binders. The chloride-induced aluminosilicate gel crystallisation was also observed in the affected geopolymeric mortars/concretes in Chapter 6, which was attributable to the decreased macroscopic interfacial bonding strength and mortar/concrete compressive strength.

This chapter, therefore, aims to understand the effects of anions in the processes of geopolymerisation as well as the nature of the secondary products by employing the various reaction models developed in Chapter 7, within which Gladstone fly ash was used as a case study. The chloride-induced aluminosilicate gel precipitation and crystallisation as observed in Chapters 5 and 6 will also be revisited and reconfirmed in this chapter. As will be shown later in the chapter, anions that have strong affinities for Ca\(^{2+}\) can be used as reaction probes to better understand the processes of geopolymerisation from a chemical mechanistic point of view.
8.1 INTRODUCTION

As discussed in Chapter 2, aluminosilicate gel formation in geopolymeric systems is initialised by mineral dissolution of the solid starting raw materials. Hence, increasing solution ionic strength by inorganic salt addition, which is otherwise known to enhance or exert no effects on the silicate/aluminosilicate dissolution according to the current geochemistry [8.1-3], should be expected to accelerate or have no effects on the early geopolymeric (aluminosilicate) gel formation. This expectation, however, was found to contradict the experimental observations from Chapter 4, or from Brough et al.’s publication [8.4]: Dissolved sodium and/or potassium chloride salts were effective in retarding the setting processes of geopolymeric gels. If assuming electrolytes should play a similar role in geopolymeric conditions as in geochemical environments, then it is obvious that the setting rate of geopolymeric gels should not be controlled by the kinetics of aluminosilicate dissolution alone. The first part of this chapter, therefore, is designed to investigate the effects of common electrolytes (KCl and K₂CO₃) on the nature of chemical interactions between glassy aluminosilicates and alkaline aqueous solutions by employing the reaction models developed in Chapter 7. In addition, the secondary products produced from the reaction models will also be characterised and used to mechanistically explain the chloride-induced gel deterioration processes observed in Chapters 5 and 6.

As postulated in Chapter 7, the limited chemical interactions between the glassy contents of Gladstone fly ash and the various soluble silicate-deficient activating solutions could be attributed to the Ca-induced interfacial precipitation of polysialates, which subsequently prevented direct contact of the glassy aluminosilicates to the activating solutions. Removal of Ca from the fly ash/activating solution interface, hence, is expected to increase the extent of the mass transfer processes across the microscopic interfaces. Consequently, the second part of this chapter is aimed to test this postulate through the addition of K₂C₂O₄·H₂O and K₂HPO₄, whose constituent anions (C₂O₄²⁻ and PO₄³⁻) are well documented to possess very high affinities for Ca²⁺ [8.5-8], and reduce the formation of the interfacial Ca-poly-sialate believed to be responsible for the limited reactivity of the Gladstone fly ash in soluble silicate-deficient activating solutions.
Note that since the chemical dosage used for the various salt contaminations is small relative to the solution alkalinity used, the effects of potassium from the added salts can be regarded as insignificant. Hence, this chapter in effect studies the effects of anionic contamination on the processes of chemical interactions between glassy aluminosilicates and alkaline aqueous solutions using Gladstone fly ash as a case study. As will be discussed in Section 8.7, the anions Cl\(^{-}\), CO\(_3^{2-}\), C\(_2\)O\(_4^{2-}\) and PO\(_4^{3-}\), if used appropriately, could serve as very effective reaction probes to study the mechanism of geopolymerisation in general.

### 8.2 MATERIALS AND EXPERIMENTAL METHODS

#### 8.2.1 Materials

Gladstone fly ash, Vitrosol N(N40)\(^{\circledR}\) sodium silicate solution and laboratory-grade reagents (NaOH, KOH, KCl, K\(_2\)CO\(_3\), K\(_2\)C\(_2\)O\(_4\),H\(_2\)O, and K\(_2\)HPO\(_4\)) were used to study the effects of anionic contamination on the chemical interactions between a typical glassy aluminosilicate and the various activating solutions of varying soluble silicate dosages.

#### 8.2.2 Leaching Experiments

The reaction model used in this chapter was similar to that of Chapter 7. See Sections 3.3.3.1 and 7.2.2 for the detailed accounts of the reaction model as well as the sampling techniques. The anionic-contaminated activating solutions of the designated compositions were prepared according to Table 8.1 at pH = ~13.95, which were equilibrated to 20 ± 0.5°C. The fly ash was then added to the cooled activating solutions at a solid/solution of 0.1 to make up the leaching slurries at 20 ± 0.5°C. At a designated time, the reacted solids were separated from the solutions using the sampling techniques described in Section 3.3.3.1.

#### 8.2.2.1 Solution analysis

The rate and extent of mass transfer across the ‘microscopic’ interface between the fly ash and the activating solutions were measured by analysing the reacted solutions from the
reaction model using inductively-coupled plasma coupled with optical emission spectroscopy (ICP-OES). See Section 3.3.3.2 for the detailed analytical methods. The pH of all the activating solutions was found to remain very constant throughout the leaching experiments at 13.93-13.98.

Table 8.1 The calculated molar compositions of the activating solutions

<table>
<thead>
<tr>
<th>System</th>
<th>Anion</th>
<th>[SiO$_2$] (mM)</th>
<th>SiO$_2$/M$_2$O $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A $^a$</td>
<td>---</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td>B $^a$</td>
<td>Cl$^-$</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td>C $^a$</td>
<td>CO$_3^{2-}$</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td>D $^a$</td>
<td>(COO)$_2^{2-}$</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td>E $^a$</td>
<td>HPO$_4^{2-}$</td>
<td>0</td>
<td>---</td>
</tr>
<tr>
<td>F $^a$</td>
<td>---</td>
<td>14.24</td>
<td>0.0237</td>
</tr>
<tr>
<td>G $^a$</td>
<td>Cl$^-$</td>
<td>14.24</td>
<td>0.0237</td>
</tr>
<tr>
<td>H $^a$</td>
<td>CO$_3^{2-}$</td>
<td>14.24</td>
<td>0.0237</td>
</tr>
<tr>
<td>I $^a$</td>
<td>C$_2$O$_4^{2-}$</td>
<td>14.24</td>
<td>0.0237</td>
</tr>
<tr>
<td>J $^a$</td>
<td>HPO$_4^{2-}$</td>
<td>14.24</td>
<td>0.0237</td>
</tr>
<tr>
<td>K $^a$</td>
<td>---</td>
<td>28.48</td>
<td>0.0475</td>
</tr>
<tr>
<td>L $^a$</td>
<td>Cl$^-$</td>
<td>28.48</td>
<td>0.0475</td>
</tr>
<tr>
<td>M $^a$</td>
<td>CO$_3^{2-}$</td>
<td>28.48</td>
<td>0.0475</td>
</tr>
<tr>
<td>N $^a$</td>
<td>C$_2$O$_4^{2-}$</td>
<td>28.48</td>
<td>0.0475</td>
</tr>
<tr>
<td>O $^a$</td>
<td>HPO$_4^{2-}$</td>
<td>28.48</td>
<td>0.0475</td>
</tr>
<tr>
<td>P $^a$</td>
<td>---</td>
<td>213.60</td>
<td>0.356</td>
</tr>
<tr>
<td>Q $^a$</td>
<td>Cl$^-$</td>
<td>213.60</td>
<td>0.356</td>
</tr>
<tr>
<td>R $^a$</td>
<td>CO$_3^{2-}$</td>
<td>213.60</td>
<td>0.356</td>
</tr>
<tr>
<td>S $^a$</td>
<td>C$_2$O$_4^{2-}$</td>
<td>213.60</td>
<td>0.356</td>
</tr>
<tr>
<td>T $^a$</td>
<td>HPO$_4^{2-}$</td>
<td>213.60</td>
<td>0.356</td>
</tr>
<tr>
<td>U $^a$</td>
<td>---</td>
<td>569.60</td>
<td>0.949</td>
</tr>
<tr>
<td>V $^a$</td>
<td>Cl$^-$</td>
<td>569.60</td>
<td>0.949</td>
</tr>
<tr>
<td>W $^a$</td>
<td>CO$_3^{2-}$</td>
<td>569.60</td>
<td>0.949</td>
</tr>
<tr>
<td>X $^a$</td>
<td>C$_2$O$_4^{2-}$</td>
<td>569.60</td>
<td>0.949</td>
</tr>
<tr>
<td>Y $^a$</td>
<td>HPO$_4^{2-}$</td>
<td>569.60</td>
<td>0.949</td>
</tr>
<tr>
<td>VII-Control $^b$</td>
<td>---</td>
<td>1000.00</td>
<td>0.250</td>
</tr>
<tr>
<td>VII-Cl $^b$</td>
<td>Cl$^-$</td>
<td>1000.00</td>
<td>0.250</td>
</tr>
<tr>
<td>VII-CO$_3^{2-}$ $^b$</td>
<td>CO$_3^{2-}$</td>
<td>1000.00</td>
<td>0.250</td>
</tr>
<tr>
<td>VII-C$_2$O$_4^{2-}$ $^b$</td>
<td>C$_2$O$_4^{2-}$</td>
<td>1000.00</td>
<td>0.250</td>
</tr>
<tr>
<td>VII-HPO$_4^{2-}$ $^b$</td>
<td>HPO$_4^{2-}$</td>
<td>1000.00</td>
<td>0.250</td>
</tr>
</tbody>
</table>

$^a$ The anion concentration used in all the activating solutions in the ‘reaction model’ was 80 mM with pH = 13.95.
$^b$ The anion concentration used in all the activating solutions for ‘real’ geopolymeric binder synthesis was 400 mM at [OH$^-$] = ~10M.
$^c$ M = Na and K with molar Na/K = 1.50.
8.2.2.2 Solid analysis

X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS) were used to characterise the unreacted and the reacted solids microstructurally. See Section 3.3.3.3 for the detailed analytical methods. Samples for all SEM imaging were carbon-coated using secondary electron detection.

8.2.3 Synthesis and Characterisations of Geopolymeric Binders

System VII geopolymeric binders were synthesised using the same procedure as described in Section 7.2.3.2, which were cured under 20 ± 3°C, 50 ± 5% relative humidity and atmospheric pressure until testing. The activating solutions were prepared in accordance with Table 8.1 and were allowed to cool to room temperature before geopolymeric binder synthesis. Samples were labelled using the same system as those in Chapters 4 and 5.

The yield stress of the early geopolymeric pastes before setting was determined on a Haake vane rheometer attached with vane C. An arbitrary gel setting time was set at a yield stress of 5 kPa where the gel was reasonably hard and was unable to be moulded thereafter. Compressive strength tests were obtained conforming to ASTM C39 on an ELE compression machine using a pace rate of 1 kN/s.

8.3 MICROSCOPIC CHEMICAL INTERACTIONS IN THE CONTAMINATION-FREE REACTION MODELS

8.3.1 Mass Transfer Across the Fly Ash/Activating Solution Microscopic Interface

The results of the ICP-OES solution analyses from the various contamination-free reaction models (i.e. the leaching slurries) are presented in Figure 8.1 and Table 8.2. It is clear that addition of soluble silicates had indeed caused significant changes to the fly ash
dissolution/precipitation characteristics as compared to the one without any soluble silicates (System A).

When less than 200 mM of soluble silicates were used (Systems F and K), it was observed that there was an initial net precipitation of the added soluble silicates, followed by a net Si dissolution as shown in Figure 8.1. This indicates that the apparent fly ash dissolution was a result of the competition between the primary phase dissolution and the secondary phase precipitation processes. In general, it was observed that increasing soluble silicate dosage had decreased the apparent dissolution of all the elements studied including Al, Si, Ca and Mg (Table 8.2) at [Si]₀ < 200 mM. The dissolution inhibition in these systems (Systems F and K) could be a result of the formation of aluminosilicate secondary precipitates (polysialates) with charge-balancing cations of Na and K and network modifiers of Ca and/or Mg. As will be discussed later, scanning electron microscopy of the reacted solids had revealed that there were secondary precipitates of aluminosilicates scattered on top of the fly ash particles. It seems that, at [Si]₀ < 200 mM, the greater the initial soluble silicate
Table 8.2 The maximum apparent dissolution observed from the reaction models

<table>
<thead>
<tr>
<th>System</th>
<th>Al</th>
<th>Si</th>
<th>Ca</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>6.89 (168)</td>
<td>4.49 (168)</td>
<td>0.81 (2)</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>7.52 (168)</td>
<td>4.31 (168)</td>
<td>0.91 (2)</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>7.08 (168)</td>
<td>7.01 (96)</td>
<td>0.56 (6)</td>
<td>0</td>
</tr>
<tr>
<td>D</td>
<td>9.93 (96)</td>
<td>11.93 (48)</td>
<td>0.02 (168)</td>
<td>0</td>
</tr>
<tr>
<td>E</td>
<td>14.12 (96)</td>
<td>19.47 (96)</td>
<td>0.10 (96)</td>
<td>0</td>
</tr>
<tr>
<td>F</td>
<td>9.56 (168)</td>
<td>--- b</td>
<td>0.13 (24)</td>
<td>0</td>
</tr>
<tr>
<td>G</td>
<td>9.97 (168)</td>
<td>--- b</td>
<td>0.14 (48)</td>
<td>0</td>
</tr>
<tr>
<td>H</td>
<td>9.82 (168)</td>
<td>--- b</td>
<td>0.38 (6)</td>
<td>0</td>
</tr>
<tr>
<td>I</td>
<td>5.15 (96)</td>
<td>5.30 (48) c</td>
<td>0.02 (96)</td>
<td>0</td>
</tr>
<tr>
<td>J</td>
<td>8.04 (96)</td>
<td>14.99 (96) c</td>
<td>0.11 (168)</td>
<td>0</td>
</tr>
<tr>
<td>K</td>
<td>7.75 (168)</td>
<td>---</td>
<td>0.08 (48)</td>
<td>0</td>
</tr>
<tr>
<td>L</td>
<td>7.45 (168)</td>
<td>--- b</td>
<td>0.08 (48)</td>
<td>0</td>
</tr>
<tr>
<td>M</td>
<td>8.04 (168)</td>
<td>--- b</td>
<td>0.30 (168)</td>
<td>0</td>
</tr>
<tr>
<td>N</td>
<td>2.75 (48)</td>
<td>1.07 (24) c</td>
<td>0.02 (168)</td>
<td>0</td>
</tr>
<tr>
<td>O</td>
<td>4.89 (96)</td>
<td>12.46 (96) c</td>
<td>0.14 (96)</td>
<td>0</td>
</tr>
<tr>
<td>P</td>
<td>0.92 (48)</td>
<td>6.05 (8)</td>
<td>3.77 (8)</td>
<td>0</td>
</tr>
<tr>
<td>Q</td>
<td>1.56 (48)</td>
<td>76.18 (48)</td>
<td>4.02 (6)</td>
<td>0</td>
</tr>
<tr>
<td>R</td>
<td>2.04 (24)</td>
<td>78.68 (48)</td>
<td>3.74 (24)</td>
<td>0</td>
</tr>
<tr>
<td>S</td>
<td>1.69 (24)</td>
<td>103.24 (24)</td>
<td>4.54 (4)</td>
<td>0</td>
</tr>
<tr>
<td>T</td>
<td>1.54 (96)</td>
<td>118.19 (96)</td>
<td>2.25 (49)</td>
<td>0</td>
</tr>
<tr>
<td>U</td>
<td>3.65 (8)</td>
<td>154.86 (8)</td>
<td>23.25 (8)</td>
<td>0</td>
</tr>
<tr>
<td>V</td>
<td>4.08 (48)</td>
<td>323.96 (8)</td>
<td>23.02 (8)</td>
<td>0</td>
</tr>
<tr>
<td>W</td>
<td>6.12 (24)</td>
<td>601.64 (24)</td>
<td>30.44 (24)</td>
<td>0</td>
</tr>
<tr>
<td>X</td>
<td>4.71 (8)</td>
<td>205.77 (8)</td>
<td>18.24 (6)</td>
<td>0</td>
</tr>
<tr>
<td>Y</td>
<td>3.85 (24)</td>
<td>277.68 (96)</td>
<td>20.58 (24)</td>
<td>0</td>
</tr>
</tbody>
</table>

Theoretical max. dissolution 548.7 832.3 62.1 32.8

a The parenthesis denotes the time of leaching in hours when the value of the maximum apparent dissolution was taken. The maximum apparent dissolution was obtained by subtracting the elemental concentration at the designated time by the initial concentration.

b Only precipitation was observed.

dosage, the greater was the surface coverage and the denser was this secondary layer. The formation of this aluminosilicate layer, a phenomenon known as polysialation according to Phair and Van Deventer [8.9], was favoured in a system of high pH (~14) and less than 1 M soluble silicate concentration. Within these conditions, monomeric silicates were predominant in the solution [8.9-12]. Since the conditions specified were not very different from the conditions used in this chapter (Systems A, F and K), it was possible that a similar reaction mechanism was involved, where monomeric silicates polymerised via a heterogeneous nucleation mechanism and blocked the direct contact between the fly ash primary phase and the surrounding activating solution. This prevented further dissolution and hence a very limited solubility was observed in Systems A, F and K.
If more than 200 mM of the soluble silicates were added to the initial activating solution (System P and U), the fly ash dissolution characteristics were found to deviate even more from System A. See Figure 8.1 and Table 8.2. Apart from the initial rapid dissolution of the added soluble silicates, there was a clear but greatly enhanced net dissolution of Si and Ca. For example, the extent of the apparent dissolution was 8.87 mole% for Si and 27.36 mole% for Ca in System U. These values were about 30 times greater than for System A. In other words, increasing soluble silicate dosage over 200 mM was effective in promoting significant structural breakdown of the primary phases within the fly ash. The dissolved species later polymerised and precipitated to form secondary phase(s) with a quantity large enough to be detected by FTIR and SEM, which will be presented in the next section.

In summary, the effects of soluble silicate addition on the mass transfer processes across the microscopic interface in this chapter are found to closely resemble those observed in Chapter 7: The results obtained from the pure Na or K reaction models were almost the same as the mixed-alkali models with molar Na/K ratio = 1.5 in this chapter. It therefore seems that the effects of soluble silicate addition on the microscopic chemical interactions were not critically affected by the nature of the alkali cations present in the activating solution. They are, however, controlled by the soluble silicate dosages used, or the SiO$_2$/M$_2$O ($Rm$) ratio present in the activating solution, as was discussed in Section 7.5.

### 8.3.2 Evidence of Chemical Interactions from the Reacted Solids

Similar to Chapter 7, the reacted solids obtained from the various reaction models (Systems A, F, K, P and U) were characterised microstructurally using XRD, FTIR and SEM & EDS. These results were then compared to the mass transfer measurements obtained from the ICP-OES solution measurements. In ideal situations, the results from both the solid and the solution analyses should agree well with each other.

From the XRD (Figure 8.2) and the FTIR analyses (Figure 8.3), it was found that the fly ash reactivity was very limited in Systems A, F and K as the infrared spectral bands and the x-ray diffraction peaks of Systems A, F and K-reacted solids were almost identical to those of the unreacted fly ash (Systems F and K are not shown). The very limited chemical interactions
Figure 8.2  The XRD diffractograms of the unreacted Gladstone fly ash (Gdf) and the various reacted solids after 168 hours of leaching under (a) Systems A to E and (b) Systems U to Y (b). Q = α-quartz. M = mullite. W = whewellite.

between the fly ash and the Systems A, F and K activating solutions have been attributed to the interfacial secondary precipitation of polysialates in Section 8.3.1. This had been experimentally confirmed by the SE-SEM images collected: Secondary precipitates were
Figure 8.3  The FTIR spectra of the unreacted Gladstone fly ash (Gdf) and the various reacted solids after 168 hours of leaching under (a) Systems A to E and (b) Systems U to Y (b).

indeed present on the surfaces of the reacted solids of Systems A (Figure 8.4), F and K (Figure 8.5). Furthermore, it seems that, within the concentration range of 0 ≤ [Si]₀ < 200 mM, the greater the soluble silicate dosage, the denser and the more complete was the surface coverage of this secondary layer. According to the SEM-EDS analyses, the secondary layer on the fly ash particles of System A was an aluminosilicate (polysialate), with an averaged elemental composition of 51.46% O, 20.39% Al, 22.64% Si, 3.78% Ca, 0.94% Na and 0.66% K. The Ca content was about 10 times greater than that of the untreated fly ash due to the surface precipitation of the dissolved Ca as shown in Figure 8.4.

When the soluble silicate dosage used in the activating solution was more than 200 mM, Figure 8.6 shows that the secondary precipitation product of System U-reacted fly ash was markedly different from that of System A (Figure 8.4). All the remaining fly ash particles of System U were interconnected by gel-like structures, which according to the SEM-EDS
Figure 8.4  SE-SEM image of System A-reacted fly ash after 168 hours of leaching. The block arrow indicates where typical SEM-EDS analyses were performed.

Figure 8.5  SE-SEM image of System K-reacted fly ash after 168 hours of leaching.

analyses were aluminosilicates with an averaged composition of 60.76% O, 3.18% Al, 20.73% Si, 6.59% Ca, 3.28% Na and 1.97% K. From Figure 8.2 as well as from Chapter
7, the formation of these aluminosilicate gels in System U could be a result of the greatly enhanced primary dissolution, which was followed by the polymerisation and the eventual gellation of the solutes in the bulk solution. This newly formed aluminosilicate gel could be assigned to the new vibrational band located at $1042 \text{ cm}^{-1}$ in the System U reacted solids (Figure 8.3 (b)) and should be amorphous in nature as no new crystalline phase was detected from the XRD analysis as shown in Figure 8.2 (b). The little change in peak intensities of the crystalline phases originally present in Gladstone fly ash such as $\alpha$-quartz (Q) and mullite (M) also suggests that the chemical interactions of the fly ash with the activating solutions were only limited to the glassy phase(s) of the fly ash, as was also suggested in Chapter 7.

Thus, from the above experimental observations, the chemical interactions between the fly ash and the various contamination-free activating solutions of varying soluble silicate dosages were similar to those observed in Chapter 7. The mass transfer processes across the microscopic interface were not affected significantly by the mixed-alkali nature of the activating solutions employed in this chapter.
8.4 Cl\(^-\) & CO\(_3\)\(^{2-}\)–AFFECTED MICROSCOPIC CHEMICAL INTERACTIONS

8.4.1 Mass Transfer between Glassy Aluminosilicates and Activating Solutions

The effects of KCl and K\(_2\)CO\(_3\) addition on the microscopic chemical interactions between the fly ash and the various activating solutions are summarised in Figures 8.7 to 8.9 and Table 8.2. It was found that soluble silicates in the initial activating solution might play a major role in determining the effects of the inorganic salt contaminations.

When the inorganic salts KCl and K\(_2\)CO\(_3\) were added to the activating solution initially free of soluble silicates, the chloride-affected system (System B) was shown to exhibit the same dissolution characteristics as System A. Carbonate (System C), however, was found to accelerate dissolution of Al and Si initially while at the same time lowered the solubility of Ca. See Figure 8.7.

When the activating solution was dosed with less than 200 mM of soluble silicates, it was found that the dissolution of Al and Si of the chloride-affected (Systems G and L) and the carbonate-affected (Systems H and M) systems was the same as that of the salt-free systems (System F and K). See Figures 8.7 and 8.8 and Table 8.2.

If, on the other hand, the soluble silicate dosage was greater than 200 mM, the dissolution and the secondary precipitation characteristics of all the inorganic salt-affected systems (Systems Q, V and R, W) were very different from the salt-free systems (Systems P and U). In particular, when 569.60 mM of soluble silicates was used (Figure 8.9 and Table 8.2), it was found that both Cl\(^-\) and CO\(_3\)\(^{2-}\) investigated were effective in either slowing down or delaying the apparent Al and Si secondary precipitation processes.
Figure 8.7  The leaching characteristics of Systems A to E for (a) aluminium, (b) silicon and (c) calcium. \([\text{Al}] = \text{concentration of Al in the solution at time } t. \ [\text{Al}]_0 = \text{concentration of Al at the start of leaching. Same notations for Si and Ca.}\)
Figure 8.8  The leaching characteristics of Systems F to J for (a) aluminium, (b) silicon and (c) calcium. $[\text{Al}] = \text{concentration of Al in the solution at time } t$. $[\text{Al}]_0 = \text{concentration of Al at the start of leaching. Same notations for Si and Ca.}$
Figure 8.9  The leaching characteristics of Systems U to Y for (a) aluminium, (b) silicon and (c) calcium. $[Al] = $ concentration of Al in the solution at time $t$. $[Al]_0 = $ concentration of Al at the start of leaching. Same notations for Si and Ca.
8.4.2 Evidence of Chemical Interactions from the Reacted Solids

According to the SE-SEM images collected, when the fly ash was reacted with a solution free of soluble silicates (System A), or of low soluble silicate dosages (< 200mM, such as Systems F and K), there appeared some secondary precipitates randomly scattered on top of the fly ash particles. See Figures 8.4 and 8.5. These secondary precipitates were also observed on the chloride and the carbonate-contaminated systems (Systems B, G, L and C, H, M, not shown). It seems that the greater the soluble silicate dosage, the denser and the more complete was the surface coverage of this secondary layer, which was not affected by the inorganic salt additions (KCl and K₂CO₃).

On the other hand, when the soluble silicate dosage was raised to 560 mM, the effects of Cl⁻ and CO₃²⁻ on the gel-like secondary products of System U (Figure 8.6) were varied according to the nature of the contamination. From the SE-SEM micrographs taken, the carbonate-affected gel (System W, not shown) was similar to that of System U. The chloride-affected gel (System V, see Figure 8.10), however, was markedly different to those of the salt-free system or the carbonate-contaminated system: The chloride anion Cl⁻ was found to cause crystallisation within the gel matrix, which otherwise resembled that of System U. Furthermore, this chloride-induced crystallisation was reproducible. According to the SEM-EDS elemental analyses, the chloride-induced crystal was calculated to have an averaged composition of 32Na₂O·K₂O·0.8CaO·AlO₂·(SiO₂)₂·Fe₂O₃·NaCl·nH₂O, assuming all of the Al was in fourth coordination. This chloride-induced crystal could be assigned to the new IR spectral shoulder at 991 cm⁻¹, which is normally attributable to silicate/aluminosilicate with significant alkali inclusion (see Section 3.1.2.4), of the System V-reacted solids as shown in Figure 8.3 (b) The non-inclusion of the Cl⁻ within the newly formed aluminosilicate crystals suggests that (a) Cl⁻ was not structurally bound; and/or (b) it was washed away via ion-exchange with the washing water as described in Section 3.3.3.1. The chloride-induced crystalline phase, however, could not be detected by XRD (Figure 8.2 (b)) possibly because it was below the detection limit (~5%).

The mechanisms and the implications of the Cl⁻ and CO₃²⁻-contaminated chemical interactions between the fly ash and the activating solutions will be discussed below in Section 8.6 together with the results obtained from the C₂O₄²⁻ and PO₄³⁻-contaminated systems.
8.5 C$_2$O$_4^{2-}$ & PO$_4^{3-}$—AFFECTED MICROSCOPIC CHEMICAL INTERACTIONS

8.5.1 Mass Transfer between Glassy Aluminosilicates and Activating Solutions

The effects of K$_2$C$_2$O$_4$.H$_2$O and K$_2$HPO$_4$ additions on the rate and extent of the mass transfer processes across the microscopic interface between the fly ash and the various activating solutions are shown in Figures 8.7 to 8.9 and Table 8.2. Similar to what was observed in the chloride and the carbonate-contaminated systems, the effects of these simple organic salts could be controlled by the soluble silicates in the initial activating solutions.

In the soluble silicate-free activating solution, both the oxalate (System D) and the phosphate (System E) anions were found to be very effective in initiating earlier Al dissolution as well as increasing the extents of apparent Al and Si dissolution from the fly ash as compared to the salt-free system (System A). See Figure 8.7 and Table 8.2. Furthermore, the very low solubility of Ca observed in these systems could be attributed to the fact that both of these
anions, $C_2O_4^{2-}$ and $PO_4^{3-}$, have strong affinities for $Ca^{2+}$ to produce Ca-containing precipitates through the following simplified complexation reactions [8.5-8]:

$$Ca^{2+} (aq.) + C_2O_4^{2-} (aq.) \leftrightarrow CaC_2O_4 (s.); \quad \log(K_{sp1}) = 8.59 \quad (8.1)$$

$$HPO_4^{2-} (aq.) + OH^- (aq.) \leftrightarrow PO_4^{3-} (aq.) + H_2O (l); \quad (8.2a)$$

$$10Ca^{2+} (aq.) + 6PO_4^{3-} (aq.) + 2OH^- (aq.) \leftrightarrow Ca_{10}(PO_4)_6(OH)_2 (s); \quad \log(K_{sp2}) = 58.59 \quad (8.2b)$$

where $K_{sp1}$ and $K_{sp2}$ are the thermodynamic stability products of $CaC_2O_4$ [8.5, 8.6] and $Ca_{10}(PO_4)_6(OH)_2$ (hydroxyapatite) [8.7, 8.8] at 25°C respectively. These values are much higher than that of $Ca(OH)_2$ ($\log(K_{sp}) = 5.26$) [8.5]. Hence it is expected that the dissolved calcium from the fly ash should be precipitated out either as calcium oxalate or hydroxyapatite (HAP) if $K_2C_2O_4.H_2O$ or $K_2HPO_4$ was added to the soluble silicate-free activating solution. The confirmation of the existence of these phases in Systems D and E will be further discussed in Section 8.5.2.

From Figure 8.8 and Table 8.2, when the activating solution was dosed with less than 200 mM of soluble silicates, both the oxalate (System I and N) and the phosphate (System J and O) anions were found to significantly alter the dissolution/precipitation characteristics of the fly ash. In particular, both $C_2O_4^{2-}$ and $PO_4^{3-}$ were very effective in decreasing the solubility of Ca within the first 24 hours of leaching through whewellite ($CaC_2O_4.H_2O$) and hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) precipitation. See Section 8.5.2 for the identification of these phases. As a result, the initial Si precipitation stage of the salt-free Systems F and K (see Section 8.3) was eliminated because of the presence of the $C_2O_4^{2-}$ and $PO_4^{3-}$ anions, which subsequently increased the dissolution of Al and Si from the fly ash, if assuming the solubility of Si, hence Al, was indeed controlled by the dissolved $Ca^{2+}$ according to Iler [8.3]. The above experimental observation is extremely useful in understanding the role of $Ca^{2+}$ from Ca-containing aluminosilicates in the overall geopolymerisation processes. See Section 8.6.
If, on the other hand, a soluble silicate dosage of greater than 200 mM was used, it was again observed that the primary phase dissolution and the secondary precipitation characteristics of all the salt-contaminated systems (Systems S, X and T, Y) were very different from the salt-free systems (System P and U). See Figure 8.9 and Table 8.2. Of particular interest, the phosphate anion $\text{PO}_4^{3-}$ was very effective in slowing down the dissolution of all the elements analysed by ICP-OES at the soluble silicate dosage of 569.60 mM (System Y). This is supported by the fact that the time needed for System Y to reach the maximum apparent dissolution of Al, Si and Ca was lengthened by the presence of $\text{PO}_4^{3-}$ as compared to the contamination-free System U. Phosphate was therefore very effective in retarding the dissolution of the fly ash in a high soluble silicate environment through a still unknown mechanism. As set retardation is extremely important in the technology of geopolymerisation (see Chapter 4) so that extensive future investigations on the role of phosphate in delaying extensive glassy aluminosilicate dissolution will be well justified.

8.5.2 Evidence of Chemical Interactions from the Reacted Solids

8.5.2.1 Crystalline phase identification from XRD

New XRD peaks ($d$-spacing = 2.97, 3.65 and 5.93 Å) were identified only in the oxalate-reacted solids when activated with soluble silicate-deficient activating solutions (Systems D, I and N). See Figure 8.2 (a). By comparing the diffractograms of these solids with the literature [8.13-15], with the assistance of the software Xplot for Windows and PCPDFWIN, a match was found between the new crystalline peaks observed in Systems D, I and N-reacted solids ($d$-spacing = 2.97, 3.65 and 5.93 Å) and the three strongest peaks from the literature ($d$-spacing = 2.97 Å, 3.65 Å and 5.93 Å) of calcium oxalate monohydrate (whewellite, abbreviated as W) with a chemical formula of $\text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O}$ and cell parameters of $a = 12.088$ Å, $b = 14.634$ Å and $c = 10.112$ Å. The similarity between the reaction conditions of Levchenko and Knat'ko [8.16], in which whewellite was reportedly detected in a system containing aluminosilicate clay and lime solution, and the reaction conditions of this work (Systems D, I and N), further strengthened the suggestion that the new crystalline phase was indeed whewellite.

If the soluble silicate dosage used for activating the fly ash had exceeded 200 mM, where significant chemical interactions between the fly ash glassy phase and the activating
solutions had been observed from the ICP-OES solution analyses (Table 8.2), it was found that whewellite (W) was absent in the reacted solids in Systems S and X (Figure 8.2 (b)). From Table 8.1, the soluble silicate dosages used in the activating solutions of Systems S and X were significantly greater than that of the oxalate (80 mM). It is therefore likely that there was competition between the soluble silicates and the oxalate anions for the dissolved calcium. The competition could favour the soluble silicates when their dosage exceeded 200 mM.

In any case, phosphate was found to cause no significant effect on the sample crystallinity as shown in Figure 8.2, suggesting that hydroxyapatite (HAP) that could have formed in the phosphate-contaminated systems could be amorphous in nature.

8.5.2.2 Phase identification from FTIR

From Figure 8.3, the oxalate anion was included in the oxalate-reacted solids if the activating solution was initially free of soluble silicates (System D) or the soluble silicate dosage was less than 200 mM (Systems I and N). The infrared vibrational bands at 781 cm\(^{-1}\) (m, O-C-O asymmetric bending), 1318 cm\(^{-1}\) (s, C-O asymmetric stretching), 1622 cm\(^{-1}\) (s, C-O asymmetric stretching) and 1650 cm\(^{-1}\) (s, sh, HOH bending) were indicative of the presence of calcium oxalate monohydrate \(\text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O}\) (whewellite) \[8.17\]. These vibrational bands, however, were absent in the oxalate-reacted samples if the soluble silicate dosage was greater than 200 mM (Systems S and X). See Figure 8.3 (b). The results obtained from FTIR analyses, therefore, are consistent with the results obtained from the XRD analyses. A separate experiment, in which the reacted solutions were analysed using FTIR photoacoustic spectroscopy (PAS), had shown that oxalate ion was absent in the reacted solutions of Systems D, I and N but was present in the reacted solutions of Systems S and X. This suggests that the oxalate ion was strongly associated with the reacted solids or the size of the independent whewellite crystal was large enough to be retained by the 0.2-\(\mu\)m Minisart\textsuperscript{®} membrane filter during the solid-solution separation stage (see Section 3.3.3.1). On the other hand, the oxalate ion might remain as a soluble form or it was associated with some independent species, which was small enough to pass through the filter membrane.

As was discussed earlier, phosphate anion (PO\(_3\)\(^{3-}\)) has a strong tendency to form complexes with Ca. Under the conditions specified in this work at pH = \(~13.95\), HPO\(_4\)\(^{2-}\) from the parent
K$_2$HPO$_4$ salt would dissociate into PO$_4^{3-}$ and complex with the dissolved Ca$^{2+}$ to form amorphous calcium phosphate (ACP), which later transformed into Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ (hydroxyapatite, HAP) as the most likely secondary product [8.8, 8.18, 8.19]. This was confirmed by the existence of the IR bands 565 cm$^{-1}$, 601 cm$^{-1}$ and 1058 cm$^{-1}$ attributable to HAP [8.20] (Figure 8.3 (a)). The fact that HAP was not shown in the XRD diffractograms (Figure 8.2 (a)) suggests that XRD was not sensitive enough, or crystallization of ACP did not occur (which is less likely due to the IR evidence and the solubility products involved). As was observed with the oxalate-treated systems, HAP was only detected in soluble silicate-deficient systems (Systems E, J and O). If the soluble silicate dosage was greater than 200 mM, the phosphate bands were absent in the respective infrared spectra (Systems T and Y). The different effects of the oxalate and the phosphate anions on the chemical interactions within the systems of different soluble silicate dosages suggest that the reaction mechanisms might have been changed. These mechanisms might be controlled by the nature and the concentration of the soluble silicates in the activating solutions, as will be further discussed in Section 8.6.

8.5.2.3 Sample topography and surface compositions from SEM & EDS

As discussed in Section 8.3.2, when the fly ash was reacted in soluble silicate-deficient and contamination-free activating solutions (Systems A, F, and K), polysialate precipitates were responsible for the limited mass transfer observed. See Figures 8.4 and 8.5. These polysialate precipitates, however, could be largely removed from the fly ash particles if K$_2$C$_2$O$_4$.H$_2$O and K$_2$HPO$_4$ were added to the soluble silicate-deficient activating solutions (Systems D, E, I, J, N and O). See for example Figures 8.11 and 8.12. The surface compositions of these reacted spherical particles were similar to those of the unreacted with 55.97% O, 20.30% Al, 22.28% Si, 0.80% Ca, 0.04% Na and 0.35% K. As the dissolved calcium, which is known to reduce the solubility of silicates in alkaline aqueous solutions [8.10], was taken out from the solution phase by C$_2$O$_4^{2-}$ and PO$_4^{3-}$ as whewellite and hydroxyapatite respectively, an increased Si dissolution without the apparent Si precipitation
was observed in Systems D, E, I, J, N and O (Table 8.2). These experimental observations suggest that Ca was important to cause heterogeneous nucleation at the fly ash surfaces and might control the surface reactions involved if the solution was deficient in soluble silicates.
Figure 8.13  SE-SEM image of System X-reacted fly ash after 168 hours of leaching. The block arrow indicates where typical SEM-EDS analyses were performed.

Figure 8.14  SE-SEM image of System Y-reacted fly ash after 168 hours of leaching. The block arrow indicates where typical SEM-EDS analyses were performed.

On the other hand, when soluble silicate-rich activating solutions were used, it was found that the anionic contamination of oxalate (C$_2$O$_4^{2-}$) could induce crystallisation to the System U aluminosilicate gel (Figure 8.13). As a result, some of the aluminosilicate gel was
transformed into an oxalate-induced aluminosilicate crystalline phase with an averaged chemical composition of $48\text{Na}_2\text{O}-0.8\text{K}_2\text{O}-0.4\text{CaO}[(\text{AlO}_2)_{2-}(\text{SiO}_2)_3]\cdot\text{Fe}_2\text{O}_3\cdot\gamma\text{H}_2\text{O}$ with the assumption that all of the Al was in the fourth coordination. It is, however, not known whether the oxalate anion was included in the crystal structure as SEM-EDS was insensitive to carbon. Other analytical techniques are required for such a purpose.

On the other hand, the phosphate-affected solid at a soluble silicate dosage of 569.60 mM ($\text{System Y}$) is shown in Figure 8.14. It seems that the undissolved fly ash particles were covered by layers of amorphous aluminosilicates and the sample morphology was very different from that of the $\text{System U}$ gel. What caused these morphological differences is still unknown and deserves future investigation.

### 8.6 MECHANISM OF GEOPOLYMERISATION USING ANIONS AS REACTION PROBES

The research objective of this chapter is to understand the effects of anionic contamination on the processes of geopolymerisation from a chemical mechanistic perspective. To achieve this, it is important to test the validity and suitability of the reaction model described in Section 8.2.2 for the various anionic contaminations. Hence, the effects of the various anions ($\text{Cl}^-, \text{CO}_3^{2-}, \text{C}_2\text{O}_4^{2-}$ and $\text{PO}_4^{3-}$) on the macroscopic properties of a ‘real’ geopolymeric binder were firstly characterised. These results were then compared to those observed from the various anionic-contaminated reaction models from Sections 8.4 and 8.5.

The effects of the various potassium salts ($\text{KCl}$, $\text{K}_2\text{CO}_3$, $\text{K}_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$ and $\text{K}_2\text{HPO}_4$) on the rate of geopolymeric gel solidification (or setting), which can be measured by vane rheometer in terms of yield stresses as discussed in Chapter 4, are summarised in Figure 8.15. The phosphate salt ($\text{VII-PO}_4$) was clearly the most effective gel solidification retarder, followed by the chloride ($\text{VII-Cl}$), the oxalate ($\text{VII-C}_2\text{O}_4$), and then the carbonate ($\text{VII-CO}_3$). At the chemical dosage used (400 mM), these salts were found to exert no adverse effects on
Figure 8.15  Yield stress developments of the various System VII geopolymeric binders under 20 ± 3°C, 50 ± 5 % relative humidity and atmospheric pressure.

<table>
<thead>
<tr>
<th></th>
<th>VII-Control</th>
<th>VII-Cl</th>
<th>VII-CO$_3$</th>
<th>VII-C$_2$O$_4$</th>
<th>VII-PO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive strength (MPa)</td>
<td>25.10</td>
<td>25.80</td>
<td>31.14</td>
<td>23.81</td>
<td>25.51</td>
</tr>
</tbody>
</table>

Table 8.3 Compressive strengths of the various System VII geopolymeric binders at the sample age of 28 days under 20 ± 3°C, 50 ± 5 % relative humidity and atmospheric pressure

the product early compressive strength of System VII geopolymeric binders (Table 8.3). Hence, these potassium salts could act as effective gel solidification controllers for geopolymeric products as was also reported in Chapter 4.

From the various reaction models, it is clear that the retarding effects of the anionic contaminations within the System VII geopolymeric binders cannot be explained by following the dissolution/precipitation characteristics of the fly ash using soluble silicate-deficient activating solutions ([Si]$_0$ < 200 mM). On the other hand, an activating solution containing 569.60 mM of soluble silicates (Systems U) was demonstrated to be a good reaction model for studying gel solidification processes within System VII geopolymeric binders, which were also activated with soluble silicate-rich activating solutions (Table 8.1).
From Figure 8.15, the gellation time (defined as the time required for a geopolymeric paste to start gaining sufficient strength) for VII-Cl, VII-CO$_3$ and VII-C$_2$O$_4$ was slightly longer than that of VII-Control. This corresponds well to the results obtained from the reaction models Systems V, W and X: The time for the apparent Si precipitation to take place in Systems V, W and X was also slightly longer than that of System U (Figure 8.9 and Table 8.2). The effect of the phosphate salt on delaying the fly ash primary phase dissolution (Figure 8.9) was probably the reason that gave rise to the extended gellation time of VII-PO$_4$ (Figure 8.15). From the reaction models Systems V and W, the chloride and carbonate salts were found to decrease the rate of the secondary precipitation processes of Si. This can be translated to the smaller tangents associated with the chloride and carbonate-affected yield stress curves (VII-Cl and VII-CO$_3$, Figure 8.15). In other words, the retarding effects of simple electrolytes, such as KCl and K$_2$CO$_3$, on the rate of geopolymeric gel solidification before final set as observed in Chapter 4 and in this chapter can be two-fold: (a) the initiation of the aluminosilicate gel formation is delayed in the presence of Cl$^-$ and CO$_3^{2-}$, although not to a great extent; and (b) the growth rate of the aluminosilicate gel was retarded by Cl$^-$ but not CO$_3^{2-}$. As the reaction models of Systems U, V and W had revealed that the rate of the glassy aluminosilicate dissolution was not retarded in the presence of the electrolytes KCl and K$_2$CO$_3$, it appears that the retarding effects of Cl$^-$ and CO$_3^{2-}$ anions should be concentrated at the gellation step of geopolymerisation (see Section 2.2.4).

According to Iler [8.3], after colloidal polysilicates have been formed through polymerisation of lower oligomeric silicates, the colloidal silicate particles are then linked together by aggregation, which is facilitated by the interparticle attractive/repulsive forces. Depending on the nature of the aggregation processes, three major types of products can be produced:

1. Gels, where colloidal particles are linked together in branched chains that fill the whole volume of a colloidal suspension. As a result, there is no associated change in silicate concentration in a macroscopic sense across the medium. In this case, the overall medium becomes viscous and then is solidified by a coherent network of colloidal particles which, by capillary actions, retains the solution in the gel structure (or pore solution);
2. Precipitates, where colloidal particles are concentrated into closely packed clumps through the expulsion of the solution; and

3. Flocculates, where the particles are linked together by bridges of the flocculating agent, which are sufficiently long so that the aggregates structure remains open and voluminous.

As there is no flocculation agent present in *System VII* geopolymeric conditions, it leaves gellation and precipitation (coagulation) of silicates/aluminosilicates as the only two possible outcomes of geopolymerisation of glassy aluminosilicate solids in soluble silicate-rich activating solutions.

In highly alkaline regime, i.e. pH > 11, it is known that surface silanol groups of silicates are deprotonated so that the negatively charged colloidal particles are prevented from aggregation. Addition of electrolytes to colloidal suspensions therefore is known to accelerate both gellation and coagulation as it lowers the surface charge of the charged colloidal particles [8.3]. If assuming the increase of the yield stress of the geopolymeric paste as shown in Figure 8.15 is mainly due to the formation of the silicate/aluminosilicate gels (this assumption is reasonable as the yield stress measured after the so-called gellation time is relatively high for colloidal suspensions without extensive gellation), the retarding effects of the electrolytes especially KCl on the gel solidification retardation as shown in Figure 8.15 can then be understood as their accelerating effects on colloidal silicate coagulation rather than gellation. In other words, precipitation of silicate/aluminosilicate was enhanced in the presence of electrolytes. As CO$_3^{2-}$ was shown to cause no observable effects on the yield stress development of *System VII* geopolymeric paste after the initiation of gel solidification (Figure 8.15), it is possible that CO$_3^{2-}$ was not as effective a coagulation agent as Cl$^-$, or it was precipitated out with the dissolved Ca$^{2+}$ to form CaCO$_3$ precipitates, which are highly insoluble in aqueous environments. The chloride-induced precipitates then crystallised to yield aluminosilicate crystallites [8.21] such as those shown in Figures 6.13, 6.15 and 8.10.

As was discussed in Section 7.5, gellation of silicates or aluminosilicates is more favourable in a solution composed of higher oligomeric polysilicates/colloidal silicates. On the other hand, if a solution is composed of lower oligomeric silicates, which could be a result of low
Rm ratio, decreased solution pH, or accelerated rate of aggregation before significant colloidal growth is allowed to take place, precipitation is a more likely outcome. Therefore, the chloride-induced aluminosilicate precipitation and crystallisation in the reaction model System V can be explained by the accelerated coagulation rate of small-sized colloidal silicates, which is facilitated by the decreased surface charge of the colloidal particles in the presence of KCl electrolyte [8.3]. In real geopolymeric conditions, as the soluble silicate dosage used in System VII geopolymeric binder synthesis was substantially higher than the reaction model System V, it is possible that gellation could still proceed in the chloride-contaminated environment without much aluminosilicate precipitation. However, as the gellation was initiated earlier in the presence of KCl before substantial colloidal growth was achieved, these chloride-contaminated systems could give rise to structurally weaker gels [8.3], which was prone to hydrolytic attack as suggested in Chapter 5. This conclusion is of critical significance in the technology of geopolymerisation as it implies that any activating solution that does not allow sufficient time for colloidal particle growth before gellation will cause silicates/aluminosilicate precipitation or gel weakening, which then reduce the interparticle strength as well as the macroscopic strength, as was observed in the System V geopolymeric binders (activated with a solution with relatively low Rm ratio) in Chapter 5.

From Section 8.5, additions of K₂C₂O₄·H₂O and K₂HPO₄ to activating solutions deficient in soluble silicates ([Si]₀ < 200 mM, pH = ~13.95) had been observed to be very effective in removing the dissolved Ca²⁺ from the dissolving fly ash surfaces to form Ca-containing precipitates of whewellite and hydroxyapatite. As a result, the interfacial secondary precipitates of Systems A, F and K (see Figures 8.4 and 8.5) were not observed in Systems D, E, I, J, N and O (Figures 8.11 and 8.12). This absence of secondary precipitates had been attributed to the increased apparent fly ash dissolution of Systems D, E, I, J, N and O as compared to that of the salt-free counterparts (Systems A, F and K). See Table 8.2. Without the presence of C₂O₄²⁻ and PO₄³⁻, the dissolved Ca²⁺ from the fly ash would be adsorbed back to the dissolving SiO₂ surface at high solution pH (> ~10) to form layers of calcium hydroxides or calcium silicate hydrates [8.3, 8.22] or polysialates as suggested in Chapter 7, which nucleated from the dissolving surface and blocked the direct contact between the aluminosilicate surface and the activating solutions. Therefore, it seems that the reactivity of Ca-aluminosilicates was indeed controlled by the dissolved Ca²⁺ concentration in the activating solutions. This implies that if there is a ‘reaction sink’ present in the activating solutions that draws the dissolved Ca²⁺ away from the aluminosilicate/alkaline aqueous
solution interface, the extent of chemical interactions between the Ca-aluminosilicates and the activating solutions will be greatly enhanced. As was observed in Chapter 7 as well as in this chapter, increasing the soluble silicate dosage to over 200 mM in the activating solutions of Na\(^+\), K\(^+\) and Na\(^+\)/K\(^+\) at pH = ~13.95 at 20°C was indeed very effective in promoting the extent of fly ash glassy phase dissolution as compared to the soluble silicate-free systems. As silicates of higher degrees of polymerisation, such as colloidal silicates, are known to readily adsorb Ca\(^{2+}\) and Al\(^{3+}\) for gellation (not precipitation) and growth [8.3, 8.23-27], the soluble silicates of higher degrees of polymerisation could serve as a reaction sink that draws Ca\(^{2+}\) and Al\(^{3+}\) from the dissolving Ca-aluminosilicate surfaces and thus promotes dissolution.

8.7 CONCLUSIONS

Soluble silicates were found to play a very important role in determining the processes of primary phase dissolution and secondary phase precipitation of a Class F fly ash in alkaline silicate solutions (~ pH 13.95) at 20°C. They also determined how the potassium salts (KCl, K\(_2\)CO\(_3\), K\(_2\)C\(_2\)O\(_4\)H\(_2\)O and K\(_2\)HPO\(_4\)) could affect the nature of chemical interactions between the fly ash and the various alkaline aqueous solutions. It was found that reaction model System U with a soluble silicate dosage of 569.60 mM and molar SiO\(_2\)/M\(_2\)O = 0.949 at pH = ~13.95 was suitable to model the gel solidification processes within a real System VII geopolymeric binder. The greatly affected dissolution and precipitation processes within the salt-affected reaction models were found to agree well with the observed gel solidification characteristics of the salt-affected System VII geopolymeric binders. The phosphate salt (K\(_2\)HPO\(_4\)) was the most effective retarder for geopolymer synthesis among all. The fact that aluminosilicate crystallisation was identified in the chloride and the oxalate-contaminated reaction models suggests that these salts may also induce crystallisation within real geopolymeric systems as observed in Chapters 5 and 6.

From the above experimental observations, the mechanism of the chloride-induced aluminosilicate precipitation and crystallisation in the reaction model System V could be attributed to the acceleratory effects of KCl on the rate of colloidal coagulation due to its
charge neutralisation effects on the negatively-charged deprotonated silanol groups. In ‘real’
geopolymeric conditions, contamination of chlorides could give rise to structurally weaker
aluminosilicate gel also attributable to the acceleratory effects of Cl⁻ on colloidal
aggregation, which prevented growth of colloidal particles before gellation. As a result, the
aluminosilicate gels in the chloride-contaminated systems were prone to hydrolytic attack as
observed in Chapter 5.

Through the use of K₂C₂O₄.H₂O and K₂HPO₄ as reaction probes, it was further found that
the dissolved Ca²⁺ content in the activating solutions should control the chemical reactivity
of the fly ash. Soluble silicate of high dosages, which resulted in the formation of higher
oligomeric silicates/colloidal silicates that readily adsorbed dissolved Ca²⁺ from the fly ash,
could be responsible for the enhanced chemical interactions between the glassy Ca-
aluminosilicate phase(s) and the soluble silicate-rich activating solutions. The role of soluble
silicates in geopolymerisation will be further investigated through the use of infrared
frequency shift in the next chapter.

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CHAPTER 9

Geopolymerisation of Glassy Aluminosilicates

This chapter is based on the publication: The Use of Infrared Spectroscopy to Study Geopolymerisation of Heterogeneous Amorphous Aluminosilicates, submitted to Langmuir 2002.

The microscopic chemical interactions between a typical heterogeneous glassy aluminosilicate and the various activating solutions have been extensively studied in Chapters 7 and 8 through the use of the novel reaction models that have been developed for the first time in this thesis. The dosage of soluble silicates of an activating solution at a constant solution alkalinity was found to critically determine the extent of the microscopic chemical interactions as well as the nature of the secondary products. From Chapters 5 and 6, solution alkalinity of activating solutions at a constant soluble silicate dosage also seems to play an important role in the synthesis of the various geopolymeric products. This chapter therefore is aimed to understand the role of solution alkalinity as well as the role of soluble silicates in the overall geopolymerisation processes using a novel in situ and in real time analytical procedure developed for the first time in this thesis. As will be shown in this chapter, geopolymerisation should consist of three major processes: (1) cation-exchange with the activating solutions; (2) alkali-activation, which hydrolyses the aluminosilicate solids and releases the dissolve species into the nearby activating solutions; and (3) polymerisation of the dissolved species. Without extensive amounts of soluble silicates present in the initial activating solution, geopolymerisation would terminate at the cation-exchange step without much alkali-activation or polymerisation, thus reducing the amount of the principal binding phase of a geopolymeric system – the aluminosilicate gel – being produced regardless of the solution alkalinity. This could be used to mechanistically explain the experimental observations as presented in Chapters 5 and 6, which is extremely important for the purposes of efficient process optimisation in the technology of geopolymerisation.
9.1 INTRODUCTION

The term geopolymerisation has been used by a number of investigators to describe all the chemical processes that are involved in producing geopolymeric binders [9.1-4]. As discussed in Chapter 2, these may include (1) OH- promoted hydrolytic reaction, or alkali-activation, that releases dissolved species into the so-called activating solutions; (2) polymerisation of the dissolved species; (3) gellation of the polymerised aluminosilicates; (4) gel setting and hardening; and (5) gel solid-state transformation. Although these reaction steps may sound reasonable by considering the chemistry of soluble silicates and zeolites, direct experimental proof on each of the proposed geopolymerisation steps is still lacking in the field of geopolymer technology. This can be mainly attributed to the difficulties in separating the solid from the gel/solution phase during reaction and the lack of methods for in situ analyses. See Section 3.3.3. As understanding the chemistry of geopolymerisation is of vital importance for its efficient process optimisation, this chapter therefore is aimed to investigate the effects of solution alkalinity and soluble silicate dosage on the processes of geopolymerisation in situ and in real time.

To achieve the above research objective, a novel analytical procedure was developed for the first time in this thesis by taking advantage of the results obtained from the reaction models in Chapters 7 and 8. In Chapters 7 and 8, the infrared vibrational band of the Gladstone fly ash originally located at ~1074 cm\(^{-1}\) was found to shift to the lower frequency end of an infrared spectrum when significant apparent fly ash dissolution was observed. This observation can be understood by considering the chemical changes that should be imposed on the solid raw materials after alkali-activation. With the assumption that Al is always in the fourth coordination, a simplified hydrolytic reaction on an aluminosilicate is shown in eq (9.1):

\[
\text{M}^+-(\text{Al}^3-\text{O}^-\text{Si})_{\text{raw}}^- + 2\text{M}^+\text{OH}^- \rightarrow \text{M}^+-(\text{Al}^3^-\text{O}^-\text{M}^+) + (\text{M}^+\text{O}^-\text{Si})^- + \text{H}_2\text{O} \quad (9.1)
\]

where M = Na or K.
From eq (9.1), it is clear that during alkali-activation, every bridging oxygen atom (BO) of the original aluminosilicate is replaced by two negatively charged non-bridging oxygen atoms (NBO), which are charge compensated by the alkalis. Microstructurally, this is similar to adding alkalis to synthetic silicate or aluminosilicate glasses, whose alkali and water contents can be artificially controlled. From the literature [9.5-10], addition of alkalis as network modifiers to an (alumino)silicate is known to generate a greater concentration of NBO’s within the structure. During such a process, the TO$_4$ (T = Al or Si) units within the silicate network have become more isolated with increasing alkali inclusion and thus lowers the molecular vibration force constant of the T-O bond. As a result, an infrared (IR) band attributable to T-O-Si asymmetric stretching vibration of the TO$_4$ tetrahedra of an (alumino)silicate glass has been found to shift to a lower frequency end with increasing alkali content, and the extent of the infrared frequency shift is approximately linear to the alkali content within the glass structure [9.6-9.10]. See also Section 3.1.2.4. With the view that a greater extent of alkali-activation on aluminosilicates should also give rise to products of greater NBO concentrations, it is expected that similar trends should be observed during geopolymerisation of aluminosilicates especially at the early stages, as was partially observed in Chapters 7 and 8.

This chapter, therefore, employs infrared spectroscopy to test the above hypothesis with the aim to quantitatively measure the extent of alkali-activation of the glassy phase(s) within a typical Gladstone fly ash as a case study. As will be presented later in this chapter, following the progressive change of the infrared vibrational band of real geopolymeric binders in real-time can also yield semi-quantitative information on the extent of polymerisation of the dissolved species after the initial alkali-activation. This can be used to mechanistically explain the macroscopic setting and hardening characteristics of geopolymeric binders, mortars and concretes.
9.2 MATERIALS AND EXPERIMENTAL METHODS

9.2.1 Materials

Gladstone fly ash, Vitrosol N(N40)® sodium silicate solution, KASIL® 2236(K32) potassium silicate solution, laboratory-grade reagents NaOH and KOH and distilled/deionised water were used throughout the investigation.

9.2.2 Leaching Experiments

Leaching was performed to accurately measure the extent of fly ash dissolution as a result of alkali-activation. In each leaching experiment (or reaction model), 100 g of the pre-dried fly ash was added to 1000 mL of the leaching solution (or the activating solution). All leaching tests were run in parallel at 20 ± 0.5°C to minimise experimental errors. The activating solutions were prepared by dissolving calculated amounts of the silicate solution (Vitrosol N(N40) or KASIL® 2236(K32)) and MOH (M = Na and/or K) in distilled/deionised water. The final compositions of the activating solutions are presented in Table 9.1. Note that the reaction models Systems A to P of this chapter were the same as the reaction models Systems A to P in Chapter 8. At the designated time internal, 10 mL of the suspensions was collected until 168 hours of leaching. The reacted, or alkali-activated, solids and the respective activating solutions were separated according to the procedure described in Section 3.3.3.1.

9.2.2.1 Solution analysis

The compositions of the reacted activating solutions were determined by ICP-OES as described in Section 3.3.3.2.

9.2.2.2 Solid analysis

The reacted fly ash was analysed by powder XRD analysis, FTIR spectroscopy and BSE-SEM & EDS topographical characterisations. Spectral decomposition (or deconvolution) of the complex infrared bands collected over the 1350-800 cm⁻¹ spectral region was performed
Table 9.1 The calculated molar compositions of the activating solutions

<table>
<thead>
<tr>
<th>System</th>
<th>Alkali Cation (M)</th>
<th>[SiO$_2$] (mM)</th>
<th>[OH$^-$] (mM)</th>
<th>SiO$_2$/M$_2$O ($R_m$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A $^a$</td>
<td>Na</td>
<td>0</td>
<td>~600 $^d$</td>
<td>---</td>
</tr>
<tr>
<td>B $^a$</td>
<td>Na</td>
<td>14.24</td>
<td>~600 $^d$</td>
<td>---</td>
</tr>
<tr>
<td>C $^a$</td>
<td>Na</td>
<td>28.48</td>
<td>~600 $^d$</td>
<td>---</td>
</tr>
<tr>
<td>D $^a$</td>
<td>Na</td>
<td>42.72</td>
<td>~600 $^d$</td>
<td>---</td>
</tr>
<tr>
<td>E $^a$</td>
<td>Na</td>
<td>71.20</td>
<td>~600 $^d$</td>
<td>---</td>
</tr>
<tr>
<td>F $^a$</td>
<td>Na</td>
<td>213.60</td>
<td>~600 $^d$</td>
<td>---</td>
</tr>
<tr>
<td>G $^a$</td>
<td>Na</td>
<td>427.60</td>
<td>~600 $^d$</td>
<td>---</td>
</tr>
<tr>
<td>H $^a$</td>
<td>Na</td>
<td>569.60</td>
<td>~600 $^d$</td>
<td>---</td>
</tr>
<tr>
<td>I $^a$</td>
<td>K</td>
<td>0</td>
<td>~600 $^d$</td>
<td>---</td>
</tr>
<tr>
<td>J $^a$</td>
<td>K</td>
<td>14.24</td>
<td>~600 $^d$</td>
<td>---</td>
</tr>
<tr>
<td>K $^a$</td>
<td>K</td>
<td>28.48</td>
<td>~600 $^d$</td>
<td>---</td>
</tr>
<tr>
<td>L $^a$</td>
<td>K</td>
<td>42.72</td>
<td>~600 $^d$</td>
<td>---</td>
</tr>
<tr>
<td>M $^a$</td>
<td>K</td>
<td>71.20</td>
<td>~600 $^d$</td>
<td>---</td>
</tr>
<tr>
<td>N $^a$</td>
<td>K</td>
<td>213.60</td>
<td>~600 $^d$</td>
<td>---</td>
</tr>
<tr>
<td>O $^a$</td>
<td>K</td>
<td>427.60</td>
<td>~600 $^d$</td>
<td>---</td>
</tr>
<tr>
<td>P $^a$</td>
<td>K</td>
<td>569.60</td>
<td>~600 $^d$</td>
<td>---</td>
</tr>
<tr>
<td>Q $^a$</td>
<td>Na/K $^c$</td>
<td>0</td>
<td>~600 $^d$</td>
<td>---</td>
</tr>
<tr>
<td>R $^a$</td>
<td>Na/K $^c$</td>
<td>14.24</td>
<td>~600 $^d$</td>
<td>---</td>
</tr>
<tr>
<td>S $^a$</td>
<td>Na/K $^c$</td>
<td>28.48</td>
<td>~600 $^d$</td>
<td>---</td>
</tr>
<tr>
<td>T $^a$</td>
<td>Na/K $^c$</td>
<td>213.60</td>
<td>~600 $^d$</td>
<td>---</td>
</tr>
<tr>
<td>U $^a$</td>
<td>Na/K $^c$</td>
<td>569.60</td>
<td>~600 $^d$</td>
<td>---</td>
</tr>
<tr>
<td>V $^a$</td>
<td>Na/K $^c$</td>
<td>1,000.00</td>
<td>1,000.00</td>
<td>1.0</td>
</tr>
<tr>
<td>W $^a$</td>
<td>Na/K $^c$</td>
<td>2,000.00</td>
<td>2,000.00</td>
<td>1.0</td>
</tr>
<tr>
<td>X $^a$</td>
<td>Na/K $^c$</td>
<td>0</td>
<td>5,000.00</td>
<td>0</td>
</tr>
<tr>
<td>Y $^a$</td>
<td>Na/K $^c$</td>
<td>2,500.00</td>
<td>5,000.00</td>
<td>0.5</td>
</tr>
<tr>
<td>Z $^a$</td>
<td>Na/K $^c$</td>
<td>0</td>
<td>10,000.00</td>
<td>0</td>
</tr>
<tr>
<td>AA $^a$</td>
<td>Na/K $^c$</td>
<td>2,500.00</td>
<td>10,000.00</td>
<td>0.25</td>
</tr>
</tbody>
</table>

**X-Control**

<table>
<thead>
<tr>
<th>System</th>
<th>Alkali Cation (M)</th>
<th>[SiO$_2$] (mM)</th>
<th>[OH$^-$] (mM)</th>
<th>SiO$_2$/M$_2$O ($R_m$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VIII-Control $^b$</td>
<td>Na/K $^c$</td>
<td>0</td>
<td>5,000.00</td>
<td>0</td>
</tr>
<tr>
<td>IX-Control $^b$</td>
<td>Na/K $^c$</td>
<td>2,500.00</td>
<td>5,000.00</td>
<td>0.5</td>
</tr>
<tr>
<td>X-Control $^b$</td>
<td>Na/K $^c$</td>
<td>0</td>
<td>10,000.00</td>
<td>0</td>
</tr>
<tr>
<td>XI-Control $^b$</td>
<td>Na/K $^c$</td>
<td>2,500.00</td>
<td>10,000.00</td>
<td>0.25</td>
</tr>
</tbody>
</table>

$^a$ The activating solution was prepared for leaching at a solid/solution ratio of 0.1.
$^b$ The activating solution was prepared for synthesising geopolymeric binders at a solid/solution ratio of 2.
$^c$ Molar Na/K = 0.2.
$^d$ The solution was adjusted to pH = 13.95.

by using the CurveFit function of the BioRad Win-IR program (Version 4.14 Level II Galactic Industries Corporation). The deconvolution procedure used in this work was in accordance with those described by Handke et al. [9.11]. Briefly, the starting calculation parameters for the curve fitting process, such as number of component bands, band positions, width at half-maximum, relative intensities and shape, were predetermined by combined procedures of the secondary derivative method and Fourier self-deconvolution from Griffiths and Pariente [9.12]. The accurate positions of the band maxima were
determined by the second derivative of the spectra at the inflection points. Similar information together with other calculation parameters were obtained by the deconvolution process and compared with the second derivative method. The actual curve fitting process was performed using the Levenberg-Marquardt algorithm from the BioRad Win-IR program to iteratively minimise the weighted difference between the actual (or the curve fitted) and the measured data, with the aim to minimise the number of component bands.

9.2.3 Synthesis and Characterisations of Geopolymeric Binders

Systems VIII, XI, X and XI geopolymeric binders (or VIII-Control, IX-Control, X-Control and XI-Control) were synthesised using the same procedure as described in Section 7.2.3.2, which were cured under 20 ± 3°C, 50 ± 5% relative humidity and atmospheric pressure until testing. The activating solutions were prepared in accordance with Table 9.1 and were allowed to cool to room temperature before geopolymeric binder synthesis. Samples were labelled using the same system as those in Chapters 4 and 5.

The final setting time was determined using the modified Vicat needle as in Section 3.2.4.2. The compressive strength was tested in accordance with Section 3.2.4.3. Furthermore, the various geopolymeric binders were microstructurally characterised by XRD and FTIR using the procedure as described in Section 9.2.2.2.

9.3 ALKALI-ACTIVATION

9.3.1 Mass Transfer Across the Fly Ash/Activating Solution Microscopic Interface

As the results of Systems A to P have already been presented and discussed in Chapter 7, it will not be discussed in detail again in this chapter. From Figure 9.1, it is clear that the addition of significant amount of soluble silicates to the activating solution of Na/K = 0.2 at pH ~13.95 (System U) could induce significant changes to the fly ash dissolution/reprecipitation characteristics as compared to the system without any soluble
Figure 9.1  The Si and Ca dissolution profiles of Systems Q and U reaction models. $[\text{Si}] = \text{concentration of Si in the activating solution at time } t$. $[\text{Si}]_0 = \text{concentration of Si in the initial activating solution. Same notation for Ca.}$

Silicates (System Q). $[\text{Si}]_0$ denotes the initial soluble silicate concentration in the activating solution. A positive ($[\text{Si}] - [\text{Si}]_0$) value means the overall process is dissolution and vice versa. This is similar to what have been observed in Chapters 7 and 8 on the reaction models of varying alkali contents. Hence, the effects of soluble silicates on the mass transfer processes between the fly ash and the activating solutions are not affected by the nature of the alkali cations present in the solutions.

In general, the effects of soluble silicates on the extent of apparent Al dissolution can be divided into 3 major intervals as shown in Table 9.2. At $0 \leq [\text{Si}]_0 \leq 14.24 \text{ mM (Systems A to B, I to J and Q to R)}$, the presence of soluble silicates was found to increase the maximum apparent dissolution of Al. At $14.24 < [\text{Si}]_0 < 213.60 \text{ mM (Systems C to E, K to M and S to T)}$, the maximum apparent Al dissolution decreased with increasing soluble silicate dosage.
Table 9.2 The maximum apparent dissolution observed from the reaction models

<table>
<thead>
<tr>
<th>System</th>
<th>Maximum apparent dissolution (mM) *</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>A</td>
<td>7.0 (168)</td>
</tr>
<tr>
<td>B</td>
<td>9.1 (168)</td>
</tr>
<tr>
<td>C</td>
<td>7.3 (168)</td>
</tr>
<tr>
<td>D</td>
<td>1.7 (168)</td>
</tr>
<tr>
<td>E</td>
<td>0.6 (97)</td>
</tr>
<tr>
<td>F</td>
<td>1.1 (26)</td>
</tr>
<tr>
<td>G</td>
<td>2.3 (10)</td>
</tr>
<tr>
<td>H</td>
<td>3.5 (8)</td>
</tr>
<tr>
<td>I</td>
<td>6.9 (168)</td>
</tr>
<tr>
<td>J</td>
<td>9.6 (168)</td>
</tr>
<tr>
<td>K</td>
<td>7.7 (168)</td>
</tr>
<tr>
<td>L</td>
<td>2.2 (168)</td>
</tr>
<tr>
<td>M</td>
<td>0.9 (168)</td>
</tr>
<tr>
<td>N</td>
<td>0.9 (48)</td>
</tr>
<tr>
<td>O</td>
<td>1.9 (48)</td>
</tr>
<tr>
<td>P</td>
<td>3.7 (8)</td>
</tr>
<tr>
<td>Q</td>
<td>6.9 (168)</td>
</tr>
<tr>
<td>R</td>
<td>9.6 (168)</td>
</tr>
<tr>
<td>S</td>
<td>7.8 (168)</td>
</tr>
<tr>
<td>T</td>
<td>0.9 (48)</td>
</tr>
<tr>
<td>U</td>
<td>3.7 (8)</td>
</tr>
<tr>
<td>V</td>
<td>13.4 (48)</td>
</tr>
<tr>
<td>W</td>
<td>52.3 (72)</td>
</tr>
<tr>
<td>X</td>
<td>53.0 (168)</td>
</tr>
<tr>
<td>Y</td>
<td>164.6 (120)</td>
</tr>
<tr>
<td>Z</td>
<td>78.2 (168)</td>
</tr>
<tr>
<td>AA</td>
<td>123.5 (168)</td>
</tr>
</tbody>
</table>

Theoretical max. dissolution c

|        | 375.4   | 704.6  | 62.1  | 32.8 |

* The parentheses denote the time of leaching in hours when the value of the maximum apparent dissolution was taken. The maximum apparent dissolution was obtained by subtracting the initial concentration from the elemental concentration at the designated time, i.e. ([Si] – [Si]₀).

b No apparent dissolution but only precipitation was observed.

Values were obtained by assuming α-quartz and mullite were insoluble. See Section 3.1.2.2 for the mass compositions of these crystalline phases within Gladstone fly ash.

If the soluble silicate dosage was increased still further ([Si]₀ ≥ 213.60 mM, Systems F to H, N to P and T to U), the maximum apparent Al dissolution was found to increase again with increasing soluble silicate dosage. The maximum apparent Al dissolution was observed at the end of each leaching experiment at 168 hours. No Mg dissolution was observed at all except when the activating solutions were highly concentrated in alkali and soluble silicate concentrations (Systems W and Y).
The dissolution characteristics of Si and Ca, on the other hand, were very different from those of Al. See Table 9.2. When the soluble silicate dosage was less than 213.60 mM (Systems B to E, J to M and R to S), the presence of soluble silicates in the initial activating solution evidently decreased the extents of Si and Ca dissolutions due to the formation of the interfacial precipitates of (Na,K,Ca)-polysialates (see Chapters 7 and 8). In these systems, the time to reach the maximum apparent dissolution of Si and Ca was always observed at the end of the leaching experiments at the 168th hour. If, however, more than ~200 mM of soluble silicates were added (Systems F to H, N to P and T to U), both the maximum apparent dissolutions of Si and Ca were found to increase with increasing soluble silicate dosage. At \([\text{Si}]_0 = 569.60 \text{ mM} \) (Systems H, P and U), the maximum apparent dissolutions of Si and Ca, which occurred at approximately 12 hours, were significantly greater than those without soluble silicates (Systems A, I and Q). See Figure 9.1. After the maximum dissolution was achieved, Si (including the dissolved and the added soluble silicates) and Ca then precipitated out as secondary phase(s), the nature of which was highly dependent on the nature of the alkali cation in the activating solutions as shown in Chapter 7.

From the above it can be concluded that addition of soluble silicates to an activating solution at pH ~13.95 could be effective in promoting fly ash dissolution if the soluble silicate dosage was over ~200 mM. Similar trends could also be observed when the alkali concentration of the activating solution was increased. The maximum apparent dissolutions of Si and Ca for Systems Y ([\text{MOH}]_0 = 5 \text{ M}, [\text{Si}]_0 = 2.5 \text{ M}) and AA ([\text{MOH}]_0 = 10 \text{ M}, [\text{Si}]_0 = 2.5 \text{ M}) were significantly greater than those of Systems X ([\text{MOH}]_0 = 5 \text{ M}, [\text{Si}]_0 = 0 \text{ M}) and Z ([\text{MOH}]_0 = 10 \text{ M}, [\text{Si}]_0 = 0 \text{ M}), respectively. See Table 9.2.

### 9.3.2 Evidence of Chemical Interactions from the Reacted Solids

Figure 9.2 shows that, regardless of the activating solutions used, the alkali-activating process employed in this work did not cause any observable changes to the XRD diffractograms of the fly ash. No new crystalline peaks could be identified and the peak intensity remained unchanged before and after the alkali-activation. Hence, it can be assumed that the chemical interactions associated with the alkali-activation were only involved with the amorphous glassy phase(s) of the fly ash throughout the duration of the present work. Furthermore, the products of alkali-activation and/or geopolymerisation were x-ray amorphous as were also reported by other investigators [9.1-4, 9.13, 9.14].
Figure 9.2  The XRD diffractograms of the unreacted fly ash (Gdf) and the various alkali-activated solids (Systems Q and U, IX-Control and XI-Control) after 168 hours of activation.

Figure 9.3  The FTIR spectra of the unreacted fly ash (Gdf) and the various alkali-activated solids (Systems Q and U, VIII-Control, IX-Control, X-Control and XI-Control) after 168 hours of activation.
The IR spectra of some representative samples of the alkali-activated fly ash are presented in Figure 9.3. The major IR vibrational bands were assigned and summarised in Table 3.3 by referring to numerous previous studies (see the references associated with Table 3.3). It can be seen that with limited apparent fly ash dissolution, such as Systems Q, the IR spectrum of the alkali-activated fly ash at the end of the leaching experiment was almost identical to that of the unreacted fly ash (Gdf). On the other hand, significant spectral differences could be observed from the solids that had demonstrated significant apparent dissolution from the ICP-OES analyses such as System U (Table 9.2). The vibrational band with a maximum at 1077 cm\(^{-1}\) was found to shift towards a lower wavenumber at 1047 cm\(^{-1}\) in the System U-activated fly ash. This indicates that the original silicate and/or aluminosilicate structures in the fly ash had been significantly depolymerised [9.15-17]. The significant reduction in intensity of the spectral shoulder at \(\sim 560 \text{ cm}^{-1}\), which is attributable to silicate and/or aluminosilicate glasses with long-range structural order such as rings of tetrahedra and/or octahedra [9.11, 9.18, 9.19], further suggests that the System U activating solution was effective in destroying the glassy content(s) of the fly ash. The results of the IR analyses on the activated fly ash are consistent with those obtained from the ICP-OES analyses.

### 9.3.3 FTIR Spectral Deconvolution

Figure 9.4 shows the result of the spectral deconvolution of the unreacted fly ash. It is clear that one principal band and several satellite bands should comprise the more complex original band over the 1350-800 cm\(^{-1}\) region. The 1077 cm\(^{-1}\) principal band should be assigned to the T-O-Si (T = Si or Al) asymmetric stretching vibration within the TO\(_4\) tetrahedra typical of amorphous aluminosilicate glass [9.20]. The three satellite bands at 1203, 1167 and 1117 cm\(^{-1}\) could be the spectral shoulders of the principal band at 1077 cm\(^{-1}\), which are typical in silicate and aluminosilicate glasses [9.18, 9.21] and could be attributed to different structural units within the same silicate structure [9.22]. They could also be a result of the combination of the spectral shoulders of the 1077 cm\(^{-1}\) principal band and the bands attributable to \(\alpha\)-quartz and mullite. The low abundance of \(\alpha\)-quartz (4.2 wt%) and mullite (12.3 wt%) in the unreacted Gladstone fly ash, as determined by quantitative XRD in Section 3.1.2.2, and the low sensitivity used during spectrum acquisition of this work may altogether prevent these satellite bands to be completely resolved. By comparing the result of spectral deconvolution of the unreacted fly ash (Figure 9.4) with those of the various
Figure 9.4  The FTIR spectral deconvolution of the unreacted Gladstone fly ash.

Figure 9.5  The FTIR spectral deconvolution of the System $U$-activated fly ash after 168 hours of activation.
Figure 9.6  The FTIR spectral deconvolution of the *IX-Control* geopolymeric binder after 48 hours of activation.

Figure 9.7  The FTIR spectral deconvolution of the *XI-Control* geopolymeric binder after 48 hours of activation.
alkali-activated fly ash and geopolymeric binders (Figure 9.5 to 9.7), it is clear that the frequency changes of the satellite bands were relatively small. Only the position of the principal band originally at 1077 cm\(^{-1}\) was shifted significantly and systematically after alkali-activation. This observation is extremely important as spectral deconvolution can easily yield a number of different solutions. Only the right set of deconvolution solutions will give the same number and the same position of the spectral bands among different samples as shown in Figures 9.4 to 9.7.

9.3.4 Extent of Alkali-Activation vs. Infrared Frequency Shift from the Reaction Models

McMillan and Wolf [9.10] had stated previously that as the concentration of alkali metal oxide increased in a silicate structure, a fully polymerised tetrahedral framework would become increasingly “depolymerised” – a result of an increased number of non-bridging oxygen atoms (NBO) in the structure. The bonding between the TO\(_4\) tetrahedral units in this case should become more ionic at a higher NBO concentration. Consequently, the T-O bonds in the tetrahedra should possess smaller molecular vibration force constants [9.7]. As a result, the T-O-Si asymmetric stretching vibration band should appear at a lower wavenumber with an increasing alkali metal oxide inclusion and/or a greater extent of silicate depolymerisation. See Section 3.1.2.4 for a more detailed account on the subject of infrared frequency shift with the alkali metal oxide, alkaline metal oxide, transition metal oxide contents of various natural and industrial silicates.

As pointed out earlier, the effect of alkali-activation on aluminosilicates, from a structural point of view, is to introduce alkali cations to the existing aluminosilicate structure while the framework is being destroyed through OH\(^{-}\)-promoted hydrolytic reactions. See eq (9.1). The product of alkali-activation, therefore, should exhibit a decreased Al/M (M = Na or K) ratio. From the literature [9.23], an aluminosilicate with Al/R = 1 (the amount of alkali equals the amount of the negatively-charged and tetrahedrally-coordinated Al) was reported to contain no NBO’s. NBO’s, however, were generated if Al/R was less than 1. Hence, it can be anticipated that with increasing extent of alkali-activation, the NBO concentration of the aluminosilicate (assuming that the Al is in the fourth coordination) should also increase. By considering the results of McMillan and Wolf [9.10] and others [9.6-9.9], it can be
anticipated that with increasing extent of alkali-activation on a silicate or aluminosilicate, the T-O-Si asymmetric stretching vibration band should be increasingly shifted to the lower energy end of an infrared spectrum.

By performing spectral deconvolution as shown in Section 9.3.3, and by taking the advantage of the measurable mass transfer processes from the various reaction models, a calibration curve such as Figure 9.8 can then be constructed. Note that the extent of alkali-activation was calculated as \[ \frac{100 \times \text{maximum apparent Si dissolution}}{\text{theoretical maximum Si dissolution}} \], where the values were obtained from the reaction models as shown in Table 9.2. Figure 9.8 shows that the frequency shift of the T-O-Si asymmetric stretching maximum of the IR principal band originally located at 1077 cm\(^{-1}\) was approximately linear to the extent of the alkali-activation of the glassy content within the fly ash. The greater the extent of activation, the lower was the wavenumber of this principal band maximum. This is consistent with the hypothesis raised earlier and the assignment of the T-O-Si asymmetric stretching vibration “principal” band to the glass phase(s) of the fly ash being correct.
Figure 9.9  The position of the T-O-Si stretching vibration principal band versus the soluble silicate dosage of Na-activating solutions Systems A to H and K-activating solutions Systems I to P after 168 hours of leaching.

Also from Figure 9.8, the exact position of the principal band at a certain extent of alkali-activation seems to be unaffected by the type of the alkali cations in the starting activating solution, or the effects of the alkali cations on the molecular force constant of T-O bond was insignificant. Therefore, Figure 9.8 can be used as a calibration curve for estimating the extent of alkali-activation of the glassy content within the fly ash, regardless of the type of the alkali(s) present in the initial activating solutions. This is despite the fact that, at the same alkali concentration and soluble silicate dosage, the Na-activating solutions (Systems A to H) were more effective in destroying the glassy content of the fly ash than the K-counterparts (Systems I to P). See Table 9.2 and Figure 9.9. This implies that less solution alkalinity, or less dosage of soluble silicates, was required to achieve the same extent of alkali activation as compared to the K-counterpart(s).

9.3.5 Alkali-Activation within Real Geopolymeric Binders

The study of the alkali-activating processes within real geopolymeric binders in situ and in real time was facilitated by acquiring the infrared spectra of the freshly-made geopolymeric binders at the designated intervals. After performing the spectral deconvolution as described
in Section 9.3.3, the position of the T-O-Si asymmetric stretching vibration “principal” band attributable to the glassy phase(s) of the fly ash at time t was then compared to the calibration curve of Figure 9.8 to yield the extent of alkali-activation of the glassy phase(s) within the geopolymeric binders in real time.

As shown in Table 9.1, the only difference between the reaction models Systems Y and AA and the geopolymeric binders IX-Control and XI-Control is the solid/solution ratio. In the reaction models, the solid/solution ratio was 0.1 whereas it was 2 in geopolymeric binders. Table 9.2 shows that almost complete Si dissolution was achievable in both Systems Y and AA within 2 hours of leaching even when the solution alkalinitities of these two systems were significantly different. This suggests that these reaction models (solid/solution ratio = 0.1) could be saturated with the activator – the hydroxyl ions. See Table 9.1 for the compositions
of the activating solutions. On the other hand, if the solid/solution ratio was increased to 2 as in *IX-Control* and *XI-Control*, which is typical for the synthesis of geopolymeric binders while affixing the solution alkalinity, the soluble silicate dosage as well as the Na/K ratio in the activating solutions, very different activation characteristics were observed. See Figure 9.10. *XI-Control* attained complete dissolution in ~48 hours. On the other hand, *IX-Control* had reached only 80% activation in ~5 hours and the alkali-activation process(es) was terminated thereafter. The obvious differences between *IX-Control* and *XI-Control* perhaps could be explained by considering the relative concentrations of the solid and hydroxyl contents in these systems. *XI-Control* could be saturated, or even over-saturated with the activator, while *IX-Control* was under-saturated. The fact that the activation curves (Figure 9.10) for both *IX-Control* and *XI-Control* were almost the same from the start of the activation up to ~5 hours suggests that (1) the alkali concentration within the concentration range of 5 M ≤ [OH]₀ ≤ 10 M did not affect the kinetics of the alkali-activation process(es); and (2) the alkali-activation process(es) could be the same in both geopolymeric systems until the activator was run out, as in the case of *IX-Control*.

Clark *et al.* [9.9], through the use of IR reflection spectroscopy, stated that the first step of sodium silicate glass corrosion in water or aqueous environment was the diffusion of the network modifying Na⁺ ion from the glass structure into the surrounding solution through an ion-exchange process (the Si-ONa⁺ bond was replaced by Si-OH⁺) before the silicate structural backbone was destroyed. The Si-O asymmetric stretching vibration band was found to firstly shift to the higher frequency end attributable to the loss of Na⁺ before shifting back to the lower energy end as the corrosion continued. As the first step of alkali-activation was also the diffusion of Ca²⁺ from the fly ash into the activating solution (see Figure 9.1 as well as Chapters 7 and 8), the process of ion-exchange could also occur before the T-O bonds were hydrolysed. From Figure 9.10, the T-O-Si asymmetric stretching principal band of *System U* was found to shift to the higher energy end of the IR spectrum at the start of the alkali-activation before moving back to the lower energy end. This two-step infrared frequency shift was also observed in the other systems activated with soluble silicate-rich activating solutions (*IX-Control* and *XI-Control*, *Systems F* to *H*, *N* to *P*, *T* to *W*, *Y* and *AA*). In other words, ‘true’ alkali-activation, which involves T-O bond breakage and dissolution of network formers such as Si⁴⁺ and Al³⁺, was found to follow the initial ion-exchange of the network modifiers with the activating solutions.
On the other hand, if no or little dosages of soluble silicates were used (VIII-Control and X-Control, Systems A to E, I to M, Q to S, X and Z), the T-O-Si asymmetric stretching principal band was only shifted to the higher frequency end without shifting back to the lower frequency end. It is therefore possible that without significant soluble silicate additions, major structural breakdown was inhibited after the initial ion-exchange process. This is consistent with the observations in Chapters 7 and 8 that in soluble silicate-deficient activating solutions, interfacial precipitation of Ca-containing polysialates, which was facilitated by the Ca\(^{2+}\) released from the fly ash, was responsible to stop further chemical interactions between the fly ash primary phase and the activating solutions.

9.4 POLYMERISATION/SOLID-STATE TRANSFORMATION

As discussed in Chapter 2, it is generally assumed in the field of geopolymer technology that extensive alkali-activation on the solid raw materials is required to release enough reactants into the activating solution so that polymerisation of the dissolved aluminate and silicate species can proceed, which then leads to gel setting and hardening. Figure 9.11 shows for the first time that a glassy aluminosilicate in a geopolymeric binder such as XI-Control, which was activated by an activating solution of high solution alkalinity and high soluble silicate dosage, could be significantly activated (∼65% of activation) even before setting. After setting, the compressive strength and the extent of activation were clearly not related: The geopolymeric binder XI-Control continued to gain strength while no further dissolution of the fly ash was observed after ∼48 hours. This result is not surprising as the extent of activation measures the degree of “depolymerisation” of the original glassy content(s) whereas the compressive strength is an indication of the degree of “polymerisation” of the newly formed aluminosilicate gel. A careful examination of the results of the IR spectral deconvolution (Figure 9.7) reveals that a new spectral band at 1107 cm\(^{-1}\) could be identified in XI-Control. A similar band was also observed at 1102 cm\(^{-1}\) in IX-Control (Figure 9.6) as well as in the geopolymeric binders synthesised from metakaolin [9.14]. In this work, this new IR band was found to grow in intensity with age without significant band shift. According to Furukawa et al. [9.24], this new band can be assigned to the Si-O asymmetric
Figure 9.11  The extent of activation and the compressive strength versus the duration of activation for IX-Control.

stretching vibrational band attributable to a highly polymerised sheet and/or framework structure, which in nuclear magnetic resonance (NMR) terminology can be denoted as Q$_3$ and Q$_4$ respectively (meaning the tetrahedral silicon is surrounded by 3 bridging oxygen (BO) for Q$_3$ and 4 BO for Q$_4$). Since this work does not intend to structurally identify the alkali-activated products, this new phase is denoted as a Q$_3$ structure, for convenience’s sake.

An attempt was thus made to correlate the observed compressive strength of IX-Control and XI-Control with the relative intensity of this new IR band. The results are summarised in Figure 9.12, where $I_{\text{new}} = \text{intensity of the newly formed and highly polymerised Q}_3$ T-O-Si asymmetric stretching vibration band at $\sim 1105 \text{ cm}^{-1}$, and $I_{\text{principal}} = \text{intensity of the T-O-Si asymmetric stretching vibration principal band}$, which was found to shift with the extent of activation (see Section 9.3.4).
Figure 9.12  The compressive strength versus the relative intensity of the new phase at ~1105 cm\(^{-1}\) for IX-Control and XI-Control. The numbers within the figure denote the duration of activation when the alkali-activated fly ash was taken for IR analysis.

From Figure 9.12, the Q\(^3\) T-O-Si asymmetric stretching band of both IX-Control and XI-Control was found to grow in intensity while little physical strength was observed before setting. Both mixtures obtained final set when the \(I_{\text{new}}/I_{\text{principal}}\) ratio of ~0.13 was reached at ~2 hours. After setting, it seems that as the intensity of the Q\(^3\) T-O-Si asymmetric stretching band became stronger, the geopolymeric binders also became physically stronger. This is true for IX-Control throughout the entire investigation as well as for the early stage of XI-Control. In fact, when the \(I_{\text{new}}/I_{\text{principal}}\) ratio was the same, both geopolymeric binders appeared to possess similar compressive strength. XI-Control had a higher strength than IX-Control at the end of this investigation possibly because more Q\(^3\) phase was formed in XI-Control after ~7 hours. The Q\(^3\) new phase continued to form in XI-Control thereafter until 100% activation was reached at ~48 hours (Figure 9.10).

If it is assumed that the new phase of the new Q\(^3\) T-O-Si asymmetric stretching band was responsible for the early strength of IX-Control and XI-Control, the “extra” strength of XI-Control after 48 hours of activation must come from other source(s). Figure 9.10 shows that
after ~48 hours of activation, and hence after 100% activation of the glassy content(s) of the fly ash was achieved, the T-O-Si asymmetric stretching “principal” band of XI-Control, which is attributable to the hydrolysed glassy content of the fly ash, then began to shift back to a higher energy field. This means that the once depolymerised species due to alkali-activation was somehow triggered to repolymerise again. The increased polymerisation could be responsible for the extra strength observed in XI-Control after ~48 hours of activation. It is possible that as time went on, excessive water was evaporated from the geopolymeric binder. The solubility limit of the dissolved species was thus exceeded once again and ultimately caused further precipitation/gellation to enhance the strength of geopolymeric binders. This, however, does not explain why the repolymerisation process did not occur in IX-Control and thoroughly deserves future investigation. Nevertheless, the solution used for activating XI-Control is far more efficient in promoting (1) fly ash dissolution (Figure 9.10), (2) formation of highly polymerised $Q^3$ phase (Figure 9.12), and (3) repolymerisation of the once depolymerised phase (Figure 9.10), than IX-Control.

Finally, it is important to note that the $Q^3$ T-O-Si asymmetric stretching band of IX-Control and XI-Control is different in nature from the high frequency principal band of VIII-Control and X-Control as shown in Figure 9.3. The principal band was shifted to the higher energy end of the IR spectrum after the initial ion-exchange reaction (see Section 9.3.5), which then stayed at 1082 and 1091 cm$^{-1}$ for VIII-Control and X-Control respectively without apparent fly ash dissolution even after 672 hours of activation. Though highly polymerised, these phases did not contribute to significant physical strength of the geopolymeric binders. Both of these binders only attained a compressive strength of less than 2 MPa at the end of this investigation.

### 9.5 MECHANISM OF GEOPOLYMERISATION

In Chapters 7 and 8, the chemical interactions between glassy aluminosilicates and activating solutions have been categorised into two major groups through the use of the various reaction models: Those that are activated by soluble silicate-deficient activating solutions, and those that are activated by soluble silicate-rich activating solutions. From the
experimental observations obtained in this chapter, these categories are also applicable in the real geopolymeric binders through the use of the novel in situ and in real time infrared spectroscopy with the aid of the calibration curve obtained from the reaction models. In other words, the reaction models developed in this thesis are very closely related to the real geopolymeric systems.

Rahier et al. [9.14] and Felche and Luger [9.25] showed that when a sodium alkaline aqueous solution containing no soluble silicates was used, the reacted metakaolin and kaolinite contained both the amorphous aluminosilicates as well as hydroxysodalite crystallite. Though no quantitative information was given, it seems the crystalline content was significant in the soluble silicate-free activating solutions. If a potassium alkaline solution was used instead, the crystalline reaction product was illite [9.26]. It is therefore expected that alkali-activating aluminosilicate solids, crystalline or amorphous, with an alkaline solution without soluble silicates should give rise to a reaction mixture of aluminosilicate crystallite(s) as well as amorphous aluminosilicate(s). In this chapter, only highly polymerised and x-ray amorphous phase(s) was identified in the fly ash activated by solutions containing little or no soluble silicates (VIII-Control and X-Control). See Figure 9.2 and 9.3. It is likely that the highly polymerised phase(s) of VIII-Control and X-Control may be precursors to a crystalline phase(s) such as hydroxysodallite and/or illite. This will have to be investigated in the future. Nevertheless, the analytical procedure developed in this thesis showed that the initial ion-exchange reaction of Ca$^{2+}$ of the Ca-containing glassy aluminosilicate of the Gladstone fly ash was responsible for the formation of the highly polymerised structure with decreased NBO concentration. This structure, however, demonstrated little interparticle strength crucial for the macroscopic strength of the hardened paste possibly because the alkali-activation step on the reactive phase(s) of the fly ash (and the subsequent gel formation and hardening) was terminated by the secondary phase precipitation of Ca-containing polysialates on the activated fly ash surfaces that limited direct contact between the reactive fly ash primary phase(s) and the soluble silicate-deficient activating solutions.

On the other hand, when soluble silicate-rich activating solutions were used (IX-Control and XI-Control), the early geopolymerisation process could be similar to the corrosion of alkali and alkaline earth silicate glasses [9.9]. The network modifiers of alkali and/or alkaline earth cations were released into the surrounding activating solutions through ion-exchange
reactions, which disturbed the silicate/aluminosilicate structures and rendered the inner T-O bonds more accessible to hydrolytic attack [9.9, 9.17-29]. As the T-O bonds were hydrolysed, the dissolved network formers Si\(^{4+}\) and Al\(^{3+}\) were released into the surrounding activating solutions to form a highly polymerised (gel) phase, which could be responsible for the early macroscopic (yield stress and compressive) strength of geopolymeric binders. Furthermore, this highly polymerised phase was unaffected by the solution alkalinity (IX-Control and XI-Control, Figures 9.6 and 9.7) and could also be attributed to the excellent macroscopic interfacial bonding strength observed in the geopolymeric mortars and concretes activated by soluble silicate-rich activating solutions. See Chapters 6 and 10. After 100% activation was achieved such as in XI-Control, the repolymerisation of the less polymerised phase attributable to the hydrolysed glassy aluminosilicates could be responsible for the later (ultimate) strengths of geopolymeric binders, mortars and concretes. Further investigations on this repolymerisation process(es) of the hydrolysed glassy aluminosilicates are of critical importance for process optimisation of geopolymeric products including binders, mortars and concretes.

Rahier et al. [9.14] reported that when a metakaolin was reacted with alkaline silicate solutions, whose SiO\(_2\)/M\(_2\)O (Rm) ratios were between 0.2 and 0.8, there was a phase separation within the resultant geopolymeric binders. A small quantity of crystalline material(s) (not identified) and a highly polymerised phase were found within the mainly amorphous and less polymerised aluminosilicate gel matrix. Since the Rm ratio of the activating solutions used in this work for the synthesis of IX-Control (Rm = 0.5) and XI-Control (Rm = 0.25) was also within the range of 0.2 and 0.8, it can be concluded that phase separation should be common for all geopolymeric binders synthesised by alkali-activating various (glassy) aluminosilicates with alkaline silicate solutions of 0.2 ≤ Rm ≤ 0.8. Within this Rm range, solution alkalinity could be critically important in determining whether 100% activation on the glassy aluminosilicate can be achieved, which could subsequently lead to the repolymerisation step (or gel solid-state transformation) responsible for later macroscopic strengths of geopolymeric products.

According to Serrano and Van Grieken [9.30], the reaction mechanism of heterogeneous zeolite synthesis is governed by the nature of the solution employed. See Section 2.2.4 for a more detailed discussion. At high Rm ratio and high solution alkalinity (M\(_2\)O/H\(_2\)O), the nucleation of zeolite precursors is of a through-solution type. In this system, solutes are
transported across the hydrogel/solution interface and nucleation of zeolite precursors is situated in the solution phase. If on the other hand, a low $Rm$ ratio and low solution alkalinity solution was used, the solid-state transformation is highly localised within the hydrogel to yield highly polymerised phases. By comparing Derouane et al.’s observation [9.30] and the observations presented in this chapter, zeolite synthesis and geopolymerisation seem to share a similar set of reaction mechanisms. The reaction mechanism of geopolymerisation in a high $Rm$ ratio and high solution alkalinity activating solution, i.e. IX-Control and XI-Control, also seems to be a through-solution type, whereas the solid-state transformation (if there was any after the initial ion-exchange reaction) in VIII-Control and X-Control, which were activated without any soluble silicates, was highly localised and resulted in little interparticle bonding throughout the whole reaction mixture. This will have to be clarified by future investigations.

9.6 CONCLUSIONS

A new analytical procedure was developed in this thesis to study the processes of alkali-activation and geopolymerisation of a typical heterogeneous amorphous aluminosilicate in situ and in real time. This novel analytical procedure involves firstly constructing a calibration curve of infrared T-O-Si asymmetric vibration ‘principal’ band attributable to glassy aluminosilicate versus extent of alkali-activation from a set of well-designed reaction models. As the type of alkali cation(s) present in the activating solutions was found to exert insignificant effects on the positioning of this IR band, this calibration curve can be used to approximate the extent of activation (OH’-promoted hydrolysis) of the glassy aluminosilicate in many different applications.

From the use of the calibration curve and with the aid of IR deconvolution, it was found that at a solid/solution ratio of 2, geopolymerisation was initiated by ion exchange between the glassy aluminosilicate and the activating solution. The subsequent reactions were then controlled by the concentration of soluble silicates. If an activating solution of $Rm < \sim 0.2$ was used, a highly polymerised phase with little interparticle bonding was formed. No apparent hydrolysis on the aluminosilicate was observed due to the formation of the
interfacial Ca-polysialate that hinders mass transport across the solid/solution interface. Phase separation, on the other hand, was found in the geopolymeric binders activated by solutions of $0.2 \leq R_m \leq 0.8$, which resulted in the formation of a highly polymerised phase and a less polymerised phase. In these geopolymeric binders, the early macroscopic (compressive) strength was attributed to the highly polymerised phase. The degree of repolymerisation of the less polymerised phase attributable to the once hydrolysed aluminosilicate then controlled the later strength. It was found that without achieving 100% activation (or hydrolysis), repolymerisation of the hydrolysed aluminosilicate did not occur. High concentrations of alkalis as well as soluble silicates were both required to hydrolyse the aluminosilicate to completion.

9.7 REFERENCES


CHAPTER 10

Chemical Interactions Between Crystalline Aluminosilicates and Activating Solutions

- This chapter is based on the publication: The Mechanism of Interface Formation Between Siliceous Aggregates and Geopolymers, submitted to J. Mater. Sci. 2002.

The nature and the reaction mechanism of the microscopic chemical interactions between a typical heterogeneous glassy aluminosilicate and the various activating solutions have been studied extensively in Chapters 7, 8 and 9. It has been concluded that soluble silicates of high dosages are effective in eliminating interfacial precipitation of Ca-polysialates and thus promoting mass transfer of the dissolved species from the glassy aluminosilicates across the microscopic interface, which is critical for the subsequent polymerisation and gellation of the dissolved species in the solution phase to yield the critical interparticle bonding across the gel matrix. However, it is still not sure if the same reaction mechanism should also apply to crystalline aluminosilicates such as clays or feldspars. This chapter, therefore, employs the various reaction models similar to those used in Chapters 7, 8 and 9 to examine the crystalline aluminosilicate chemical interactions with various activating solutions. The macroscopic interface formation between natural siliceous aggregates and soluble silicate-rich geopolymeric binders will also be proposed.

10.1 INTRODUCTION

In Chapter 6, geopolymeric binders synthesised by alkali-activating a mixture of Gladstone fly ash and HR1-grade kaolinite (fly ash/kaolinite = 9) with soluble silicate-rich activating solutions were shown to demonstrate excellent macroscopic interfacial bonding to natural siliceous aggregates. The macroscopic interface produced as such, according to the SEM
topographic analysis in Chapter 6 and in some other studies [10.1-3], was similar to those observed in the bulk geopolymeric binder. This is in stark contrast to ordinary Portland cement (OPC) systems where the macroscopic interface (or interfacial transition zone, ITZ) is characterised by higher concentrations of large portlandite crystals and long ettringite needles with a lower calcium silicate hydrate gel concentration than the bulk cement paste [10.4-6]. See Section 2.1.6 for a more detailed discussion on the OPC ITZ.

As geopolymeric systems are synthesised by employing highly alkaline aqueous solutions, it is often speculated that the extent of chemical interactions between siliceous aggregates and the highly alkaline activating solutions can be quite extensive. In Chapter 6, it has been shown that siliceous aggregates could be seriously corroded if a soluble silicate-deficient activating solution was used for geopolymeric concrete synthesis. This soluble silicate-deficient alkali corrosion, however, was phase specific. In other words, alkalis only attacked some specific phases of a siliceous aggregate, which in Chapter 6 were undifferentiated between clays or feldspars. This chapter, therefore, is aimed to differentiate the possible alkali-reactive phase(s) within siliceous aggregates using kaolinite (clay) and albite (feldspar) as a case study as well as to reconfirm the experimental finding presented in Chapter 6: (1) alkali corrosion was absent in soluble silicate-rich geopolymeric systems; and (2) a macroscopic interface was absent in soluble silicate-deficient geopolymeric systems. Furthermore, the formation mechanism of the macroscopic interface between siliceous aggregates and soluble silicate-rich geopolymeric binder will also be proposed and discussed by employing various reaction models similar to those used in Chapters 7, 8 and 9.

10.2 MATERIALS AND EXPERIMENTAL METHODS

10.2.1 Materials

Gladstone fly ash, HR1-grade kaolinite, high purity albite (Minerals Corporation Limited, Broken Hill, Australia), basalt, siltstone, Vitrosol N(N40)® sodium silicate solution, and laboratory-grade reagents NaOH and KOH, were used.
From the elemental compositions of Table 3.1, the mineralogical XRD examination in Section 3.1.2.2, and by taking account of the ideal chemical formula of kaolinite (Al₂Si₂O₅(OH)₄), the HR1-grade kaolinite sample was estimated to contain ~88 wt% of pure kaolinite and ~12 wt% of quartz, assuming all the excessive SiO₂ is crystalline. Similarly, the albite was estimated to contain ~97 wt% of pure albite (NaAlSi₃O₈) and ~3 wt% of quartz. The Brunauer-Emmett-Teller (BET) surface area, using a six-points nitrogen adsorption (Micromeritics ASAP 2000), is 15.7 m² g⁻¹ for the HR1-grade kaolinite and 0.24 m² g⁻¹ for the high purity albite.

10.2.2 Synthesis and Characterisation of Geopolymeric Products

10.2.2.1 Synthesis

Only one geopolymeric binder was synthesised to bind the natural siliceous rocks throughout the investigation. This geopolymeric binder was the same as the binder I-10-2.5 in Chapter 6. See Section 6.2.2. for the method of synthesis. The sandwich specimens used for the examination of the macroscopic interface between the siliceous rocks and the geopolymeric binder I-10-2.5 were also prepared in the same way as those of Section 6.2.2. See Figure 10.1 for the schematic illustration of the sandwich specimens. The geopolymeric products were labelled using the same labelling system as in Chapter 6 and were cured at 40 ± 3°C for 24 hours and then demoulded. Subsequently, the samples were cured at 20 ± 3°C and a relative humidity of 50 ± 5% under atmospheric pressure until testing.

10.2.2.2 Macroscopic interfacial characterisation

BSE-SEM images were collected from the sandwich specimens as shown in Figure 10.2. Other material characteristics of the I-10-2.5 binder and the related products are presented in Chapter 6. SEM-EDS line scan, which is conceptually the same as SEM-EDS dot analyses taken at small and regular intervals along a straight line, was used to measure the change of elemental compositions across the interface between natural siliceous aggregates and the I-10-2.5 geopolymeric binder. The intervals were chosen so that at least 10 individual dot
Figure 10.1  The sandwich specimen used for examining the interface between rock slices and geopolymer.

Figure 10.2  The BSE-SEM image of the sandwich specimen. S = siltstone slice, I = 1-10-2.5 geopolymeric binder. The locations where the SEM-EDS line analyses were taken were marked as white dotted lines as an example.

analyses were taken within a 5 μm distance. The results of the SEM-EDS line scans presented in this work were averages of 5 separate analyses at 5 different locations. The locations of each line scans were carefully selected so as to avoid visible fly ash particles and other mineral fragments within the geopolymeric gel as demonstrated in Figure 10.2. Note that all the samples were carbon coated before BSE-SEM images were taken.
10.2.3 Leaching Experiments and Analyses

Leaching was performed to accurately measure the mass transfer processes between HR1-grade kaolinite, albite, basalt and siltstone and the various activating solutions. In each leaching experiment (or reaction model), 100 g of the pre-dried pulverised solids was added to 1000 mL of the activating solution. All leaching experiments were run in parallel at 25 ± 0.5°C to minimise experimental errors. The activating solutions were prepared by dissolving calculated amounts of the silicate solution (Vitrosol N(N40)) and MOH (M = Na and K, Na/K = 0.2) in distilled/deionised water. The final compositions of the activating solutions are presented in Table 10.1. At the designated time interval, 10 mL of the suspensions was collected until the 168th hour of leaching. The reacted, or alkali-activated, solids and the respective activating solutions were separated according to the procedure described in Section 3.3.3.1. The compositions of the reacted activating solutions were determined by ICP-OES as described in Section 3.3.3.2 whereas the reacted solids were analysed by powder XRD analysis, FTIR spectroscopy and SEM & EDS topographical (carbon coated) characterisation. See Section 3.3.3.3.

<table>
<thead>
<tr>
<th>System</th>
<th>Activating Solution (M)</th>
<th>Solid</th>
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<tbody>
<tr>
<td></td>
<td>[OH]_0 (^a)</td>
<td>[SiO_2]_0</td>
</tr>
<tr>
<td>Kao 1</td>
<td>0.6</td>
<td>0</td>
</tr>
<tr>
<td>Kao 2</td>
<td>0.6</td>
<td>0.5</td>
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<tr>
<td>Kao 3</td>
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<td>0</td>
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<tr>
<td>Kao 4</td>
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<td>0.5</td>
</tr>
<tr>
<td>Kao 5</td>
<td>10</td>
<td>0</td>
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<tr>
<td>Kao 6</td>
<td>10</td>
<td>0.5</td>
</tr>
<tr>
<td>Alb 1</td>
<td>0.6</td>
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<tr>
<td>Alb 2</td>
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<tr>
<td>Alb 3</td>
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<tr>
<td>Alb 4</td>
<td>5</td>
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<tr>
<td>Alb 5</td>
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<td>Alb 6</td>
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<td>B 1</td>
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<td>B 6</td>
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\(^a\) Na/K = 0.2.
10.3 CHEMICAL INTERACTIONS BETWEEN CRYSTALLINE ALUMINOSILICATES AND ACTIVATING SOLUTIONS

10.3.1 In Soluble Silicate-Deficient Activating Solutions

Chemical interactions between aluminosilicate minerals (or crystalline aluminosilicates) and aqueous solutions have been under extensive investigation throughout the field of geochemistry. Despite significant advances being made in recent years, the reaction mechanism that governs the mineral dissolution kinetics is still under intense debate. In principle, all of the developed reaction models can be categorised into three major groups [10.7]: (1) Diffusion-controlled kinetics, where the overall mineral dissolution rate is controlled by the inward and the outward diffusion of the reactants; (2) Surface reaction-controlled kinetics, where the rate of dissolution is controlled by the formation of an activated complex in accordance with the transition state theory (TST) by Eyring [10.8]; and (3) A combination of diffusion-controlled and surface reaction-controlled models.

Brady and Walther [10.9] have recently reviewed many articles and concluded that the dissolution rates of silicate and aluminosilicate minerals, including quartz, kaolinite, albite, anorthite, forsterite, nepheline and bytownite, are proportional to the number of activated complexes on the mineral surfaces. These activated complexes are formed through acid-base reactions of the surface silanol or aluminol groups with the surrounding solutions. At pH > 8, the Si–O bonds of the surface silanol groups (≡Si–OH, whose pH_{zpc} is 2.4) are preferentially polarised and weakened over the surface aluminol groups (≡Al–OH, whose pH_{zpc} is 5-7 if Al is in IV-coordination, or 8 if it is in VI-coordination) due to the greater electronegativity of Si than Al [10.9]. In other words, reaction precursors should form primarily on the silica sites for all aluminosilicates at high pH. Hence, in the context of TST, detachment of Si from the ≡Si–O\(^{−}\) precursor should be the rate-limiting step for the initial elementary aluminosilicate dissolution in alkaline conditions, which has been experimentally confirmed [10.9]. This means that initially, more Si should be dissolved into an alkaline solution than Al. A Si-depleted and Al-rich surface, therefore, should be observed after the initial non-stoichiometric dissolution, producing a greater concentration
Figure 10.3  The leaching curves of HR1-grade kaolinite in the various soluble silicate-free activating solutions at the solution alkalinity ([OH\(^-\)]) of 0.6 M (Kao 1), 5 M (Kao 3) and 10 M (Kao 5). \([T] = \) concentration of Si or Al in the reacted activating solution at time \(t\). \([T]_0 = \) initial concentration of Si or Al in the activating solution.

of gibbsite (Al(OH)\(_3\))-like structure at the reacting surface as was suggested by Chou and Wollast [10.10]. The initial detachment of the adjacent silica should then expose the surface Al sites to the hydroxyls in the surrounding solutions and thereby increase their chance for bond polarisation. As the Al-O-Si bond is relatively weaker than the Si-O-Si bond according to Xiao and Lasaga [10.11], the detachment of Al from the \(\equiv\text{Al}^+\text{O}^-\) groups should become the rate-limiting step of the steady-state dissolution following the initial non-stoichiometric dissolution [10.9].

In this work, when kaolinite was suspended in alkaline solutions without additional soluble silicates (i.e. Kao 1, 3 and 5), it was found that the initial Si dissolution was very rapid. See Figure 10.3. It is also evident from Figure 10.3 that no Al dissolution was observed in the first 8 hours in the 0.6 M MOH solution (Kao 1). This delay in the initiation of Al dissolution was also observed in solutions of higher solution alkalinitites ([OH\(^-\)] = 5 and 10 M, Kao 3 and 5), where the concentration of Si in the solution was always higher than Al, although the time required to observe the dissolved Al became shorter with increasing
Table 10.2 The maximum apparent dissolution and the zero-order dissolution rates, with respect to Si and Al, of the kaolinite and the albite in the activating solutions at 25°C

<table>
<thead>
<tr>
<th>System</th>
<th>Log (Rate) (mole m⁻² s⁻¹)</th>
<th>Maximum Apparent Dissolution (mmole) a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si</td>
<td>Al</td>
</tr>
<tr>
<td>Kao 1</td>
<td>-11.28 (0.99) b</td>
<td>-11.75 (0.96) b</td>
</tr>
<tr>
<td>Kao 2</td>
<td>--- c</td>
<td>-12.97 (0.92) b</td>
</tr>
<tr>
<td>Kao 3</td>
<td>-10.80 (0.97) b</td>
<td>-10.67 (0.96) b</td>
</tr>
<tr>
<td>Kao 4</td>
<td>--- c</td>
<td>-10.75 (1.00) b</td>
</tr>
<tr>
<td>Kao 5</td>
<td>-10.23 (1.00) b</td>
<td>-10.18 (1.00) b</td>
</tr>
<tr>
<td>Kao 6</td>
<td>--- c</td>
<td>-10.23 (1.00) b</td>
</tr>
<tr>
<td>Alb 1</td>
<td>--- d</td>
<td>--- d</td>
</tr>
<tr>
<td>Alb 2</td>
<td>--- c</td>
<td>--- e</td>
</tr>
<tr>
<td>Alb 3</td>
<td>--- d</td>
<td>--- d</td>
</tr>
<tr>
<td>Alb 4</td>
<td>--- c</td>
<td>--- d</td>
</tr>
<tr>
<td>Alb 5</td>
<td>--- d</td>
<td>--- d</td>
</tr>
<tr>
<td>Alb 6</td>
<td>--- c</td>
<td>--- d</td>
</tr>
</tbody>
</table>

a The parentheses denote the time of leaching in hours when the value of the maximum apparent dissolution was taken. Unless otherwise indicated, only pure dissolution was observed.
b The rate constant was obtained from the best fit of the linear part of the dissolution curve against time. The parentheses denote the R² value of the best fit.
c Both apparent dissolution and precipitation were significant.
d The dissolution rate was linear against log(time).
e The dissolution rate was linear against log(time) and then levelled off.

solution alkalinity. As the Si/Al ratio of the unreacted kaolinite (Al₂Si₂O₅(OH)₄) is 1, the kaolinite dissolving surface, therefore, should be depleted in Si and enriched in Al, which is consistent with the surface reaction-controlled mechanism discussed above [10.9, 10.10].

From Figure 10.3, it was also found that steady-state kaolinite dissolution could be achieved after ~8 hours of leaching in Kao 1, 3 and 5. Both Si and Al dissolutions were linear against time. As batch reactors are not designed to avoid concentration build-up of the constituent metal cations of the dissolving mineral, the steady-state dissolution observed in this work suggests that the kaolinite dissolution could be zero order with respect to Si and Al. This implies that in the conditions of Kao 1, 3 and 5, at least within the duration of this work, the steady-state dissolution kinetics of the kaolinite were not chemical affinity-controlled. Consequently, the zero-order kaolinite steady-state dissolution rates were calculated by
Figure 10.4  The plot of log(Si dissolution rate, $r$) versus log(solution alkalinity, [OH$^-$]). The results shown were obtained from this chapter as well as from Huertas et al. [10.12].

Ignoring the results obtained in the first 8 hours of leaching, and are summarised in Table 10.2. The fact that the dissolution rates of Si and Al were similar to each other suggests that the kaolinite dissolution was approximately stoichiometric or quasi-stoichiometric at the steady-state stage, after the initial non-stoichiometric dissolution.

Huertas et al. [10.12] had previously investigated kaolinite dissolution using batch reactors from pH 1 to 13 at 25°C. Briefly, they found that the initial kaolinite dissolution was non-stoichiometric, whereas the steady-state stage was quasi-stoichiometric. This is in agreement with the results obtained in this chapter. They also found that the kaolinite dissolution rate was at the minimum at around pH 7 to 10. At either ends of this dissolution minimum, higher rates were observed. According to Huertas et al. [10.12], the pH dependence of kaolinite dissolution at constant temperature (25°C) could be mathematically expressed as:

$$r = 10^{-12.19} a_{H^+}^{0.55} + 10^{-14.36} + 10^{-10.71} a_{OH^-}^{0.75}$$

(10.1)

where $r$ = steady-state linear dissolution rate (mole m$^{-2}$ s$^{-1}$), $a_{H^+}$ = activity (M) of H$^+$, and $a_{OH^-}$ = activity (M) of OH$^-$. Replotting the results of Huertas et al. [10.12] with the present
work shows that, at steady-state, log \( r \) of Si dissolution was linear to log \( ([\text{OH}^-]) \) at pH \( \geq 9 \) as shown in Figure 10.4 and eq (10.2) with a correlation coefficient \( (R^2) \) of 0.97.

\[
\log (r) = 0.42 \log ([\text{OH}^-]) - 10.97
\]  

(10.2)

The excellent correlation coefficient obtained suggests that the results in this work were in good agreement with those from Huertas et al. This is despite the fact that the solid/solution ratios and the purity of the solids were different. As the effect of different solid/solution ratios in calculating the dissolution rates should be accounted for by the BET surface areas measured, it appears that quartz as an impurity within the kaolinite samples should have little effect on the overall kaolinite dissolution kinetics. This is consistent with other experimental observations in Chapters 7, 8 and 9. The reactivity of quartz was very limited in alkaline aqueous solutions or in geopolymeric environments.

Huertas et al. [10.12], using batch reactors, had also compared their kaolinite dissolution results with other investigators and found that their results were in good agreement with those using flow-through reactors [10.9, 10.13]. The flow-through reactors were used with the aim to minimise the chance of saturation with respect to possible secondary phases such as gibbsite and smectite so that the rate measured was the true steady-state dissolution. This implies that secondary precipitation in batch conditions such as those used by Huertas et al. [10.12] was no more than that of the flow-through reactors. As this work seems to agree well with Huertas et al., it is also possible that secondary precipitation was minimal in Kao 1, 3 and 5 conditions and the rates measured as presented in Table 10.2 were representative of the true steady-state dissolution. This observation is important in discussing the effects of soluble silicate additions on the microscopic chemical interactions of crystalline aluminosilicates with activating solutions as will be presented in the next section.

The dissolution characteristics of albite in the various alkaline solutions \((\text{Alb } 1, 3 \text{ and } 5)\) are summarised in Figure 10.5. It was found that throughout the present investigation, the albite dissolution was approximately linear against \( \log(\text{time}) \) in the solutions of various different alkalinitities \(([\text{OH}^-] = 0.6, 5 \text{ and } 10 \text{ M})\). According to Knauss et al. [10.14], it is necessary to react albite for \( \sim 14 \) days before steady-state dissolution similar to that of kaolinite (Figure
**Figure 10.5** The leaching curves of albite in the various soluble silicate-free activating solutions at the solution alkalinity ([OH\(^-\)]) of 0.6 M (Alb 1), 5 M (Alb 3) and 10 M (Alb 5). [T] = concentration of Si or Al in the reacted activating solution at time t. [T]\(_0\) = initial concentration of Si or Al in the activating solution.

10.4) can be reached if a pH 10 solution at 25 °C is used. Hence, it is possible that the albite dissolution observed in this work could still be at the initial non-stoichiometric dissolution stage even at the end of the present investigation (168 hours or 7 days). As kaolinite dissolution was observed to reach the steady-state only after ~8 hours (Figure 10.4, *Kao 1, 3* and 5), the kinetics of the initial kaolinite dissolution were much faster than that of albite. These differences could be attributed to the differences in the BET surface areas between the two minerals. (The BET surface area of kaolinite was 15.7 m\(^2\) g\(^{-1}\) whereas it was only 0.24 m\(^2\) g\(^{-1}\) for albite.) It therefore appears that the kinetics of aluminosilicate dissolution should be controlled by both the surface-controlled and the diffusion-controlled mechanisms. For a given mineral, it is the surface-controlled mechanism that is determining the rate of mineral dissolution, as concluded by Brady and Walther [10.9].

From Figure 10.5, it was also observed that the ‘initial’ dissolution of Si was faster than that of Al in *Alb 1, 3* and 5, with consideration of the stoichiometric ratio of the unreacted ideal albite (NaAlSi\(_3\)O\(_8\)). For example, at [OH\(^-\)]\(_0\) = 10 M and at the 168\(^{th}\) hour, the dissolved Si
concentration was 31.04 mM, which was 3.18 times more than the dissolved Al (9.75 mM). The albite reacting surface, therefore, should be enriched with Al. As the kaolinite reacting surface was also Si-depleted as discussed above, it appears that when exposed to highly alkaline solutions ([OH⁻] ≥ 0.6 M or pH ≥ ~13.95), the nature of the aluminosilicate mineral surfaces in general should be depleted in Si and enriched in Al by the end of the initial non-stoichiometric dissolution stage, as was also observed by Chou and Wollast [10.10] and Hamilton et al. [10.7] using x-ray photoelectron spectroscopy (XPS) albeit at much lower solution alkalinites (pH = 9-11.24) than this work. The initial non-stoichiometric dissolution, therefore, should be controlled by the =Si–O⁻ complexes until steady-state dissolution was reached. During steady-state dissolution, detachment of Al from the =Al-O⁻ activated complexes then became the rate-limiting step as the Al dissolution rate was slightly higher than that of Si in Kao 3 and 5 (Table 10.2) [10.9]. The fact that the dissolution of Al was always slower than Si in Kao 1 throughout this work suggests that the dissolution observed in the [OH⁻]₀ = 0.6 M activating solution could still be at the non-stoichiometric stage.

10.3.2 In Soluble Silicate-Rich Activating Solutions

The effects of soluble silicate addition on the microscopic chemical interactions of kaolinite and albite with activating solutions are presented in Figures 10.6 and 10.7 respectively. As the activating solutions were already dosed with 0.5 M soluble silicates before leaching had commenced ([SiO₂]₀ = 0.5 M), the notation ([Si] – [Si]₀) was adopted to describe the chemical interactions between the minerals and the activating solutions. When the ‘slope’ of the ([Si] – [Si]₀) versus leaching time curve is negative, it means the amount of Si being dissolved away is smaller than that being precipitated at that instant, therefore the chemical process involved is Si precipitation-dominant, and vice versa. When the value of ([Si] – [Si]₀) is negative, it means the ‘net amount’ of the added soluble silicates presumably being adsorbed by the minerals is more than that of the silicates dissolved away, or ‘apparent precipitation’. Similarly, when the ([Si] – [Si]₀) is positive, the process is an ‘apparent dissolution’.
Figure 10.6 The leaching curves of kaolinite in the various soluble silicate-rich activating solutions at a 0.5 M soluble silicate dosage and at the solution alkalinity ([OH⁻]) of 0.6 M (Kao 2), 5 M (Kao 4) and 10 M (Kao 6). [T] = concentration of Si or Al in the reacted activating solution at time t. [T]₀ = initial concentration of Si or Al in the activating solution.

As discussed above, aluminosilicate dissolution in highly alkaline environments should be controlled by the Si-activated complexes during the initial non-stoichiometric stage with a higher Si detachment rate than Al. According to Iler [10.15], the resulting Al-enriched reacting surface should act as an adsorbent for soluble silicate adsorption, as was observed by Siever and Woodford [10.16]. With the assumption that the nature of the ‘initial’ reacting surface in the soluble silicate-rich activating solutions (Kao 2, 4 and 6 and Alb 2, 4 and 6) and in the soluble silicate-free activating solutions (Kao 1, 3 and 5 and Alb 1, 3 and 5) should be the same, it is expected that surface adsorption of the 0.5 M added soluble silicates should be observed in Kao 2, 4 and 6 and Alb 2, 4 and 6, especially during the initial non-stoichiometric dissolution stage.

From Figures 10.6 and 10.7, it was found that, at a solution alkalinity ([OH⁻]₀) of 0.6 M and a soluble silicate dosage ([SiO₂]₀) of 0.5 M, i.e. Kao 2 and Alb 2, some of the added soluble silicates were adsorbed by the Al-enriched kaolinite and albite surfaces within the first 4 hours of leaching. This is consistent with the above hypothesis. As true dissolutions of
**Figure 10.7** The leaching curves of albite in the various soluble silicate-rich solutions at a 0.5 M soluble silicate dosage and at the solution alkalinity ([OH⁻]) of 0.6 M (Alb 2), 5 M (Alb 4) and 10 M (Alb 6). [T] = concentration of Si or Al in the reacted activating solution at time t. [T]₀ = initial concentration of Si or Al in the activating solution.

Kaolinite and albite (i.e. the apparent dissipations) were inhibited because of the soluble silicate adsorption (both the apparent Al dissipations of kaolinite and albite, and the XRD intensity reduction of the kaolinite peaks were reduced in the presence of soluble silicates, see Table 10.2 and Figure 10.8), it is likely that the subsequent dissolution-dominant stage observed in Kao 2 and Alb 2 between 4 and 96 hours could be largely attributed to the desorption of the once adsorbed soluble silicates.

At [OH⁻]₀ = 5 M and [SiO₂]₀ = 0.5 M (Kao 4), the initial Si precipitation on the kaolinite surface was also observed within the first 2-4 hours (Figure 10.6), which corresponds to the initial non-stoichiometric dissolution of Kao 3 that produced an Al-enriched surface for soluble silicate adsorption. This was followed by a Si dissolution-dominant stage until ~48 hours, which might include both the desorption of the adsorbed soluble silicates and the dissolution of the kaolinite. After ~48 hours, the Si from the added soluble silicates and/or the dissolved kaolinite were then adsorbed again by the reacted kaolinite as shown by the
**Figure 10.8** The change in XRD intensity of the kaolinite peak at \( d \)-spacing = 7.183 Å (\( \lambda_{Cu,K\alpha} = 1.54184 \) Å) versus solution alkalinity [OH\(^-\)]\(_0\) of the unreacted HR1-grade kaolinite and the reacted kaolinite in the various activating solutions with ([SiO\(_2\)]\(_0\) = 0.5 M) and without soluble silicates ([SiO\(_2\)]\(_0\) = 0 M). The XRD analyses were taken at the 168\(^{th}\) hour.

The negative slope of the ([Si] – [Si]\(_0\)) versus time curve possibly because the kaolinite reacting surface was once again saturated with Al-rich species. From the XRD analysis (Figure 10.8), addition of 0.5 M soluble silicates was very effective in promoting structural change to the kaolinite crystalline structure at [OH\(^-\)]\(_0\) = 5 M as the kaolinite peak at \( d \)-spacing = 7.183 Å (and all the other peaks as well, see Figure 10.9) had almost completely disappeared in *Kao 4* at the 168\(^{th}\) hour whereas the intensity of the same peak was only reduced to about half of the original intensity in *Kao 3*. This kaolinite structural alteration in *Kao 4* could start as early as 48 hours after leaching (when the maximum apparent dissolution was observed, see Table 10.2), or earlier, according to the FTIR analysis in Figure 10.10. The intensities of the kaolinite characteristic bands, see Table 3.3 for the detailed spectral assignments, were significantly reduced and broadened in *Kao 4* at the 48\(^{th}\) hour, whereas the FTIR spectrum of *Kao 3* was almost the same as that of the unreacted kaolinite at the end of the present work. This is despite the fact that the maximum apparent dissolution of *Kao 4* observed at the 48\(^{th}\) hour was only ~2% of the theoretical maximum value (excluding the dissolution of the silica...
**Figure 10.9** The XRD diffractogram of the unreacted HR1-grade kaolinite (*Kao*) and the reacted kaolinite in the various activating solutions. *Kao 1, 3 and 5* were taken at the 168th hour of leaching whereas *Kao 2, 4 and 6* were taken when the maximum apparent Si dissolutions were observed (Table 10.2), i.e. at the 168th hour, the 48th hour and the 4th hour respectively. K = kaolinite. Q = α-quartz.

Impurity). Hence, the structural alteration of kaolinite in the 5 M OHalkaline silicate solution (*Kao 4*) was highly localised. Furthermore, the reacted solids were x-ray amorphous as no new crystalline peaks could be identified (see Figure 10.9).

If the solution alkalinity was increased even higher to 10 M with 0.5 M soluble silicate dosage (*Kao 6*), the initial precipitation-dominant stage of *Kao 2 and 4* was not observed (see Figure 10.6). The chemical interactions between the kaolinite and the *Kao 6* activating solution, instead, was characterised by a dissolution-dominant stage from the start of the solution analysis (2 hours) to ~4 hours of leaching. Subsequently, the added and the
Figure 10.10  The FTIR spectra of the unreacted HR1-grade kaolinite (Kao) and the reacted kaolinite in the various activating solutions. Kao 1, 3 and 5 were taken at the 168\textsuperscript{th} hour of leaching whereas Kao 2, 4 and 6 were taken when the maximum apparent Si dissolutions were observed (Table 10.2), i.e. at the 168\textsuperscript{th} hour, the 48\textsuperscript{th} hour and the 4\textsuperscript{th} hour respectively. The numbers within the graph denote the IR band positions.

dissolved Si were adsorbed by the kaolinite as shown by the negative slope of the leaching curve (Figure 10.6). At this solution alkalinity, the effect of the soluble silicate addition on the kaolinite structural alteration was not obvious from the XRD analysis (Figure 10.9). The kaolinite peak at d-spacing = 7.183 Å for both Kao 5 and Kao 6 was reduced to almost the same intensity level as the background intensity at the 168\textsuperscript{th} hour. The FTIR analysis (Figure 10.10), however, indicates that soluble silicates had accelerated the structural alteration process as the kaolinite characteristic bands at 1108, 1009, 914, 698, 538 and 435 cm\textsuperscript{-1} had completely disappeared and significantly broadened at the 4\textsuperscript{th} hour of leaching in Kao 6, whereas 168 hours were required for Kao 5 to reach a similar extent of structural alteration.
Figure 10.11 The FTIR spectra of the unreacted albite and the reacted albite in the various activating solutions. All the reacted albites Alb 2, 4, 5 and 6 were taken at the 168th hour of leaching. The numbers within the graph denote the IR band positions.

From Figures 10.5 and 10.7, when activating solutions of 5 M or 10 M OH⁻ and 0.5 M soluble silicates were used for alkali-activating albite (Alb 4 and Alb 6), it was found that the effects of soluble silicate addition were not exactly the same as those observed on the kaolinite (Kao 4 and Kao 6, see Figures 10.3 and 10.6). For example, the initial precipitation of the added soluble silicates was not observed in Alb 4, which was otherwise the case in Kao 4. Nevertheless, the presence of soluble silicates still increased the maximum apparent Si dissolution of albite in both Alb 4 and 6 within a shorter reaction time. See Table 10.2. After the maximum apparent Si dissolution was reached (at ~96 hours for Alb 4 and at ~48 hours for Alb 6), a Si precipitation-dominant stage was then observed in Alb 4 and Alb 6 until the end of the present investigation.

From Figure 10.7, it seems the net amount of Si being adsorbed by the reacted albite, after the maximum apparent dissolution was observed, was greater in Alb 6 than in Alb 4, at least within the time scale of the present work. This is confirmed by the FTIR and the SEM & EDS analyses as presented in Figures 10.11 and 10.12 respectively. With the aid of spectral
deconvolution similar to that performed in Chapter 9, a new spectral band at 961 cm\(^{-1}\), attributable to the stretching vibration of the Si-O bond from the –SiO\(^-\)M\(^+\) (M = Na or K) group [10.17], or asymmetric stretching vibration of the Si-O-Al bond within a highly Al-substituted aluminosilicate structure [10.18, 10.19] (consistent with the assumption that the Al-rich albite reacted surface should be an efficient adsorbent for soluble silicates), could only be observed in the Alb 6 reacted albite but not in any other reacted albites. See Figure 10.11. Furthermore, the spectral regions at around 760 cm\(^{-1}\) (attributable to symmetric stretching of Si-O-T, T = Si or Al [10.20, 10.21]) and around 590 cm\(^{-1}\) (attributable to bending vibration of O-T-O [10.20, 10.21]) had become broadened only in Alb 6 as if the albite had transformed from the crystalline state to a glassy state [10.20]. As the XRD analysis had failed to detect any structural change throughout the entire work on Alb 1 to 6.
Figure 10.13 The XRD diffractograms of the unreacted albite and the reacted albite in the various activating solutions. All the reacted albites Alb 2, 4, 5 and 6 were taken at the 168th hour of leaching.

(Figure 10.13), it can be concluded that (1) the chemical interactions between albite and activating solutions, with and without soluble silicates, only occurred at the albite surfaces (this is different from what was observed in the kaolinite systems or in glassy aluminosilicate systems presented in Chapters 7, 8 and 9); (2) the spectrum broadening at the 760 and 590 cm⁻¹ regions in Alb 6 was caused by the deposition of the dissolved and/or added soluble silicates; and (3) the new 961 cm⁻¹ band in the Alb 6-reacted albite should be assigned to the newly adsorbed silicate species on the reacted albite surfaces, which according to the SEM-EDS analyses (from 5 separate analyses on 5 different locations and assuming all the Al was in IV-coordination), should have an averaged chemical formula of approximately 0.19Na₂O·0.01K₂O·[KAIO₃·(SiO₂)₃]·mH₂O. This newly adsorbed silicates on the Alb 6-reacted albite surface, or the Alb 6 interfacial layer, should be responsible for holding the albite particles together to form conglomerates as shown in Figure 10.12 (c), which were not observed in the unreacted albite (Figure 10.12 (a)) or any other reacted albite (e.g. Figure 10.12 (b)). The Alb 6 interfacial layer could be similar in nature to the polysialate layer described by Phair and Van Deventer [10.22,10.23], which was synthesised
by suspending zirconia particles in sodium silicate and aluminate solution and was characterised by an IR spectral band located at 976 cm$^{-1}$ attributable to the asymmetric stretching of Si-O-Al bond of an alkali modified aluminosilicate with significant Al substitution [10.18, 10.19, 10.23], which could be similar in nature to the 961 cm$^{-1}$ spectral band of the Alb 6-reacted albite (Figure 10.11). According to Phair and Van Deventer [10.23], the formation of a polysialate layer on a relatively unreactive solid surface (zirconia) is more favourable at a higher solution alkalinity due to the greater concentrations of the hydrated cationic sites (−ZrO−M$^+$) on the reacting solid surfaces and/or monomeric soluble silicates being formed in the activating solutions. As the dissolution profile of albite in Alb 3 and 5 was similar to each other (see Figure 10.5 and Table 10.2) and in the context of TST, the formation of the interfacial polysialate layer in Alb 6 should be attributed to the greater concentration of monomeric silicates present in Alb 6, not to a greater extent of deprotonation of the surface silanol and/or aluminol groups in Alb 6 than that of Alb 4.

From Figures 10.3 and 10.5 to 10.7, it appears that the general dissolution/precipitation characteristics of Al for both kaolinite and albite were unaffected by the addition of soluble silicates. The dissolution of Al was continuous in the activating solutions with and without soluble silicates whereas the Si was characterised by a series of dissolution-dominant and precipitation-dominant stages in soluble silicate-rich activating solutions. This suggests that aluminosilicate chemical interactions with soluble silicate-rich activating solutions in general are controlled by the detachment of the Si-activated complexes. This is different from those observed in the soluble silicate-free systems (Kao 1, 3, 5 and Alb 1, 3, 5), as discussed in Section 10.3.1.

10.4 PHASE IDENTIFICATION OF ALKALI-CORROSIVE MINERALS IN SILICEOUS AGGREGATES

In Chapter 6, it was found that quartz in basalt and siltstone aggregates was highly resistant to alkali attack while the mineral phase(s) of clay or feldspar (undifferentiated under SEM & EDS) was alkali corroded in soluble silicate-deficient geopolymeric environments. The results presented in Section 10.3 indicate that the crystal structure of the feldspar content
(albite) within a siliceous aggregate was highly alkali-resistant regardless of the nature of the activating solution (see Figures 10.11 and 10.13). On the other hand, the crystal structure of the clay content (kaolinite) was highly alkali-reactive especially in soluble silicate-rich activating solutions (see Figures 10.9 and 10.10). Hence, the alkali-corroded mineral phase(s) within the siltstone (and basalt) aggregate as shown in Figure 6.6 should be attributed to the clay mineral(s). As shown in Figure 10.3, the dissolution of kaolinite appears to be continuous without apparent precipitations in soluble silicate-deficient activating solutions. Hence, it is expected that kaolinite, or the clay content within a siliceous aggregate, can proceed to a significant extent in soluble silicate-deficient activating solutions as shown in Figure 6.6. In soluble silicate-rich and high solution alkalinity environments (Kao 4 and Kao 6), however, the kaolinite crystal structure was significantly destroyed before the maximum apparent dissolution was observed (Table 10.2, Figures 10.9 and 10.10). This was followed by a Si precipitation dominant stage where the dissolved Si and the added soluble silicates were adsorbed back to the kaolinite reacting surface (Figure 10.6). As a result, it is possible that in soluble silicate-rich geopolymeric conditions, the clay content of siliceous aggregates can undergo some structural transformation without causing significant morphological change as in Figure 6.11. This aspect will have to be further investigated in the future. On the other hand, an alkali-resistant aluminosilicate mineral such as albite was an effective adsorbent for soluble silicate adsorption and the subsequent polysialate interface formation after alkali-activation in the various activating solutions without significant structural alteration to the parent crystal structure.

10.5 MECHANISM OF MACROSCOPIC INTERFACE FORMATION

10.5.1 General Characteristics of the Macroscopic Interface

The typical morphological feature of the macroscopic interface between natural siliceous aggregates (basalt and siltstone) and I-10-2.5 geopolymeric binder is presented in Figure 10.2. The morphology of the geopolymeric gel in proximity to the aggregate surfaces, or the macroscopic interface, was found to resemble very closely that of the bulk geopolymeric
Figure 10.14 The results of SEM-EDS line scan across the interface of quartz (Q) and the I-10-2.5 geopolymeric binder (I) from the siltstone-geopolymeric binder sandwich specimen.

gel, as was reported in Chapter 6 (Figure 6.11). No apparent crystalline interfacial products could be identified in the macroscopic interface. Furthermore, good interfacial cohesion and bonding between the aggregates and the geopolymeric binder were found everywhere along the macroscopic interface. The elemental compositions of the samples across the macroscopic interface using SEM-EDS line scans along the white dotted lines as shown in Figure 10.2 are presented Figures 10.14 to 10.17.

From Figure 10.14, quartz was found to remain alkali-resistant throughout the duration of the present investigation. The concentration of Si was constant throughout the entire quartz structure and there was an abrupt decrease in Si concentration at the macroscopic interface.
Figure 10.15 The results of SEM-EDS line scan across the interface of anorthite (A) and the 1.10-2.5 geopolymeric binder (I) from the basalt-geopolymeric binder sandwich specimen.

This indicates that very limited Si dissolution was present possibly because alkali penetration (Na⁺ and K⁺, accompanied by OH⁻) into the quartz structure was not extensive (Figure 10.14). At the geopolymer side of the macroscopic interface, however, an interfacial layer of ~5 μm thick was found near the quartz surfaces. This macroscopic interfacial layer showed a Si concentration gradient from the high of ~28 % at the quartz surfaces and decreased to the low of ~18 % at the bulk gel. A macroscopic interfacial layer of approximately 5 μm thick was also identified at other parts of the aggregate surfaces. The Si concentration was always higher at the mineral surfaces (albite (~21 %, not shown), anorthite (~24 %, Figure 10.15), sanidine (~27 %, not shown), augite (~23 %, Figure 10.16) and clinochlore (~23 %, Figure 10.17)) than in the bulk gel (~18 %).
Figure 10.16 The results of SEM-EDS line scan across the interface of augite (Au) and the I-10-2.5 geopolymeric binder (I) from the basalt-geopolymeric binder sandwich specimen.

Also from Figures 10.14 to 10.17, it seems that the silicate minerals network modified by non-Group 1 alkali cations, such as Mg$^{2+}$, Ca$^{2+}$ and Fe$^{3+}$ (anorthite, augite and clinohlore), are prone to alkali corrosion. Concentration gradients of the network modifiers (Mg$^{2+}$, Ca$^{2+}$ and Fe$^{3+}$) were quite prominent within the rock-forming minerals near the macroscopic interface, as well as within the macroscopic interfacial layer. These concentration gradients indicated that the network modifiers were leached out from the silicate structure by alkali-activation. The SEM-EDS study as shown in Figures 10.14 to 10.17 also suggests that the chemical composition of the macroscopic interfacial layer is highly localised. For example, the macroscopic interfacial layer of the siltstone-geopolymeric binder specimen as shown in Figure 10.14, by assuming all of the Al was in the fourth coordination, had an averaged molar composition of 1.5Na$_2$O·1.6MgO·CaO·[KAlO$_2$·(SiO$_2$)$_{2.6}$]$_{10}$·4.4Fe$_2$O$_3$·xH$_2$O at the
Figure 10.17 The results of SEM-EDS line scan across the interface of clinochlore (C) and the 1:10-2.5 geopolymeric binder (I) from the basalt-geopolymeric binder sandwich specimen.

clinochlore surface, whereas the macroscopic interfacial layer at the quartz surface only ~15 μm away had an averaged composition of 0.5Na2O·2K2O·1.7CaO[KAIO2·(SiO2)2·3]·yH2O. In any case, the molar Si/Al ratio of the macroscopic interfacial layer was approximately 2.5~3 at any mineral surfaces of both the basalt and siltstone aggregates whereas the molar Si/Al ratio of the bulk geopolymeric binder was ~2 with an averaged composition of 2.1Na2O·0.24MgO·3CaO·[Na0.15K0.85AlO2·(SiO2)1.5]20·0.5Fe2O3·zH2O. This implies that studying the reactions of the individual rock-forming minerals with activating solutions with or without soluble silicates (such as in Section 10.3) could provide an understanding of the ‘overall’ macroscopic interface formation processes between natural siliceous aggregates and geopolymeric binders. This will be further discussed together with more experimental results in Section 10.5.2.
10.5.2 Chemical Interactions Between Basaltic Aggregates and Activating Solutions

Pulverised basalt was used as a case study to study the chemical interactions between siliceous aggregates and various activating solutions. From Figure 10.18 and Table 10.3, it was found that the general characteristics of the chemical interactions between pulverised basalt and the various activating solutions, with and without soluble silicates, were similar to what was observed in the systems containing kaolinite and albite (see Figures 10.3 and 10.5 to 10.7 and Table 10.2). In activating solutions without soluble silicates (B 1, 3 and 5, Figure 10.18), the dissolutions of Si and Al from the basalt were continuous without apparent precipitation. On the other hand, when 0.5 M soluble silicates were added, the chemical interactions between the basalt and the activating solutions (B 2, 4 and 6) were characterised by an initial Si precipitation-dominant stage, where the added soluble silicates were adsorbed by the basalt. This is followed by a Si dissolution dominant stage, within which, the once adsorbed soluble silicates might be desorbed together with the dissolution of the basalt (similar to Kao 2, 4 and 6 and Alb 2, 4 and 6, see Figure 10.6 and 10.7). As the dissolution process was non-stoichiometric, an Al-rich surface was formed and triggered the second Si precipitation-dominant stage as was seen in B 4 and 6. Note that at low solution alkalinity ([OH]_0 = 0.6 M, B 2), the second Si precipitation-dominant was not observed as was also the case in Kao 2 and Alb 2.

The SEM topographical study shows that, similar to the formation of the Alb 6 interfacial layer, the surface adsorption of the dissolved and/or the soluble silicates on the B 4 and B 6-reacted basalt should be responsible for the formation of the interfacial layers that held the pulverised basalt particles together to form conglomerates as demonstrated in Figure 10.19 (b), which was absent in the unreacted basalt (Figure 10.19 (a)). The SEM-EDS analysis shows that the averaged chemical composition of the B 4 interfacial layer should be approximately 1.2Na_2O·0.8MgO·[KAlO_2·(SiO_2)_2·3]_6·1.7Fe_2O_3·nH_2O, whereas the B 6 interfacial layer should be 0.6Na_2O·MgO·[KAlO_2·(SiO_2)_2·3]_6·1.6Fe_2O_3·pH_2O. By comparing to that of the Alb 6 interfacial layer, it seems the interfacial layer that was formed by reacting the various aluminosilicate minerals in the alkaline silicate solutions should, in general, have a Si/Al ratio of ~3, which is similar to what was observed in the interfacial
layer between the real siliceous aggregates (basalt and siltstone) and the geopolymeric

![Graph showing leaching curves of basalt in various activating solutions.](image)

**Figure 10.18** The leaching curves of the pulverised basalt in the various activating solutions. $[\text{Si}] = \text{concentration of Si in the reacted activating solution at time } t$. $[\text{Si}]_0 = \text{initial concentration of Si in the activating solution.}$

**Table 10.3** The maximum apparent dissolutions of the pulverised basalt and siltstone in the activating solutions at 25°C

<table>
<thead>
<tr>
<th>System</th>
<th>Si</th>
<th>Al</th>
<th>Ca</th>
<th>Mg</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>B 1</td>
<td>10.9 (168)</td>
<td>5.0 (168)</td>
<td>0.3 (168)</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>B 2</td>
<td>10.7 (168)</td>
<td>3.0 (24)</td>
<td>0.4 (168)</td>
<td>0.8 (168)</td>
<td>0.1 (168)</td>
</tr>
<tr>
<td>B 3</td>
<td>24.6 (168)</td>
<td>9.8 (168)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>B 4</td>
<td>21.4 (8)</td>
<td>9.0 (168)</td>
<td>0.4 (24)</td>
<td>1.3 (168)</td>
<td>0.7 (168)</td>
</tr>
<tr>
<td>B 5</td>
<td>23.9 (168)</td>
<td>8.2 (168)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.2 (168)</td>
</tr>
<tr>
<td>B 6</td>
<td>10.7 (4)</td>
<td>9.0 (168)</td>
<td>0.0</td>
<td>0.2 (4)</td>
<td>0.5 (168)</td>
</tr>
</tbody>
</table>

*The parenthesis denotes the time of leaching in hours when the value of the maximum apparent dissolution was taken.*
Figure 10.19  The SEM images of (a) unreacted pulverised basalt using BSE detection, and (b) reacted pulverised basalt under B 6 for 168 hours using SE detection.

Figure 10.20  The XRD diffractograms of the unreacted basalt and the reacted basalt in the various activating solutions. All the reacted basalt B 3, 4, 5 and 6 were taken at the 168th hour of leaching.
binder 1-10-2.5 as presented previously. The interfacial layers of \textit{Alb} 6, B 4 and B 6 should be x-ray amorphous as all of the XRD diffractograms of the reacted solids resembled very closely those of the unreacted solids (see Figures 10.13 and 10.20).

Since the chemical interactions between albite and the real basaltic rock (pulverised or in slice) and the various activating solutions, or \textit{I-10-2.5} geopolymeric binder, were found to share similar general characteristics (i.e. the leaching characteristics and the Si/Al ratios of the interfacial layers formed), as well as the fact that albite is one of the constituents in basalt, it is likely that the polysialate-like interfacial layer observed in the albite systems could also exist on the real siliceous aggregates. From this reasoning, the mechanism of the macroscopic interface formation between siliceous aggregates and soluble silicate-rich geopolymeric binders (such as \textit{I-10-2.5}) is a result of soluble silicate-promoted heterogeneous reactions that consist of accelerated surface dissolution followed by surface adsorption/deposition of the dissolved and added soluble silicate on the reacted aggregate surface, which then led to the formation of polysialate interface responsible for the macroscopic interfacial bonding. This implies that an activating solution consisting of high concentrations of alkali (MOH) and soluble silicates is an essential prerequisite for the formation of a strong interface between siliceous aggregates and geopolymeric binders, which is crucial to the overall macroscopic properties of the geopolymeric concretes. Without soluble silicate addition, the interface between siliceous aggregates and geopolymeric binders may not exist (see Chapter 6), as the chemical interactions involved do not include significant soluble silicate adsorption.

10.6 CONCLUSIONS

The chemical interactions between crystalline aluminosilicates (kaolinite and albite) were investigated through the use of the reaction models similar to those used in Chapter 7, 8 and 9. It was found that addition of 0.5 M soluble silicates to an activating solution highly concentrated in alkalis ([OH$^-$]$_0 = 5$ to 10 M) was responsible to facilitate the formation of an Al-enriched aluminosilicate surface through accelerated and increased Si-preferential (non-
stoichiometric) dissolution of the parent crystalline aluminosilicates. This Al-enriched solid surface was crucial for the subsequent deposition of the dissolved and the added soluble silicates from the activating solution, which then led to the formation of a polysialate interface with a Si/Al ratio of ~3 resembling the real geopolymeric interface between natural siliceous aggregates (basalt and siltstone) and a geopolymeric binder (I-10-2.5) activated by an activating solution highly concentrated in solution alkalinity ([OH⁻]₀ = 10 M) and soluble silicates ([SiO₂]₀ = 2.5 M). Without soluble silicates, no polysialate interface was observed in the soluble silicate-free leaching systems or geopolymeric concretes because the aluminosilicate surface was less Al-enriched and the dissolved Si was too little to facilitate the surface deposition. Furthermore, high solution alkalinity was found to promote polysialate interface formation because the activating solution was more concentrated in lower oligomeric soluble silicates, which was more preferable for heterogeneous soluble silicate deposition than a solution concentrated in higher oligomeric soluble silicates. The results of this work suggest that both high concentration of solution alkalinitities and soluble silicates are essential for the interface formation between siliceous aggregates and geopolymeric binders.

10.7 REFERENCES


CHAPTER 11

Conceptual Model of Chemical Interactions in Geopolymers

Geopolymeric binders and the related products are synthesised by mixing aluminosilicate solids with activating solutions of high solution alkalinity. The subsequent chemical processes, collectively termed geopolymerisation, had been previously proposed to consist of 5 major reaction steps [11.1-3]: (1) aluminosilicate solid dissolution (or alkali-activation); (2) polymerisation/colloidal formation of dissolved aluminosilicates; (3) aluminosilicate gellation; (4) setting and hardening; and (5) gel solid-state transformation. As geopolymerisation was thought to be initialised by alkali-activation, it was generally assumed throughout the geopolymer research community that the product physical and chemical properties were directly proportional to the extent of alkali-activation. Consequently, increasing solution alkalinity (M₂O/H₂O ratio) was often practised in an attempt to increase the product compressive strengths albeit of limited success [11.4, 11.5]. Rahier et al. [11.6], on the other hand, reported that increasing SiO₂/M₂O (Rm) ratio of an activating solution (which is commonly known in soluble silicate chemistry to promote gellation of (alumino)silicate rather than precipitation [11.6, 11.7]) was very effective in promoting metakaolinite dissolution (indirectly proven) as well as rendering the resultant products excellent physical, mechanical and thermal properties. Based on Rahier et al.’s [11.8] and a few others’ observations [11.9-11], Xu and Van Deventer [11.2] then postulated that aluminosilicate gel formation was responsible for promoting extensive solid dissolution by avoiding accumulation of the dissolved species at the solid/solution interface. This is despite the fact that all these studies had adopted an ‘indirect’ experimental approach, which usually involved physically characterising the ‘mature’ geopolymeric products. This thesis therefore aims to investigate the nature and the mechanism of the chemical interactions between aluminosilicate solids and activating solutions using ‘direct chemical methods’. The following is a conceptual model built on the basis of the experimental observations collected in this thesis on the subject of the chemical interactions between aluminosilicate solids and activating solutions. As will be shown later in the chapter, true geopolymerisation (i.e. the
chemical processes that lead to the formation of aluminosilicate gels) are only limited to the systems containing glassy/amorphous aluminosilicates and are activated by activating solutions of high solution alkalinitities and soluble silicate dosages. This conceptual model therefore is vital for the overall understanding of geopolymerisation as well as providing suggestions for future investigations in order to improve mix design and process optimisation.

11.1 INTRODUCTION

As discussed extensively in Chapter 2, ordinary Portland cement (OPC) hydration, i.e. the microscopic chemical interactions between OPC cement and water, can be summarised as consisting of two major chemical steps. Firstly, Ca$^{2+}$ is released from the tricalcium silicate or dicalcium silicate through ion-exchange reaction to the surrounding solution, which subsequently increases the solution alkalinity as well as the extent of Si$^{4+}$ dissolution (possibly through hydroxyl-promoted hydrolysis) from the solid, i.e. mass transport of the dissolved species across the microscopic interface between tricalcium silicate and water. Secondly, the dissolved species are precipitated and/or gelled after supersaturation has been reached to form the various types of calcium silicate hydrates (crystals or gels). Similarly, the macroscopic interface formation between siliceous aggregates and an OPC binder can also be regarded as consisting of mass transport of the dissolved species from both the cement particles and the aggregates to the aggregate surfaces, which is then followed by the subsequent secondary precipitation or gellation of the dissolved species.

Through the use of novel reaction models and the associated analytical procedure developed in this thesis (see Chapters 7, 8, 9 and 10) the microscopic and the macroscopic chemical interactions between aluminosilicate solids and activating solutions can also be categorised as consisting of two major chemical steps: (1) mass transport due to hydroxyl-promoted hydrolysis, and (2) precipitation and/or gellation of the dissolved species to produce secondary products such as interfacial polysialates and aluminosilicate gels, which are the principal binding phases of geopolymers. Both of these chemical consequences are highly dependent on the nature of the starting aluminosilicate solids. As a result, the conceptual
Figure 11.1 The conceptual model of the chemical interactions between aluminosilicate solids and activating solutions. The dashed area represents the true chemical processes of geopolymerisation. ‘a’ to ‘b’ represent the various reaction pathways, which are determined by the nature of the reacting solids and the activating solutions.
model of the chemical interactions between aluminosilicate solids and activating solutions can be presented and discussed on the basis of the nature of the reacting solids and the two separate chemical phenomena, i.e. mass transport and precipitation/gellation of the dissolved species. See Figure 11.1 for the graphical presentation of this conceptual model. In the following sections, each of the reaction pathways and the associated reaction conditions of the conceptual model (marked as (a), (b), (c), … etc. in Figure 11.1) will be broadly discussed and defined based mainly on the experimental results of this thesis. Note that these reaction conditions are critical in determining the extent of the mass transport across the solid/solution interface, the extent of localised transformation of the reacting solid and the nature of the resultant secondary products formed at the solution/solution interface or at the interstitial solution. As complete investigation is not possible due to the enormous size of the experimental variables involved, it is inevitable that some literature outside the geopolymer field, such as soluble silicate and zeolite chemistry, will have to be referred to during the development of this conceptual model. This, however, does not prevent or jeopardise the use of this conceptual model as groundwork for future investigation on the reaction mechanism as well as on the process optimisation of the synthesis of geopolymeric binders and the related products.

11.2 INITIAL BRØNSTED & ION-EXCHANGE REACTIONS

As was discussed in Chapters 7, 8, 9 and 10, the first step of the chemical interactions between any silicate or aluminosilicate solids and alkaline aqueous solutions is the Brønsted acid-base reactions between the surface silanol/aluminol groups of the reacting solids and the hydroxyls (OH⁻) from the alkaline aqueous solutions [11.12-14]. At a pH approaching 14 or higher, which is typical for geopolymer synthesis, the surface silanol/aluminol groups are deprotonated through Brønsted acid-base reactions at pH > pH_{zpc} (pH of zero point of charge, which is ~2.4 for \equiv Si–OH, 5-7 for \equiv Al(IV)–OH, and ~8 for \equiv Al(VI)³–OH [11.14]):

\[
\equiv Si–OH + M^{+}OH \rightarrow \equiv Si–O^{–}M^{+} + H_{2}O \quad (11.1)
\]

\[
M^{+} (\equiv Al(IV)–OH) + M^{+}OH \rightarrow M^{+} (\equiv Al(IV)–O^{–}M^{+}) + H_{2}O \quad (11.2 \text{ a})
\]
\[
M_3^{+}\left(\equiv\text{Al}^{(VI)3-}\text{–OH}\right) + M'\text{OH}^- \rightarrow M_3^{+}\left(\equiv\text{Al}^{(VI)3-}\text{–O}M'\right) + H_2O
\]  (11.2 b)

where \(M'^+\) = monovalent alkali (\textit{Group I}) cation such as \(\text{Na}^+\) or \(\text{K}^+\) of the unreacted solid, \(M^+\) = monovalent alkali cation such as \(\text{Na}^+\) or \(\text{K}^+\) from the alkaline aqueous solution (activating solution), \(\text{Al}^{IV}\) = aluminium at the fourth coordination, and \(\text{Al}^{VI}\) = aluminium at the sixth coordination. (\(M'\) can also be divalent alkaline earth (\textit{Group II}) metals or some other multivalent transition metals. The associated Brønsted reactions will then have to be modified from eq (11.1) and (11.2) accordingly.) If the unreacted siliceous solids (silicates and aluminosilicates) are initially network modified by alkali/alkaline earth cations, \(\text{Al}^{(VI)3+}\) cation in the sixth coordination, or more rarely by transition metal cations (e.g. \(\text{Fe}^{3+}\)), dissolution of the network modifiers through ion-exchange reactions between the unreacted solids and the activating solutions should then follow the initial Brønsted acid-base reactions [11.14, 11.15].

Subsequent to the initial Brønsted/ion-exchange reactions, the network formers of siliceous solids (i.e. \(\text{Si}^{4+}\) and \(\text{Al}^{(IV)3+}\), see Section 3.1.2.4 for the definition of network modifiers and network formers) are then dissolved through hydroxyl-promoted hydrolysis, or alkali-activation [11.12-15]. See also Chapter 9 for a more detailed discussion on this subject. As \(\text{OH}^-\) has higher accessibility to the T-O-Si bonds underneath the \(\equiv\text{T-O}^{\text{Na}^+}\) surface (T = Si and Al) than the \(\equiv\text{T-O}^{\text{K}^+}\) surface due to the higher charge density and smaller ionic radius of \(\text{Na}^+\) than \(\text{K}^+\) [11.16], the frequency of successful bond rupture, hence the rate of solid dissolution, as a general trend, is higher in the Na-activating solutions than K-activating solutions. This has been experimentally confirmed in Chapter 7 as well as from numerous other investigations [11.17, 11.18].

According to the experimental results gathered from Chapters 7, 8, 9 and 10, significant chemical interactions between siliceous solids and activating solutions may not always associate with significant extent of apparent solid dissolution (or mass transfer across the solid/solution interface). A solid can extensively interact with activating solutions and undergo significant structural changes even though the observed solid dissolution is very limited (e.g. kaolinite, see Chapter 10 and Section 11.4). Therefore, as pointed out in Section
3.3.3, a better definition of the chemical interactions between siliceous solids and activating solutions should account for either the measurable mass transfer across the solid/solution interface or the extent of chemical/microstructural changes to the phases involved. Consequently, the nature of alkali-activation, i.e. hydroxyl-promoted solid transformation, and the resultant reaction products can be divided into two major categories based on the nature of the starting siliceous solids.

Depending on the nature of the activating solution, alkali-activation on glassy siliceous solids through reaction route (a) of Figure 11.1 will lead to the formation of (1) a Highly Polymerised Amorphous Phase-I suspected for its potential to become crystallised (see Chapter 9); (2) an Interfacial Polysialate-I; and/or (3) aluminosilicate gels (Gel-$\alpha$ and Gel-$\beta$) as the principal binding phases of geopolymeric systems. See Section 11.3 below for a more detailed discussion on the nature and the reaction conditions leading to these reaction products, i.e. reaction routes (c – i).

On the other hand, alkali-activation on crystalline siliceous solids, i.e. reaction route (b), will lead to the formation of an Al-Enriched Surface, which then depends on the nature of the crystal structure and the nature of the activating solutions, will result in the formation of an Interfacial Polysialate-II or a Highly Polymerised Amorphous Phase-2 through reaction route (j) or (k). See Sections 11.4 for further details.

11.3 GLASSY ALUMINOSILICATES

The microstructure of glassy materials has been under extensive investigation for many years. Generally speaking, they are the materials that possess little long-range order and unlike crystals, cannot be described by repetitive unit cell(s) that extends in three dimensions. The non-periodicity of the glass structure can be best understood to originate from the wider distributions of T-O bond lengths and bond angles as well as by the rotation of structural units about their axes as compared to the crystalline counterparts of the same chemical compositions [11.19, 11.20]. A glass therefore is generally characterised by a higher surface area and a higher free energy than a crystal. As a result, a glass is prone to
extensive alkali attack throughout the entire structure as hydroxyls are allowed to diffuse into the inner glass structure with ease, while some crystals such as albite can be considered alkali-resistant with a very small rate of diffusion.

From Chapter 9, if a soluble silicate-deficient activating solution is used ($Rm < \sim 0.2$), dissolution of network modifiers (through Bronsted/ion-exchange reactions) and network formers (through hydroxyl-promoted hydrolysis), followed by the subsequent multivalent cation (e.g. $\text{Ca}^{2+}$ and $\text{Al}^{3+}$)-promoted precipitation of interfacial polysialate layers at the solid/solution interface, i.e. reaction route (c) of Figure 11.1, is responsible for the limited solid reactivity. This is because the interfacial polysialate layer blocks direct contact between the glass primary phase and the soluble silicate-deficient activating solution. As a result, a Highly Polymerised Amorphous Phase-$I$ with little interparticle bonding is produced and the resultant binder and the related products are thus mechanical weak (see Chapters 5 and 6). Chapter 9 further shows that the infrared T-O-Si asymmetric stretching vibration band attributable to the Highly Polymerised Amorphous Phase-$I$ remains at a higher energy field (as compared to the unreacted glassy phase) for an extended period of time without significant band shift. This indicates that the Highly Polymerised Amorphous Phase-$I$ is chemically very stable, which according to Rahier et al. [11.21], can be transformed into crystalline phase(s) under some specific curing conditions, e.g. hydrothermal conditions.

If on the other hand soluble silicate-rich activating solution ($Rm > \sim 0.2$, Chapter 9) is used for the synthesis, soluble silicate-assisted and hydroxyl-promoted hydrolysis (or alkali-activation) on the T-O-Si bonds underneath the surface $=\text{T}−\text{O}−\text{M}^+$ groups, i.e. reaction route (d) and/or (e) of Figure 11.1, will release significant amounts of network formers into the activating solution. This is because the multivalent network modifiers (e.g. $\text{Ca}^{2+}$ and $\text{Al}^{(VI)3+}$) of the glassy aluminosilicate are adsorbed by the soluble silicates in the soluble silicate-rich activating solutions [11.22-27]. The soluble silicates at high dosages hence are effective in preventing the formation of the interfacial polysialate layer at the solid/solution interface, which is otherwise known to inhibit extensive alkali-activation on glassy aluminosilicates as discussed above (Chapters 7 and 8). At $Rm > 0.2$, the extent of alkali-activation on a glassy aluminosilicate can also be increased with increasing solution alkalinity at a given soluble silicate dosage (Chapter 9). Depending on the nature of the activating solution, there are two major types of reaction products that can be formed from the dissolved glassy
aluminosilicate and the added soluble silicates. Under the reaction conditions (route (e)) where lower oligomeric silicates are preferentially formed over the larger polysilicates or colloidal silicates in the early activating solution, i.e. at a higher solution alkalinity for a given soluble silicate dosage (or lower $R_m$ ratio [11.28-34]) or when sodium-rich activating solution is used (rather than potassium-rich activating solution) [11.28, 11.29, 11.31, 11.33], an aluminosilicate precipitate (network modified by the alkali and the alkaline earth cations present in the reacting systems) can be preferentially formed at the solid/solution interface (Chapters 7 and 8), hence the terminology Interfacial Polysialate-I. See Figure 11.1. On the other hand, according to Chapters 7 and 8 and numerous other investigations [11.6, 11.7], silicate/aluminosilicate gels are preferentially formed over the Interfacial Polysialate-I if the early activating solutions favour the formation of larger polysilicates or colloidal silicates via reaction route (d). Future experiments, however, are still required for the determination of the exact reaction conditions that critically determine the reaction pathways of route (d) and (e) and whether these reaction conditions are solid dependent.

From the experimental results presented in Chapter 9, there are two major types of gels that can be formed in the soluble silicate-rich geopolymeric systems ($R_m > \sim 0.2$) via reaction route (d) of Figure 11.1. Gel-$\alpha$ with a high degree of polymerisation and a low concentration of non-bridging oxygens (NBO) is formed via reaction route (f) at the very early stages of geopolymerisation independent of the solution alkalinity. The results in Chapter 9 suggest that this phase is originated from the added soluble silicates and the dissolved species from the reacted glassy aluminosilicate, which is responsible for the setting and the early strength of geopolymeric binders (Chapter 9). On the other hand, Gel-$\beta$ can only be formed/transformed via reaction route (h) from the significantly hydrolysed glassy aluminosilicate (via reaction route (g)) at high solution alkalinity ($M_2O/H_2O > \sim 5$ M). According to the results obtained from infrared spectroscopy as presented in Chapter 9, Gel-$\beta$ has a potential to ‘repolymerise’ gradually over time – a solid-state transformation of Gel-$\beta$ – and is responsible for the ultimate mechanical strength of a geopolymeric binder. If the solution alkalinity is too low ($M_2O/H_2O \leq \sim 5$ M), the hydrolysed glassy aluminosilicate cannot be transformed into Gel-$\beta$. Future experiments, however, are still required to understand the reaction mechanism(s) governing the solid-state transformation that lead to the formation of Gel-$\beta$. 
After the gels (Gel-α and Gel-β) have been formed, gel deterioration via reaction route (i), i.e. hydrolytic attack on the gel structure, will then lead to precipitation/crystallisation of the gels and then eventuate in the formation of the Precipitates/Crystals of Figure 11.1 (Chapter 8). This subsequently lowers the binder mechanical strengths from the ultimate value (Chapters 5). From Chapters 5 and 8, this gel instability can be significantly increased and accelerated if the initial activating solution is contaminated by certain electrolytes (such as chlorides), or if the solution alkalinity of the initial activating solution is too high for a given soluble silicate dosage, i.e. at a low $R_m$ ratio. From the soluble silicate chemistry [11.12, 11.28-34], the activating solution under these reaction conditions is favourable for the formation of lower oligomeric silicates before gellation, which should then result in the formation of secondary products that are more precipitates in nature than gels. This aspect will require future confirmation and is critical in understanding the gel deterioration processes as well as the commercialisation of geopolymeric products.

11.4 CRYSTALLINE ALUMINOSILICATES

In this thesis, two crystalline aluminosilicates have been used to study the chemical interactions between siliceous crystals (or minerals) and activating solutions. Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), a phyllosilicate with a sheet structure consisting of repetitive units of a ($\text{Si}_2\text{O}_5$)$_n$ layer of $\text{SiO}_4$ tetrahedra hydrogen bonded at the corners to an $\text{Al}^{\text{VI}}\text{O(OH)}_2$ layer of alumina octahedra [11.35, 11.36], is known to readily swell by absorbing water, $\text{H}_3\text{O}^+$ or $\text{OH}^-$ molecules at the hydrogen-bonded basal planes of silica tetrahedra and alumina octahedra upon contact with water or aqueous solutions. The chemical interactions between kaolinite and activating solutions can therefore be expected to be located at both the surface and at the basal planes, which should then lead to extensive alterations to the phyllosilicate crystal structure. Albite ($\text{NaAlSi}_3\text{O}_8$), on the other hand, is a tectosilicate of a three-dimensional framework structure with a relatively small BET surface area [11.35, 11.36]. This inhibits fluids to penetrate deep into the crystal structure. As a result, the chemical interactions between albite and activating solutions are mainly located at the outer albite surface with a relatively low dissolution rate [11.37]. Nevertheless, the results obtained from Chapter 10 as well as from other investigations [11.14, 11.38] show that when a crystalline
aluminosilicate makes contact with an activating solution, Si-preferential dissolution (incongruent and Si-controlled, reaction route (b)) following the initial Brønsted acid-base/ion-exchange reactions will result in the formation of an Al-Enriched Surface regardless of the starting crystal structure (Figure 11.1). The dissolution then becomes Al-controlled after steady-state dissolution is achieved if the activating solution contains no soluble silicates.

For ‘reactive’ minerals such as kaolinite, the chemical interaction between the mineral and the activating solution is insignificant if the solution alkalinity is too low ([OH\textsuperscript{-}] < 5 M) (Chapter 10). The crystal structure, however, can be significantly altered if the hydroxyl concentration of the initial activating solution is equal to or greater than 5 M ([OH\textsuperscript{-}] ≥ 5 M) through a ‘localised’ alkali-activation mechanism (reaction route (k)) to form a Highly Polymerised Amorphous Phase-2 (Figure 11.1). The alkali-activation process in this case is localised because very little mass transfer across the solid/solution interface can be observed even though the bulk crystal structure is significantly destroyed (as opposed to glassy aluminosilicates, see Section 11.3). It is also for this reason that the reaction product of route (k) is not a gel but a highly polymerised and amorphous phase. The presence of significant amounts of soluble silicates seems to be very effective in accelerating the rate of structural alteration without affecting the nature of the final secondary product(s). They are also effective in eliminating dissolution of the Highly Polymerised Amorphous Phase-2 (Chapter 10). Without the presence of soluble silicates in the initial activating solution, the Highly Polymerised Amorphous Phase-2 can be dissolved by the excessive alkalis remaining in the reactive activating solution after the alkali-activation (k) – the origin of alkali corrosion on siliceous aggregates as discussed in Chapters 6 and 10.

On the other hand, if a siliceous crystal with a framework structure and a relatively low BET surface area is used, such as albite, the bulk crystalline structure is not significantly affected regardless of the solution alkalinity or the soluble silicate dosage (Chapter 10). In other words, the chemical interactions between the less reactive crystalline aluminosilicate (albite) and an activating solution are only limited to the crystal surface. With increasing extent of Al-enrichment at the crystal surface via reaction route (b) due to higher solution alkalinity, the soluble silicates from the soluble silicate-rich activating solution then become more readily adsorbed by the Al-enriched crystal surface to form an Interfacial Polysialate-II, which is characterised by a Si/Al ratio of ~3 (Chapter 10). According to Chapter 10, this
Interfacial Polysialate-II is similar to the macroscopic interface observed at the aggregate/binder interface within a soluble silicate-rich geopolymeric mortar or concrete. Hence, Interfacial Polysialate-II is responsible for the macroscopic interfacial bonding strength between siliceous aggregates and geopolymeric (aluminosilicate) gels and is absent in soluble silicate-deficient systems as shown in Chapters 6 and 10.

11.5 CONCLUSIONS

The study of the chemical interactions between aluminosilicate solids and activating solutions in this thesis shows that a true geopolymerisation process, which by definition should lead to the formation of aluminosilicate gels (Gel-\(\alpha\) and Gel-\(\beta\)) with strong interparticle strengths, can only occur in the following reaction conditions: (1) ‘glassy/amorphous’ aluminosilicate solid; (2) high solution alkalinity ([OH\(^-\]) > 5 M); and (3) high soluble silicate dosage (\(Rm = \text{SiO}_2/\text{M}_2\text{O} > \sim 0.2\)). Similarly, Interfacial Polysialate-II can only be produced if the following reaction conditions are satisfied: (1) crystalline siliceous minerals whose internal crystal structures are not readily accessible by aqueous solutions; (2) high solution alkalinity ([OH\(^-\]) > 5 M); and (3) high soluble silicate dosage. As aluminosilicate gels (Gel-\(\alpha\) and Gel-\(\beta\)) are the principal binding phases within a geopolymeric binder and Interfacial Polysialate-II is the principal binding phase between siliceous aggregates and geopolymeric binder, reaction conditions that favour the formation of these phases, through extensive microscopic chemical interactions between aluminosilicate powders and activating solutions, or extensive macroscopic chemical interactions between siliceous aggregates and activating solutions, are vital for the process optimisation of geopolymeric products including binders, mortars and concretes. Future experiments should be directed at expanding or detailing the conceptual model presented in this chapter (Figure 11.1), by adopting the research philosophy as well as the methods of the experimentation developed in this thesis on more solids of different chemical compositions, mineralogy and microstructures and activating solutions of different solution alkalinities, \(Rm\) ratios and electrolytes.
11.6 REFERENCES


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