Assessment of Properties of Ambient Cured Geopolymer Concrete for Construction Applications

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Abstract

Geopolymer concrete can offer advantageous engineering and durability properties. Despite many years of research, the widespread usage of this new technology has been hindered due to many factors including, the difficulties in readily adopting the conventional concrete production facilities for the needs of the geopolymer concrete production, (e.g. use of liquid activator and elevated curing temperature). The main objective of this thesis is to study and develop ambient cured geopolymer concrete with a mixture of fly ash and slag.

The initial investigation was on brown coal ash because it is a widely available waste material in Victoria, Australia. A method was developed to identify optimum blends for brown coal ash with activators using data developed in this study as well as from the literature. The study did not continue with brown coal ash because it was found that the geopolymer developed using brown coal ash disintegrated in high moisture environments and the consumption alkali activators was high. The study was then continued with characterisation of six Australian class F fly ashes. The data of the study as well as from the literature was used to identify the relationships between characteristics of fly ash (i.e. particle size of fly ash, SiO₂ to Al₂O₃ ratio, Na₂O/( SiO₂ + Al₂O₃) ratio) and compressive strength of geopolymer.

This study explored the variation of the setting and workability characteristics with binder composition (fly ash to slag ratio) and alkali activator type. The calorimetric measurements showed that activation of the fly ash and slag blend using pentahydrate granular alkali activator is accompanied by negative heat flow (heat absorption) whereas anhydrous alkali activator dissolution is accompanied by release of heat. The additional heat released during the dissolution process accelerates the setting in anhydrous alkalis activated geopolymers compared to hydrated alkalis activated geopolymers.

This work included a comprehensive analysis of the short and long term mechanical properties, shrinkage and creep of ambient cured blended fly ash and slag geopolymer concrete. These long term properties of ambient cured geopolymer are also compared with properties of elevated temperature cured geopolymer binders and ordinary Portland cement (OPC) based binders. All ambient cured geopolymer concrete gained compressive strength rapidly during the early age (<28 days) and maintained the
strength afterward. The study found that the elastic modulus of ambient cured geopolymer concrete is slightly higher (32-34 GPa) than elastic modulus of previously reported heat-cured geopolymer concrete (less than 30 GPa).

The susceptibility of fly ash and slag blended geopolymer binders to alkali aggregate expansive reaction in the presence of reactive aggregates was evaluated using accelerated mortar bar and concrete prism tests. The type of reaction products and the microstructure of geopolymer with different composition are examined using XRD and NMR techniques. The analysis revealed that the fly ash and slag based geopolymer concrete containing reactive aggregates has high volume stability due to higher degree of cross-linking of the geopolymer structure (Q_2 and Q_3 type structure). The study also identified that usage of at least 30% fly ash can mitigate alkali aggregate expansive reaction (AAR) in geopolymer concrete containing reactive aggregates.

The effect of binder composition on chloride-induced corrosion of reinforced geopolymer concrete was evaluated. The results showed that the apparent chloride diffusion coefficient of blended fly ash and slag geopolymer concrete is lower than that of OPC concrete and the diffusion coefficient decreased with the slag content in the binder. Blended fly ash and slag geopolymer concrete also exhibited higher aging factor than OPC concrete indicating improved the resistance to chloride ingress with time. The study also showed that the embedded rebar in fly ash and slag based geopolymer concrete has higher protection against corrosion than a rebar in OPC concrete even when the concrete is contaminated with significant levels of chloride.

Finally, full scale reinforced geopolymer concrete beams were cast using pre-mix truck concrete. The beams were used to analyse the load carrying capacity, ductility and plastic hinge length of geopolymer concrete. The behaviour of reinforced geopolymer concrete beams was compared with that of OPC reinforced beam. The study demonstrated that for the same reinforcement configuration, the geopolymer concrete beam has lower ductility compared to OPC beam as a result of stronger bond between steel and geopolymer.

In this study, ambient cured geopolymer concrete using granular alkali activator was developed for truck mixing. The extensive study on geopolymer concrete showed that the fresh, hardened and durability properties were suitable for practical implementation.
Declaration

I hereby certify that this thesis entitled “Assessment of Properties of Ambient Cured Geopolymer Concrete for Construction Applications” contains no material which has been accepted for the award to the candidate of any other degree or diploma, except where due reference is made in the text of the examinable outcome. To the best of my knowledge, the thesis contains no material previously published or written by another person except where due reference is made in the text of the examinable outcome.

The work is based on the joint research and publications; the relative contributions of the respective authors are disclosed

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Published and Submitted Journal papers


Journal papers under preparations


Conference papers


viii
# Contents

**Publications** .......................................................................................................................... vii

1. **Introduction** ........................................................................................................................ 1

2. **Literature review** .................................................................................................................. 11
   2.1. Source materials used in geopolymers .............................................................................. 12
       2.1.1. Coal fly ash ................................................................................................................. 12
       2.1.2. Slag (GGBFS) ............................................................................................................. 14
       2.1.3. Important parameters in precursor material formation ............................................. 16
   2.2. Factors affecting geopolymer reaction .............................................................................. 21
       2.2.1. Alkali activators ......................................................................................................... 21
       2.2.2. Water content in the geopolymer .............................................................................. 22
       2.2.3. Curing regimes ........................................................................................................... 22
   2.3. Properties of geopolymer binders ..................................................................................... 23
       2.3.1. Properties of fresh geopolymer binders .................................................................... 23
       2.3.2. Properties of harden geopolymer binders ............................................................... 24
   2.4. Durability of geopolymers ............................................................................................... 28
   2.5. Behaviour of large scale reinforced geopolymer ............................................................. 34

3. **Fly ashes in Australia for geopolymer production** ................................................................. 47
   3.1. Introduction ....................................................................................................................... 47
   3.2. Analysis of brown coal fly ash based geopolymers .......................................................... 48
       3.2.1. Experimental analysis ............................................................................................... 48
       3.2.2. Results and discussion ............................................................................................ 51
   3.3. Analysis of Australian class F fly ash based geopolymers .............................................. 72
       3.3.1. Experimental analysis ............................................................................................... 72
       3.3.2. Results and discussion ............................................................................................ 75
   3.4. Concluding remarks .......................................................................................................... 83
   3.5. References for chapter 3 ................................................................................................. 85

4. **Thermal effects of activators on the setting time and rate of workability of geopolymers** ....... 89
   4.1. Introduction ....................................................................................................................... 89
   4.2. Materials and Methods .................................................................................................... 91
       4.2.1. Materials .................................................................................................................. 91
       4.2.2. Testing procedure .................................................................................................... 94
   4.3. Results and discussion ..................................................................................................... 95
       4.3.1. Fresh binder properties ............................................................................................. 95
       4.3.2. Dissolution of sodium metasilicate solids .............................................................. 97
       4.3.3. Strength development ............................................................................................. 105
       4.3.4. Reaction Kinetics .................................................................................................... 107
   4.4. Concluding remarks .......................................................................................................... 110
   4.5. References for chapter 4 ............................................................................................... 111

5. **Development of a geopolymer concrete with granular activator which is suitable for ambient temperature curing** .......................................................... 115
   5.1. Introduction ....................................................................................................................... 115
   5.2. Materials and methods ..................................................................................................... 117
       5.2.1. Precursor material .................................................................................................... 117
       5.2.2. Activator .................................................................................................................. 118
       5.2.3. Aggregate ............................................................................................................... 118
       5.2.4. Preparation of geopolymer concrete using solid alkali ............................................. 118
5.3. Results and discussion........................................ 121
5.3.1. Selecting granular alkali activator content........... 121
5.3.2. Selecting binder composition for ambient curing..... 123
5.3.3. Effect of relative humidity on the compressive strength 127
5.4. Concluding remarks........................................ 129
5.5. References for chapter 5................................. 129

6. Long term mechanical, shrinkage, and creep properties of ambient temperature cured geopolymer concrete
6.1. Introduction............................................. 133
6.2. Materials and methods..................................... 135
  6.2.1. Precursor materials.................................... 135
  6.2.2. Activator.............................................. 135
  6.2.3. Aggregates............................................ 135
  6.2.4. Preparation of geopolymer concrete.................. 135
6.3. Results and discussion..................................... 138
  6.3.1. Long term compressive strength development...... 138
  6.3.2. Flexural strength ..................................... 141
  6.3.3. Stress-strain behavior................................ 143
  6.3.4. Shrinkage.............................................. 148
  6.3.5. Creep.................................................. 150
  6.3.6. Explanation of shrinkage behavior using microstructure 153
6.4. Concluding remarks....................................... 155
6.5. References for chapter 6.................................. 156

7. Abrasion resistance of ambient temperature cured fly ash and slag based geopolymer concrete
7.1. Introduction............................................. 159
7.2. Materials and methods..................................... 161
  7.2.1. Materials.............................................. 161
  7.2.2. Preparation of concrete specimens for the test...... 161
7.3. Results and discussion..................................... 162
7.4. Concluding remarks....................................... 169
7.5. References for chapter 7.................................. 169

8. Susceptibility of geopolymer concrete to alkali aggregate reactivity
8.1. Introduction............................................. 171
8.2. Materials and methods..................................... 173
  8.2.1. Materials.............................................. 173
  8.2.2. Testing procedures..................................... 175
8.3. Results and discussion..................................... 178
  8.3.1. AAR expansion of geopolymer mortar bars.......... 178
  8.3.2. AAR expansion of geopolymer concrete prisms... 184
  8.3.3. MAS-NMR spectra variation of different binders 187
  8.3.4. X-ray diffraction of alkali activated binders....... 192
  8.3.5. Microstructural analysis of AAR products......... 193
8.4. Concluding remarks....................................... 200
8.5. References for chapter 8.................................. 200

9. Chloride ingress and steel corrosion in geopolymer concrete based on long term tests
9.1. Introduction............................................. 203
9.2. Materials and methods..................................... 206
  9.2.1. Materials.............................................. 206
9.2.2. Preparation of geopolymer concrete .......... 207
9.2.3. Testing procedures ........................................ 209
9.3. Results and discussion........................................ 210
  9.3.1. Chloride diffusion rate of concrete .............. 210
  9.3.2. Quantifying the age factor of geopolymer concrete 214
  9.3.3. Service life prediction of concrete.................. 217
  9.3.4. Corrosion rate of embedded rebar in geopolymer concrete 221
  9.3.5. Microstructural analysis of 500 days old concrete 222
9.4. Concluding remarks 224
9.5. References for chapter 9 225

10. Ductility of reinforced geopolymer concrete beams........ 231
  10.1. Introduction...................................................... 231
  10.2. Materials and methods........................................ 232
    10.2.1. Alumina-silicate source material................. 232
    10.2.2. Alkali activator............................................. 233
    10.2.3. Aggregates.................................................... 233
    10.2.4. Reinforcement details...................................... 233
    10.2.5. Casting, curing and testing procedure of beams 235
  10.3. Results and discussion....................................... 238
    10.3.1. Properties of geopolymer concrete................. 238
    10.3.2. Load-deflection of the beams...................... 239
    10.3.3. Ductility of beams......................................... 240
    10.3.4. Quantifying plastic hinge length.................. 243
    10.3.5. Moment curvature relationship of beams............ 244
    10.3.6. Comparison of the hinge length with hinge length models 248
  10.4. Concluding remarks........................................... 250
  10.5. References for chapter 10................................. 250

11. Summary and conclusions............................................. 253
List of Figures

Figure 2.1: Relationship between amorphous content of precursor material and the compressive strength of resulting geopolymer .......................................................... 20

Figure 3.1: X-ray diffraction analysis of raw materials (a) brown coal fly ashes (b) slag and GFA ..................................................................................................................... 53

Figure 3.2: Particle size distribution of fly ashes ........................................................... 54

Figure 3.3: (a) GP4 deterioration after immersed in the water (b) XRD patterns of GP4 geopolymer binder ..................................................................................................... 57

Figure 3.4: De-composition of GP13 and GP14 after water immersion ...................... 58

Figure 3.5: Calorimetric measurements for brown coal fly ash blended geopolymer binders (a) initial reaction (0-120 mins) (b) total reaction time (0-700mins)........... 59

Figure 3.6: Compressive strength development of blended brown coal fly ash geopolymers ................................................................................................................. 60

Figure 3.7: Pseudo-ternary plot of composition of brown coal fly ash blends and other commonly used construction materials (based on Scrivener et al. [23]) ............. 63

Figure 3.8: Brown coal fly ash blended geopolymer pastes after water immersion .64

Figure 3.9: XRD patterns for geopolymers (a) GP11 (b) GP12 (each pattern corresponds to 1day, 7day, and 28 days as shown) ........................................................................ 66

Figure 3.10: BSE images of geopolymer binders A) GP11 B) GP12 (different magnifications denoted 1, 2 and 3) ............................................................................................... 68

Figure 3.11: BSE image of GP12 with EDX analyses (a) unreacted particle of slag, (b) reacted binder near the unreacted particle of slag (c) binder further away from the unreacted particle of slag ........................................................................ 69

Figure 3.12: BSE image of blended geopolymer binders with EDX analyses, top- GP11, and bottom-GP12 ......................................................................................... 69

Figure 3.13: Atomic ratios of GP11 and GP12 of paste (EDX analysis data) ............ 70

Figure 3.14: BSE image and corresponding elemental maps of 1 year old GP11 blended geopolymer binder ......................................................................................... 71

Figure 3.15: BSE image and corresponding elemental maps for 1 year old GP12 blended geopolymer binder ......................................................................................... 72

Figure 3.16: Particle size distribution of fly ashes .......................................................... 74

Figure 3.17: Compressive strength of six types of fly ash based geopolymers; fly ash particle size increases from left to right ......................................................... 76
Figure 3.18: Effect of fly ash (a) particle size (b) Liquid to solid ratio on compressive strength of geopolymer pastes at different ages of curing ........................................................................77

Figure 3.19: Compressive strength variation with reactive SiO2/Al2O3 ratio for geopolymer based on previous studies Diaz et al. [41], Fernández-Jiménez et al. [29], ........................................................................................................................................79

Figure 3.20: Average 28 days compressive strength variation with Na2O/ (reactive SiO2+Al2O3) molar ratio ......................................................................................................................................80

Figure 3.21: Average 28 days compressive strength variation with Tarong fly ash content in geopolymer mix ..................................................................................................................81

Figure 3.22: Secondary electron SEM images of fracture surface of (a) Gladstone, (b) Collie, (c) Eraring, (d) Mt piper, (e) Bayswater and (f) Tarong fly ash-based geopolymers ...............................................................................................................82

Figure 4.1: Particle size distribution of (a) Slag (b) Fly ash .........................................................90

Figure 4.2: Initial and Final setting time of geopolymer pastes in the presence of PH and AH ................................................................................................................................................93

Figure 4.3: Workability loss of geopolymer mortar binders (a) 90/10 (b) 70/30 (c) 60/40 (d) 50/50 (e) 40/60 (f) 0/100 FA/S ........................................................................................................................................94

Figure 4.4: Dissolution of sodium metasilicate anhydrous and sodium metasilicate pentahydrate ..............................................................................................................................................96

Figure 4.5: Normalized heat flow of (a) 100/0 (b) 70/30 (c) 60/40 (d) 50/50 (f) 40/60 (g) 0/100 FA/S blended geopolymers during 0-1 hours. .........................................................................................97

Figure 4.6: pH variation in geopolymers (a) 50/50 fly ash and slag geopolymers (b) 100% slag ................................................................................................................................................98

Figure 4.7: Setting time with different alkali activator condition .....................................................99

Figure 4.8: Normalized heat flow due to different activator form (a) PH based binders (b) AH based binders (0-1 hour) ........................................................................................................99

Figure 4.9: Normalized heat flow of (a) 100/0 (b) 70/30 (c) 60/40 (d) 50/50 (f) 40/60 (g) 0/100 FA/S blended geopolymers during 1-30 hours of reaction .............................................101

Figure 4.10: Compressive strength development geopolymer mortars in the presence of AH and PH in (a) 1 day (b) 7 day (c) 28 day ..........................................................................................103

Figure 4.11: Normalized heat flow due to different activator form (a) PH based binders (b) AH based binders (5-40 hours) .................................................................................................................104

Figure 4.12: Compressive strength development of geopolymer binder with different alkali activator state (a) 1 day (b) 7 days (c) 28 days strength ...........................................................................105

Figure 5.1: Particle size distribution of (a) Slag (b) Fly ash .........................................................113
Figure 5.2: Particle size distribution of aggregates used in this study .................114

Figure 5.3: Effect of alkali on the (a) Slump (b) early age compressive strength of geopolymer concrete (alkali content = Na2O mass/ binder content (fly ash and slag). Mix designs are given in Table 5.2) ..............................................................118

Figure 5.4: Strength development of geopolymer concrete with binder composition ........................................................................................................119

Figure 5.5: Compressive strength development of geopolymer concrete containing 70% fly ash at different water to solid ratio (mix designs listed in Table 5.3) ...........120

Figure 5.6: Effect of sand water for (a) slump and (b) compressive strength of geopolymer ........................................................................................................122

Figure 5.7: Effect of relative humidity on the compressive strength of geopolymer binder ........................................................................................................124

Figure 6.1: Particle size distribution of aggregates used in this study. .................129

Figure 6.2: LVDT setup in the geopolymer concrete specimen (a) before the test (b) during the test ..............................................................131

Figure 6.3: Isothermal calorimetric analysis of the geopolymer paste samples with varying fly ash to slag ratio .................................................................133

Figure 6.4: Compressive strength development of the geopolymer concrete up to 600 days ........................................................................................................135

Figure 6.5: (a) Flexural strength development of geopolymer concrete (b) Measured flexural strength vs. predicted flexural strength .................................................137

Figure 6.6: Axial and radial stress-strain behaviour of (a) 60/40 FA/Slag (b) 50/50 FA/Slag (c) 40/60 FA/Slag (d) 0/100 FA/Slag ..........................................................138

Figure 6.7: (a) Elastic modulus (b) poisson’s ratio of geopolymer concrete containing different slag content (mix designs are given in Table 6.1) .........................140

Figure 6.8: Modulus of elasticity of geopolymer concrete ....................................142

Figure 6.9: (a) Shrinkage of (b) Mass loss of 50/50 FA/Slag based geopolymer concrete .................................................................................................144

Figure 6.10: (a) Shrinkage of (b) Mass loss geopolymer concrete with different binder compositions (FA/Slag ratio) .................................................................144

Figure 6.11: (a) Basic creep coefficient (b) Specific creep strain of 50/50 FA/Slag (c) Specific creep strain of 30/70 FA/Slag (d) Specific creep strain of 0/100 FA/Slag of geopolymer concrete .................................................................147

Figure 6.12: SEM images and EDX analysis of 60/40 FA/Slag geopolymer ............148
Figure 6 13: SEM images and EDX analysis of 50/50 FA/Slag geopolymer ............ 149
Figure 6 14: SEM images and EDX analysis of 0/100 FA/Slag geopolymer ............ 149
Figure 7 1: Abrasion testing procedures (a) Initial measurement (b) Abrasion test (c) After the test (d) Measurements of abraded depth ..................................................... 156
Figure 7 3: Abrasion depth of 50/50 FA/Slag (a) Bottom (b) Top Surface in 28 days (the redline indicate the median of the abraded depth, the box indicates the third and second quartile of data while the upper and lower quartiles are show as the horizontal line 159
Figure 7 4: Abrasion depth of 30/70 FA/Slag (a) Bottom (b) Top Surface in in 28 days .................................................................................................................................... 159
Figure 7 5: Abrasion depth of 0/100 FA/Slag (a) Bottom (b) Top Surface in in 28 days .................................................................................................................................... 159
Figure 7 6: Abrasion depth of 100 OPC (a) Bottom (b) Top Surface in 28 days ...... 160
Figure 7 7: Abrasion depth of 50/50 FA/Slag (a) Bottom (b) Top Surface at 200 days .................................................................................................................................... 161
Figure 7 8: Abrasion depth of 30/70 FA/Slag AB (a) Bottom (b) Top Surface at 200 days .................................................................................................................................... 161
Figure 7 9: Abrasion depth of 0/100 FA/Slag (a) Bottom (b) Top Surface at 200 days .................................................................................................................................... 161
Figure 7 10: Abrasion depth of 100 OPC (a) Bottom (b) Top Surface at 200 days ..  162
Figure 7 11: Comparison of geopolymer and OPC concrete after each test cycle ...162
Figure 8 1 : Length change of OPC mortar bar containing sand .......................169
Figure 8 2 : Average expansion of mortar bars containing NR aggregate at a) 4% Na2O b) 6% Na2O ..................................................................................................................................... 173
Figure 8 3: Average expansion of mortar bars containing R1 aggregate at (a) 4% Na2O (b) 6% Na2O ................................................................................................................... 174
Figure 8 4: Average expansion of mortar bars containing R2 aggregate at (a) 4% Na2O (b) 6% Na2O ................................................................................................................... 174
Figure 8 5: Expansion of geopolymer mortar bars containing (a) different slag content and R2 aggregate at 6% Na2O in 10 and 21 days (b) different slag content and R2 aggregate at 4 and 6% Na2O in 21 day ........................................................................... 177
Figure 8 6: Variation of expansion in geopolymer mortar bars containing reactive aggregates with the molar ratios .......................................................... 178
Figure 8.7: Length change of concrete prisms containing non-reactive aggregates at (a) 4% (b) 6% alkali level.

Figure 8.8: Length change of concrete prisms containing R2 aggregate at (a) 4% (b) 6% alkali level.

Figure 8.9: Appearance of concrete after 600 days (a) C0/100FA/S-6-R2 (b) OPC-R2.

Figure 8.10: Relationship of expansion obtained from CPT (600 days) and AMBT (60 days).

Figure 8.11: 29Si MAS NMR spectra from powders acquired at 10 kHz spinning speed and 23°C (except bottom spectrum run at 4 kHz spinning speed). Asterisks identify spinning side bands.

Figure 8.12: 27Al MAS NMR spectra from powders acquired at 10 kHz spinning speed and 23°C.

Figure 8.13: 23Na MAS NMR spectra from powders acquired at 10 kHz spinning speed and 23°C.

Figure 8.14: XRD patterns of geopolymer binders (a) 70/30 FA/S (b) 50/50 FA/S (c) 30/70 FA/S (d) 0/100 FA/S.

Figure 8.15: Reaction products found in mortars with different binders in the presence of NR basalts. Each EDX spectrum represents the composition of the area marked on the corresponding image.

Figure 8.16: Reaction products found in mortars with different binders in the presence of reactive aggregate R1. Each EDX spectrum represents the composition of the area marked on the corresponding image.

Figure 8.17: Reaction products found in mortars with different binders in the presence of reactive aggregate R2.

Figure 8.18: Products formed in mortars (a) M0100FAS-6-R2 (b) M5050FAS-6-R2.

Figure 9.1: Particle size distribution of (a) Slag (b) Fly ash. 1-10 g of source material was dispersed in water in order to obtain the particle size.

Figure 9.2: Specimens used for chloride induced corrosion testing (Dashed line shows the level of NaCl solution during the immersion process).

Figure 9.3: Chloride profiles of concrete cylinders after 5 weeks of immersion test.

Figure 9.4: The change of charged passed through concrete for concrete specimens of different ages.

Figure 9.5: Chloride penetration depth of concrete (a) 50/50 FA/S geopolymer immersed in 2.832 M NaCl solution (b) 50/50 FA/S geopolymer immersed in 0.6 M NaCl solution.
NaCl solution (c) OPC concrete immersed in 2.826 M NaCl solution (d) OPC concrete immersed in 0.6 M NaCl solution .............................................................................. 213

Figure 9 6: (a) geopolymer concrete with rebar (b) embedded rebar in geopolymer concrete (c) OPC concrete with rebar (d) embedded rebar in OPC concrete immersed in 2.826 M NaCl ............................................................................................................. 214

Figure 9 7: (a) geopolymer concrete with rebar (b) embedded rebar in geopolymer concrete (c) OPC concrete with rebar (d) embedded rebar in OPC concrete immersed in 0.60 M NaCl ............................................................................................................... 215

Figure 9 8: (a) Corrosion current (b) Corrosion rate of rebar in chloride contaminated geopolymer and OPC concrete ............................................................................................................. 216

Figure 9 9: Microstructure of 50/50 FA/Slag geopolymer concrete after 500 days .. 217

Figure 9 10: Microstructure of OPC concrete after 500 days ....................................... 218

Figure 10 1: Sieve analysis of aggregates .................................................................... 227

Figure 10 2: Layout of the reinforced beams ................................................................. 228

Figure 10 3: Casting process of geopolymer concrete beams ........................................ 230

Figure 10 4: Loading setup and instrumentation of beams ............................................. 231

Figure 10 5: Compressive strength development of geopolymer concrete measured according to AS 1012.9 .......................................................................................................................... 232

Figure 10 6: Load-deflection responses of beams under (a) 4-point loading (b) 3-point loading .......................................................................................................................... 233

Figure 10 7: Load-deflection response of Geopolymer beam and OPC beam (ρsv =0.79%) under 4-point loading .......................................................................................................................... 233

Figure 10 8: Crack patterns of beams after failure (a) 4Geo-100 (b) 4OPC-100 .... 235

Figure 10 9 : Enlarged images of crack patterns of beams after failure (a) 4Geo-100 (b) 4OPC-100 .................................................................................................................................................... 235

Figure 10 10: Beam mechanisms for the plastic analysis for (a) 4-point (b) 3-point loading [16] .......................................................................................................................... 236

Figure 10 11: Stress-Strain curves of confined and unconfined concrete (a) Geopolymer (b) OPC .......................................................................................................................... 237

Figure 10 12 : Stress and strain profiles for a beam section (the shapes of the stress profiles in the figure do not represent the calculated stress profiles) ........................................ 239

Figure 10 13: Moment-curvature relationship of OPC and Geopolymer at 100 mm stirrup spacing .......................................................................................................................... 240

xvi
Figure 10 14: Comparison between calculated and predicted plastic hinge length (Lp) (hatch angled line is for the 1:1 match)..................242
1. Introduction

The term geopolymer describes a broad class of synthetic zeolite materials that are produced by a series of reactions between alumino-silicate precursor materials and alkali activators. Precursor material for geopolymer can be a by-product from industrial processes such as coal fly ash, slag, red mud and rice husk ash (RHA) or a geological resource like metakaolinite [1]. The geopolymerisation process initiates with the dissolution of silicon and aluminium from the precursor materials in an alkali environment. The dissolved ions react to produce silicate and aluminate monomers which are converted to a poly (alumino-silicate) structure with interconnected SiO$_4$ and AlO$_4$ tetrahedral. The hardening of geopolymer is a result of poly-condensation of hydrolysed aluminate and silicate species [2]. The geopolymerisation process requires cations like Na$^+$, K$^+$, Ca$^{2+}$ to diminish charge imbalance which may be due to the coordination of aluminium or any depolymerized framework sites in whole structure [3, 4]. The properties of the final products are sensitive to factors including the characteristics of precursor materials (aluminosilicate rich materials, calcium rich materials), alkali activator type and content, curing regimes, mixing procedures. For instance, alkali activation of 100% alumina-silicate source materials produces three-dimensional N-A-S-H gels while alkali activation of calcium-bearing alumino-silicate materials produces modified geopolymer structure with two-dimensional, layer-structured C-S-H or C-A-S-H gels apart from N-A-S-H gel [5, 6].

Geopolymer, produced without the use of ordinary Portland cement (OPC), is said to be an environmentally sustainable alternative to conventional concrete. The production of one tonne OPC (i.e. calcination of clay and lime stone (CaCO$_3$) mixtures and the grinding of gypsum and clinkers) requires approximately 4.9 GJ. Furthermore, the calcination of lime stone releases high amount of CO$_2$ (greenhouse gas) into the atmosphere. Geopolymer produced with industrial by-products require far less pre-processing and McLellan et al. [7] showed that, by using geopolymer instead of OPC, the CO$_2$ emission can be reduced by approximately 44% to 64% under Australian conditions (source material availability, temperature, relative humidity etc.). Additionally, the use of industrial by-products like coal fly ash and slag reduces the accumulation of waste materials in landfills and reduce the contamination of ground water through leaching of the heavy metals. Due to the above reasons, geopolymer
binder has become prominent as a construction material among research community in recent years. Geopolymer concrete has also shown potentially advantageous engineering properties and durability compared to OPC concrete. However, the superior properties of this new concrete technology are yet to be proven to the satisfaction of the concrete industry.

Despite the fact that geopolymer concrete has a potential to replace traditional OPC based concrete, the widespread usage of this new technology is hindered due to following challenges:

1. The properties of the final geopolymer binder are highly sensitive to the characteristics of alumina-silicate source materials (i.e. chemical composition (SiO₂, Al₂O₃, CaO), amorphous content, particle size) which in-turn are highly dependent on the source of origin. Currently there is no appropriate method to predict the final properties of geopolymer binder synthesised with a specific precursor material hence each precursor composition needs to be investigated independently [8].

2. Common practices in producing geopolymer, i.e. the use of liquid activators and elevated temperature curing, limit geopolymer concrete to laboratory conditions or precast applications [8]. While the use of dry ingredients or ambient curing makes geopolymer more convenient in practice than elevated cured and liquid alkali activated geopolymers, the state of alkali activator and the curing regime significantly affect the properties of the resulting binder and there are only limited investigations on this [9, 10].

3. Suitable admixtures that enables the control of rheology and reaction kinetics in the early age of geopolymer has not been developed so far [1, 8]. Several researches have revealed that the traditional super plasticisers, setting retarders, setting accelerators and water reducers have limited success for geopolymer systems [10-12].

4. The information on the service history and durability performance of geopolymer concrete products is limited, which reduce the confidence in using this new sustainable construction material in structural applications. On the other hand OPC has around 200 year service record [8, 13].
5. The knowledge base on large scale geopolymer concrete production and in-situ casting of ambient temperature geopolymer concrete objects is limited [8].

6. Limited knowledge base on the full scale reinforced geopolymer concrete elements. Therefore, to date, geopolymer concrete has had relatively minor application in field concrete.

7. The standards that model engineering properties and procedures for geopolymer production are not yet fully developed. The usage of existing standards (developed for OPC) has not been fully validated for geopolymer concrete [1, 8, 13].

While geopolymer systems have been extensively studied, the foregoing makes it clear that geopolymer concrete materials require further investigations before they can be adopted for use in structural applications. The main objective of this thesis is to study the relevant many properties of geopolymer concrete for its practical implementations.

The main contributions of this research are as follows:

1. Identifying the suitability of waste materials in Australia as geopolymer source materials. Evaluates the properties of geopolymer systems synthesised using Australian source materials and develop a relationship between the material characteristics and the properties of resulting geopolymer binders.

2. Make geopolymer more convenient in practice compared to existing geopolymer systems.
   - Rheology and workability: Investigated the use of alkali activator type and state to control the setting time and the workability of geopolymer concrete.
   - Granular activator usage: granular activators are more convenient in practice than alkali activator solutions. The suitability of solid alkali activator in regards to properties in early age concrete as well as in later age was evaluated.
   - Ambient curing: The knowledge base on ambient cured geopolymer is limited. Therefore, this study broadens the knowledge base on ambient cured geopolymer production.

3. The evaluations on engineering properties of geopolymer in literature are mostly limited to less than one year. This thesis provides a comprehensive analysis of the properties of geopolymer concrete in the long term that enables a greater
understanding of long term properties of geopolymers i.e. mechanical, shrinkage, creep and abrasion.

4. This research evaluates the durability performance of geopolymer concrete with respect to Alkali aggregate reaction and chloride induced corrosion. The study also provides guidelines on reducing durability issues in geopolymer.

5. The knowledge based on the behaviour of reinforced full scale geopolymer concrete element is limited, in particular the post-peak behaviour of geopolymer structures which is important in ensuring the load redistribution and robustness of the structure during their service life. This work presents an in-depth investigates on the behaviour of full scale geopolymer structural elements.

The remainder of the thesis is organized as follows. Chapter 2 provides a comprehensive literature review on the precursor materials, mechanical properties, shrinkage, durability properties and behaviour of reinforced geopolymer concrete.

The potential re-use options for a suite of low rank brown coal fly ashes and class F fly ashes in Australia as feedstock for geopolymer binder synthesis are investigated in chapter 3. Fly ash suitability was evaluated using a number of conventional characterisation tools including XRF, X-Ray diffraction patterns, calorimetric and SEM/EDX microscopy. First, the variations in the brown coal fly ash based geopolymers were analysed using solid phase distribution in relation to compositional differences derived from ternary diagram analogues. Blends of brown coal ash with selected black coal fly ash (class F) and blast furnace slag were developed for compressive strength and durability tests. The study showed that brown coal fly ash with higher aluminium content improved the rate of reaction of blended binders compared to brown coal fly ashes with lower aluminium. Furthermore, high contents of sulphate and magnesium oxides available in some brown coal fly ashes induced accelerated decomposition in high moist environments. Overall, it was evident from both microscopy and mineralogical analysis of binder mixtures that brown coal fly ash participate in geopolymer network formation rather than act as filler material. Factors influencing brown coal ash reactivity and the potential for incorporating this class of ash in developing stable and usable geopolymer binder systems are also discussed. In the second part of this chapter, the characteristics of Australian class F fly ashes and the properties of their geopolymers were discussed. The study explores the role and
relationship between SiO$_2$ and Al$_2$O$_3$ contents of aluminosilicate material on the properties of geopolymer systems using Australian fly ashes and published data. The selected fly ashes, with varying amounts of amorphous and total SiO$_2$ and Al$_2$O$_3$ are assessed for their overall reactivity.

The properties of fresh geopolymer binders and early age strength development are discussed in chapter 4. Similar to the case of OPC concretes, the fresh geopolymer concrete must also exhibit desirable rheology and setting behaviours in order to be useful for field applications. Such properties can be influenced by alumino-silicate source material, alkali activator type, water to solid ratio and temperature. Use of solid alkali activators in geopolymer mixes is less hazardous than the commonly used liquid activators and yields a “cement like” mix, where only water is added for its activation and hydration. This chapter presents a study of the setting time and rate of slump loss of geopolymer binders based on fly ash and slag blends and activated with pentahydrate and anhydrous sodium metasilicate. Fly ash and slag were mixed at different ratios and activated with the two solid alkali activators mentioned above. Vicat needle test and calorimetric measurements were employed to determine the setting parameters and heat generation and sink effect of geopolymer mixes. The workability was measured using a flow table to examine the rate of slump loss. The calorimetric measurements showed that activation of the fly ash and slag blend by the pentahydrate activator is accompanied by negative heat flow (heat absorption) whereas anhydrous alkali activator dissolution is accompanied by release of heat. The additional heat released during the dissolution process accelerates the setting in anhydrous alkali activated geopolymers compared to hydrated alkali activated geopolymers. It is also observed that the strength of the geopolymers in later stage changes with changing calorimetric heat flow characteristics.
Chapter 5 of the thesis explores the workability and early age strength development in blended fly ash and slag geopolymer concrete synthesised using ambient temperature curing and granular alkali activators. Firstly, the effect of granular alkali activator content on the rheology and early age strength development of blended fly ash and slag geopolymer was discussed. Next, the effect of fly ash to slag ratio on the strength development and rheology of geopolymer concrete in the presence of granular activator at ambient temperature curing is investigated. The early age strength development and the workability of geopolymer concrete were compared (results reported chapter 4 and chapter 5) with the geopolymer concrete synthesised with liquid alkali activators. The relative humidity of the environment is identified as an important parameter in the production of OPC concrete. Therefore, the influence of relative humidity of the environment on geopolymer systems will also be discussed.

Chapter 6 provides a comprehensive analysis of the long term mechanical properties, shrinkage and creep of geopolymer concrete of ambient cured geopolymer concrete. In this study, the compressive strength changes of ambient cured geopolymer concrete were assessed over 600 days. The change of the stiffness upon aging of geopolymer concrete is evaluated using stress-strain relationship in two different ages. Flexural strength of ambient cured geopolymer concrete was obtained for ambient cured geopolymer concrete at two different ages. The measured flexural strength and modulus of elasticity of geopolymer concrete was compared with AS3600 and ACI318 standards in order to establish the applicability of existing standards to fly ash and slag based geopolymer concrete. The study also evaluates the deformation characteristics of geopolymer concrete over time using creep and shrinkage measurements of concrete.

Chapter 7 presents the study of abrasion resistance of ambient cured geopolymer concrete with different fly ash to slag ratios. Abrasion resistance of each concrete specimen was determined using the depth of wear after abrasion tested according to EN13892-4 standard. Both surfaces of the concrete specimens (i.e. top and bottom surfaces) were analysed to study the variation in abrasion resistance with surface quality and setting characteristics. The tests were carried out at two ages (28 days and 200 days) to determine the effect of age of geopolymer concrete on the abrasion resistance. The abrasion resistance of geopolymer concrete in this study was compared with OPC
control specimen and the abrasion resistance of geopolymer concrete reported in elsewhere.

Chapter 8 evaluates the susceptibility of room temperature cured blended fly ash and slag geopolymer concrete to alkali aggregate expansive reaction. Geopolymer mortar and concrete specimens with different fly ash to slag ratio, aggregates that exhibit different levels of reactivity and different alkali contents were used in this analysis. Accelerated AAR expansion tests were conducted on geopolymer mortars which were initially cured at room temperature (23°C) prior to the accelerated testing in 1M NaOH at 80°C according to RTA 363 [14]. The alkali aggregate reactivity of geopolymer concrete specimens was also evaluated using according to RTA 364 [15] test method. Microstructural information obtained through SEM/EDX, XRD and NMR techniques was used to study the causes of AAR and AAR products in geopolymer concrete.

Chapter 9 explores the resistance to chloride ingress into geopolymer concrete with varying slag to fly ash ratio. The study also evaluates the influence of maturity of concrete on the chloride ingress rate using the age factor. The corrosion behaviour of the embedded rebar the presence admixed chloride was also analysed using the geopolymer concrete specimens with added chloride. The results show that the chloride diffusion coefficient of blended fly ash and slag geopolymer concrete is significantly lower than that of OPC concrete. Geopolymer concrete also show high reduction of chloride ingress rate with maturity compared to OPC. This is due to the continual evolution of the geopolymer structure which leads to high amount of cross linking with upon aging of concrete. Embedded rebar inside chloride admixed concrete also showed better performance compared to the rebar in OPC concrete.

Chapter 10 investigates the behaviour of reinforced geopolymer concrete beams. In this study, four reinforced geopolymer concrete beams were made using blended fly ash and slag. These and one OPC beam were used to analyse the load deflection behaviour and ductility. These beams were cast in two different stirrup spacing, using a pre-mix truck and cured at ambient temperature. The analysis showed that, for the same reinforcement configuration, the geopolymer concrete beams had lower ductility compared to OPC beam, although the ultimate load carrying capacity was the same. The difference in ductility is attributed to a smaller plastic hinge length in geopolymer beams than in OPC beam, caused by the stronger bond between the steel and geopolymer concrete. In
addition, the study also found that the geopolymer concrete beams with closer stirrups provide additional confinement in turn the ductility of beams is increased.

**References for chapter 1**


2 Literature Review

Geopolymer binders are produced as a result of a series of reaction between alumina-silicate rich source materials and alkali activator. These reactions create Si-O-Al-O bonds which lead to formation aluminium and silicate monomers. The monomers are then converted into oligomers and subsequently into silicate polymers [1]. The reaction between alumna-silicate and alkali (Na$_2$O) mainly produces the amorphous sodium alumina silicate hydrate structure (N-A-S-H) gel that is three dimensional and contains SiO$_4$ and AlO$_4$ tetrahedral units interconnected by sharing oxygen atoms [1]. The charge balance of geopolymer matrix is achieved through additional cations like Na$^+$, K$^+$ and Ca$^{2+}$ [2]. The secondary products of this type of reaction are zeolites (i.e. hydroxysodalite, Na-chabazite, zeolite P, zeolite Y, faujazite) [3]. Geopolymer binders containing calcium and magnesium ions have more complicated reaction mechanisms compared to pure alumina-silicate based geopolymers. These systems produce calcium silicate hydrate (C-S-H) and calcium aluminate silicate hydrate (C-A-S-H) gel apart from amorphous N-A-S-H gel. The secondary products of these systems were identified as hydrotalcite, [Mg$_6$Al$_2$CO$_3$(OH)$_{16}$·4H$_2$O], C$_4$AH$_{13}$, CASH$_8$, C$_4$AcH$_{11}$ and C$_8$Ac$_2$H$_{24}$ [3]. A number of factors control the characteristics of the reaction products including the characteristics of alumina-silicate material, alkali activator type and the content, blending materials and curing regime, in turn, the properties of final geopolymer product can be varied widely.

This chapter provides a comprehensive review of geopolymer binders and is arranged as follows. The first section discusses the source material characteristics and the reactivity of material under different curing and alkalinity. Next, the properties of fresh geopolymer binders and methods used to adjust the properties are reviewed followed by an analysis of properties of harden geopolymer. In the final sections, the durability properties and behaviour of large scale reinforced geopolymer concrete is discussed respectively.
2.1 Source materials used in geopolymers

2.1.1 Coal Fly Ash (Dry precipitator fly ash)

Fly ash is the main by-product of coal combustion in power stations (here we focus only dry precipitator coal fly ash) and globally 480 million tons of coal fly ash is produced each year [4]. Coal fly ash mainly contains three types of particles i.e. spherical vitreous particles, Fe-oxide particles and irregular unburned coal particles [5]. The composition of each particle type varies according to the quality of coal and boiler operation conditions. Unprocessed fly ash particle size can vary in the range 0.1 to 150 μm [5]. ASTM C618 [6] categorises the fly ash into two main groups i.e. class F and class C. Harder and older anthracitic and bituminous coals are burned to obtain class F fly ash while burning of younger lignite and subbituminous coal produced class C fly ash. Table 2-1 shows the chemical composition and physical difference between two classes.

Table 2-1: ASTM-C618 standard for fly ash [6]

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Class F</th>
<th>Class C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$ + Al$_2$O$_3$ + Fe$_2$O$_3$ min%</td>
<td>70</td>
<td>50</td>
</tr>
<tr>
<td>CaO min%</td>
<td>&lt;10</td>
<td>&gt;10</td>
</tr>
<tr>
<td>SO$_3$ max%</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Moisture content max%</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Loss of ignition max%</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Physical properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fineness + 325 mesh max%</td>
<td>34</td>
<td>34</td>
</tr>
</tbody>
</table>

Class F fly ash (CFA)

Class F fly ash has been identified as the most suitable source material for geopolymer binders because of its reactivity and availability. The mass ratio of SiO$_2$ and Al$_2$O$_3$ in class F fly ash is in the range of 1.7-4.0 while the amorphous content is generally more than 50 % [5, 7]. Table 2-2 illustrates typical chemical composition of the class F type fly ash. Shi et al. [8] stated that class F fly ash has cleaner surface compared to class C fly ash due to the absence of alkalis and sulphates ions [8]. As class F fly ash has low CaO level, the main reaction products generated by alkaline activation are amorphous geopolymer gel and sodium aluminium silicate hydrate (N-A-S-H) [8].
Table 2-2: Chemical composition variation of typical class F fly ash [9].

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>20-60</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>5-35</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>6-24</td>
</tr>
<tr>
<td>CaO</td>
<td>1-12</td>
</tr>
<tr>
<td>MgO</td>
<td>0-5</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0-3</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0-4</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>0-4</td>
</tr>
<tr>
<td>LOI</td>
<td>0-15</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>1-2</td>
</tr>
</tbody>
</table>

Moreno et al. [10] analysed 23 fly ash types and found that 50-90% of the phases in the fly ashes consist of amorphous aluminosilicate glass [5]. This was also confirmed by Ying et al. [11]. Chen-Tan et al. [12] analysed the rate the dissolution of class F fly ash in NaOH solution and concluded that only 39% out of 52% of amorphous content reacts with alkali. Temuujin et al. [13] analysed Australian class F and Mongolian class C fly ashes. They found that class F based geopolymer structure has not been affected by chemical attacks whereas; class C based geopolymer structure changes after the chemical attacks. Furthermore, low calcium based geopolymer binder are not dehydrated when subject to high temperature [14]. Compared to class C fly ash class F has higher aluminium content, therefore class F creates durable geopolymer matrix [7, 13].

**Class C fly ash (CCA)**

Class C fly ash can be further segmented considering the percentage of calcium in it i.e. intermediate calcium fly ash has calcium 10-19.9% and high calcium fly ash has more than 20% calcium [15]. High calcium fly ash has crystalline phases like free CaO, C$_3$A, C$_2$S, CaSO$_4$, MgO and 4CaO.3Al$_2$O$_3$.SO$_3$ [8] which are not available in class F. Class C fly ash gives different geopolymer structure compared to class F fly ash due to the availability of significant level of calcium [16]. Temuujin et al. [13] reported that class C fly ash has self-cementing properties which enable alkali activated class C fly ash to harden at room temperature. Table 2-3 shows the chemical composition and physical difference between two classes.
Table 2-3: Chemical composition of class C fly ash [9]

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>15-45</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>20-25</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>4-15</td>
</tr>
<tr>
<td>CaO</td>
<td>15-40</td>
</tr>
<tr>
<td>MgO</td>
<td>3-10</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0-4</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0-6</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>0-10</td>
</tr>
<tr>
<td>LOI</td>
<td>0-5</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

Chindaprasirt et al. [16] researched on the characteristics of alkali activated class C fly ash mixes. They found that when the mix has high pH level (>13), CaO/SiO$_2$ ratio in the range of 0.59-0.69 and SiO$_2$/Al$_2$O$_3$ is in the range of 2.57-4.79, the final geopolymer binder has mainly C-S-H or C-A-S-H. Furthermore, they reported that at low pH level with lower Ca$^{2+}$ concentration formed N-A-S-H as the major reaction product. Later, the above results were confirmed by Somna et al. [17] and Ying et al. [11]. However, the utilisation of class C fly ash in geopolymer is limited because of its fast setting. Class C based geopolymer can have final setting time in the range of 1-2 hours or even less at room temperature [7]. Moreover, class C fly ash based geopolymer has higher susceptibility to durability problems compared to class F geopolymers (This is mainly because of dehydration of C-S-H like Portland cement binders) [16, 18]. Other main drawback in the class C fly ash is the presence of higher loss of ignition content (or unburned carbon percentage) (LOI) [19]. Diaz et al. [19] stated that unburned particles in fly ash tend to absorb the activator solution due to their higher porosity, in turn, the performance of harden geopolymer concrete is reduced. Furthermore, class C fly ash is limited to some countries like New Zealand, Thailand; therefore, the production of geopolymer using this material is not popular in Australia.

2.1.2 Slag (GGBFS)

Finely ground granulated blast furnace slag (GGBFS) has been used as a blending material with alumina-silicate material in geopolymer production to enhance the properties of fresh and geopolymer binder [20]. The main chemical constituent of slag is CaO-SiO$_2$-MgO-Al$_2$O$_3$ and GGBS is a glassy coarse material with unprocessed
particle size greater than 4.5 mm [20, 21]. Since slag contains significant level of reactive aluminium, silica and calcium, blending of slag with alumina silicate source material improves the reactivity with alkali [22]. As a result, setting time of geopolymer at room temperature (ambient curing) decreases [21]. Oh et al. [23] stated that calcium in slag is more reactive than CFA calcium because Ca in CFA does not dissolve in alkali activator as easily as the Ca in slag. Table 2-4 shows the chemical composition of slag.

Table 2-4: Typical Chemical composition of GGBFS [20]

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>(Wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>31-38</td>
</tr>
<tr>
<td>CaO</td>
<td>38-44</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>9-13</td>
</tr>
<tr>
<td>MgO</td>
<td>7-12</td>
</tr>
</tbody>
</table>

Despite the fact that slag has high glass content, it was found that there is no direct correlation between glass content and the reactivity of slag [20]. Duxson et al. [7] indicated that the molar ratio between free Ca and free Si (degree of depolymerisation see the equation below) is the most important parameter in determining the reactivity of slag. GGBFS contains main phases: gehlenite (2CaO.Al₂O₃.SiO₂), akermanite (2CaO.MgO.2SiO₂) and depolymerized calcium silicate glass and this ratio typically lies between 1.3-1.5 for GGBFS.

\[
\frac{\text{Free Ca}}{\text{Free Si}} = \frac{\text{Total Ca in gehlenite} - \text{Ca in akermanite} - \text{Ca associated with S}}{\text{Total Si} - \text{Si in gehlenite} - \text{Si in akermanite}} \quad [7]
\]

Addition of slag to alumina-silicate source material in a geopolymer system results in calcium aluminate silicate hydrate and calcium silicate hydrate phases apart from the geopolymer gel. Kumar et al. [21] reported that alkali activation of fly ash and slag blend produce C-S-H as the dominate phase at 25°C curing temperature. They also observed that when the slag content is increased C-S-H products also increase while there were no C/N-A-S-H or C-S-H in pure fly ash based geopolymer. Furthermore, Kumar et al. [21] found that alkali activation of slag and fly ash blend at 60°C curing temperature can form N/C-A-S-H when Si/Al ratio is around 2 and C-S-H when Si/Al
ratio is 2.5 and Ca/Si ratio is 0.8. Coexistence of these products, improve compactness of microstructure. Puertas et al. [24] reported that alkali activation of 50/50 FA/slag mainly form C-S-H products. Authors found that the C-S-H products formed in the alkali activated systems have lower calcium content compared to calcium in C-S-H formed in OPC binders. This result is in agreement with Yunsheng et al. [25]. Li et al. [26] conducted X-ray photoelectron spectroscopy (XPS) and found that in the presence of slag the binding energy is decreased. In addition, the authors reported that the corresponding peaks were broader for Si 2p, Al 2p, and O 1s in geopolymers containing slag. The authors stated that the new binding energy was more favorable to zeolite formation. This implies that amorphous phases in geopolymer can transfer into zeolite crystalline phases easier in the presence of slag.

Heidrich [27] reported that 3.1 million tonnes of slag were produced in 2001, of which 75% was utilised in various applications. The corresponding figures for fly ash productions (Heidrich, [27]) were 12 M tonnes/year, of which 5.5 million tonnes were utilised, a significant proportion being in blended cement concrete. These figures show that fly ash is produced far in excess of what gets used, and is, therefore, a good candidate for utilisation in geopolymer concrete. Since incorporation of a source of calcium can improve the strength properties of fly ash-based geopolymers (Results are shown in chapter 4 and chapter 5), slag could be blended with fly ash for geopolymer production. Based on the above, the fly ash and blast furnace slag blended geopolymer is more convenient in practice and economical in countries like Australia.

2.1.3 Important parameters in precursor material for geopolymer formation

Silicon

Silicon is the main ingredient in the precursor materials used for geopolymerisation. Hajimohammadi et al. [28] stated that instant availability of soluble silicon ions in an alkali-activated system leads to a geopolymer network structure with enhanced aluminium corporation. Furthermore, silica availability in the early stage of the reaction assists nucleation of aluminium and silicon from unreacted particles in the source material. If a source material releases silicon ions slowly into synthesis, high silicon based crystalline phases like analcime can be formed during alkali activation of precursor material [28]. XRD patterns and Infra-red patterns show that silica availability in the early stage help to produce geopolymer that has a uniform array [29]. Weng et al.
stated that initial silicon based species formed in a alkali activated binders are $[\text{SiO}_2(\text{OH})_2]^- \text{ and } [\text{SiO(OH)}_3]^-. \text{ The concentration of each species depends on the alkalinity of the system. These } [\text{SiO(OH)}_3]^- \text{ and } [\text{Al(OH)}_4]^- \text{ then start to condense forming stable large oligomers and polymers.}

Thockhom [31] used three different Si/Al ratios (1.7, 1.9 and 2.2) in the geopolymer binder and found that the binder with the highest Si/Al has higher thermal resistance than other binders. However, Fletcher et al. [32] reported that high fine silica in geopolymer requires higher water demand and as a result Al species can be hydrated which are predominately octahedral. In addition to this the same authors observed that geopolymers containing very high silicon (Si/Al >24) is more unstable at higher temperatures.

**Aluminium**

Aluminate species are an essential component in geopolymerisation reaction to achieve irreversible chemical hardening [33, 34]. Presence of sufficient aluminium species in the synthesis help initiate quick condensation with silicate species [35]. Fernández-Jiménez et al. [36] stated that during the initial state of reaction (2-8 hours after the alkali activation of precursor material) aluminium is more reactive than silicon. They also observed that the almost total reactive alumina in the material is consumed by the geopolymerisation. After 8 hours of reaction, the materials with low level of reactive (amorphous) aluminium slow down the reactivity which suggests that there should be minimum amount of reactive aluminium content in the precursor material for geopolymer reaction. These results are in line with the results obtained by Rattnasak et al. [34]. Weng et al. [35] reported that aluminium atom has higher positive charge than silicon atom in the same alkaline environment. Therefore, $[\text{Al(OH)}_4]^- \text{ tetrahedral tend to attract more hydroxyl ions which will encourage more aluminate species to participate in condensation reaction. Since condensation rate largely depend on the aluminate content, the geopolymer reaction is accelerated [35]. Silva et al. [37] confirmed this by showing enhancement in setting of geopolymer when aluminium content is increased. They revealed that geopolymers with the same SiO$_2$/Al$_2$O$_3$ ratio have different setting characteristics due to different Al$_2$O$_3$/Na$_2$O ratios [37]. However, Hajimohammadi et al. [38, 39] showed that high availability of Al$^{3+}$ limits the entering of Si$^{4+}$ for geopolymer reaction in the early stage which result the unstable geopolymer gel. In addition, they
found that the excess aluminium ions are absorbed into undissolved silica particles creating a barrier for continual geopolymerisation [38]. This results are in agreement with Fernández-Jiménez et al. [36]. Furthermore, Fernández-Jiménez et al. [36] reported that aluminium bonds produced during the early age geopolymer reactions are easier to break. In the presence of high aluminium content, production of Al-O-Si products is higher than Si-O-Si and therefore the mechanical strength of resulting geopolymer can be lower. Due to the above reasons, it is important to have precursor material that has an appropriate balance between SiO$_2$ and Al$_2$O$_3$ content [40].

**Calcium**

Calcium enhances the setting characteristics and mechanical properties of the geopolymer binder. Alkali activation of calcium rich source materials result in a mixture of calcium silicate hydrate and partially aluminium substituted calcium silicate hydrate gels [41]. Yip [42] presented a conceptual mapping for possible products in alkali activated binders in the presence of calcium i.e. Na/K-geopolymer, Ca-geopolymer, C-S-H and C-A-S-H. The author reported that a combination of C-S-H and amorphous geopolymer gel are formed in the presence of low alkali while in a high alkali environment (>7.5M) N-A-S-H is formed. Lee et al. [43] stated that the double charged calcium ions introduced by slag combines with hydroxyl to form hydroxide precipitates. This causes a pH reduction around the hydroxide precipitates and helps to form silicate polymers which are comparatively large solid particle with lower surface energy. The above process enhances the nucleation and polymerization between the soluble silicate and solid particles leading to an increase in the rate of hardening. These above results are in line with [41, 44]. Dombrowski et al. [45] stated that significant level of initial calcium availability in the synthesis produces C-S-H products in the later stage of reaction (at 40°C curing). The authors found that optimum calcium content that can add into the mix is 8% because this addition improved the strength of the geopolymer at ambient and elevated temperature. Higher calcium in the geopolymer can result conversion of amorphous into crystalline in the geopolymer [45].

Li et al. [25] reported that slag addition reduces the pore structure by creating combined products of C-S-H and geopolymer [25]. These observations are confirmed by the work done by Xie et al. [22], Khater [41] and Dombrowski et al. [45]. Guo et al. [46] investigated the effect of calcium containing admixtures on class C based geopolymers.
They suggested that soluble calcium ions can be transformed to their hydroxides and bonded with geopolymer matrix in order to charge balance. Ca$^{2+}$ ions accelerate the setting time of the synthesis and rapid setting can initiate hardening before completing the reaction stages systematically. Temuujin et al. [44] showed that ambient/room temperature curing is more favourable for geopolymer with high calcium content. Khater [41] also observed when calcium containing alkali activated mixtures are cured at elevated temperature, the pore water of the binder evaporates quickly compared to at room temperature curing, in turn, the geopolymer is more porous. Addition to this, Xiaolu et al. [46] found that calcium solubility is decreased at elevated temperature.

**Amorphous content**

The substitution of Si ions with other ions and depolymerisation for charge balance are important parts of a geopolymerisation reaction and both mechanisms require disordered structures (amorphous behaviour). Chen-Tan et al. [12] examined the behaviour of amorphous phases in the precursor after alkali activation and found that amorphous phases dissolved comparatively faster than crystalline phases. These results are in agreement with those of Fernández-Jiménez et al. [47]. Álvarez-Ayuso et al. [48] stated that high amorphous content lead to geopolymer binder that are more stable and strong. If high contents of mullite and quartz (crystalline phases) are present in the fly ash, the reactivity of Al-Si bearing fraction decreases drastically [48]. Williams et al. [49] synthesised geopolymer binders using both bulk and amorphous chemical composition of precursor material (maintaining constant Si/Al, Na/Al and H/Si ratio for both cases) and showed that when binder was synthesised with amorphous chemical composition, has higher compressive strength. Figure 2-1 shows the effect of amorphous content of fly ash on the mechanical strength of the geopolymer binders. Most of the fly ashes with high amorphous content (<50%) show higher than 30 MPa compressive strength. It is important mention that the fly ashes (with high amorphous content) that showed lower compressive strength had higher particle size (>60μm). Oh et al. [50] used two types of class F fly ash in their geopolymer mixes and observed that fly ash containing higher content of amorphous phases and lower particle size lead to higher compressive strength.
Particle size of the material

Reduction of the particle size through a grinding process is an economical way to increase the reactivity of precursor material without changing the chemistry [51], [52]. Payá et al. [52] stated that grinding crushes the cenospheres and porous carbon particles which help to increase the specific gravity. Stutzman et al. [53] reported that there is a high probability to increase the glassy structure of the source material when the particle size is reduced below 10 $\mu$m. These results are in line with the results obtained by Kumar and Kumar [51]. Kiattikomol et al. [54] reported that particle size fineness increases workability of the alkali activated mixtures. Furthermore, the water demand is comparatively lower in the mixtures with fine particles. The above observations were due to the reduction in porosity in the fly ash and increase of surface area in the finer particles. These results are in agreement with Li et al. [11]. Kumar et al. [51] measured the heat flow using calorimetry technique during geopolymer reaction process, and found that heat flow is higher in the geopolymers containing fine particles. Marjanović et al. [55] reported that reducing the particle size of precursor material using mechanical activation helps to generate a homogeneous geopolymer gel reducing water demand. Chindraprasirt et al. [56] studied on the properties of ultra-fine class C fly ash based geopolymer binders and concluded that fineness of the fly ash affects the workability and the strength development of the binder.
2.2 Factors affecting geopolymer reaction

2.2.1 Alkali activators

Mixtures of NaOH and sodium silicate or KOH and potassium silicates, in liquid form, are the commonly used activator in geopolymer systems that leads to improved properties (Lee & Van Deventer [43] & [43], and Lee & Van Deventer, [57]). Since KOH is more expensive than NaOH, most studies have been done using a mixture of Na$_2$SiO$_3$ and NaOH as the activator solution.

Chindaprasirt et al. [58] showed that the ratio between sodium silicate and sodium hydroxide has to be in the range 0.6-1.0 to get high mechanical properties in the resulting geopolymer binder. Davidovits [59] showed that when the NaOH concentration in the activator is below 5M the effect from the silicate is higher. Álvarez-Ayuso et al. [48] showed that when the NaOH concentration is higher, geopolymerisation can be achieved even without soluble silicate. Rangan et al. [60] proposed 0.2<Na$_2$O/SiO$_2$<0.28 and 15<H$_2$O/Na$_2$O<17.5 as the optimal oxide ratios in the activator solution in order to gain improved performance in geopolymer concrete. Provis et al. [61] stated that if the activator to binder mass ratio is in between 0.6 - 0.7 and activator has SiO$_2$/Na$_2$O ratio in the range 1 - 1.5, the resulting geopolymer binder gives better mechanical properties. However, Sindutha et al. [62] reported that very high soluble silicate content (SiO$_2$/M$_2$O>2, where M is alkali ions) can reduce the reactivity of the alkali activated mixes as the concentration of cyclic silicate species can inhibits the further condensation of aluminium ions.

Currently, common practice in geopolymer concrete research involves preparation of the activating solution by combining appropriate amounts of the two components (e.g. NaOH and sodium silicate) and allowing them to homogenise for 24 hours prior to being used for mixing of geopolymer concrete. It is argued that using dry powders and adding water does not allow for geopolymerisation reaction and the strength results may not be high as liquid based systems. However, use of geopolymer concrete for field application requires user friendly practices, and incorporation of solid activator rather than premixed solutions would be advantageous. Ismail et al. [63] used solid alkali activators in their research work but the activator was first dissolved before adding into fly ash and slag blend. Guerrieri et al. [64] also used solid sodium metasilicate activator in their work. Again, the authors first made an alkali solution and did not add into
geopolymer mix in solid form. Geopolymer concrete production using only solid source materials (including alkali activator) would create pathway towards producing large scale geopolymer concrete mixes without much practical difficulties.

### 2.2.2 Water content in the geopolymer

Fang et al. [65] stated that approximately 10.74% of added water in a geopolymer system is non-evaporable even at higher temperatures (105-1050°C). Zuhua et al. [66] found that this non-evaporable water content does not create any drying shrinkage but it helps to maintain the long term strength. Zuhua et al. [66] also reported that water acts as a reactant in geopolymer reaction. Moreover, they identified the role of water in the three stages of geopolymerisation where in the 1st stage high water based environment facilitate transferring of ions, the 2nd stage requires water for hydrolysis and 3rd stage releases water due to poly-condensation. The results are in line with [67]. Panias et al. [68] showed when the solid to liquid ratio in the binder is increased higher than 2.05g/ml, compressive strength of the binder starts to decrease. The authors also found that when the water content of the binder is very low, the compressive strength of geopolymer can be low due to casting defects (pouring difficulty due to low workability). Diaz et al. [19] showed that high alkaline liquid weakens the geopolymer binders due to high porous structure in the harden concrete.

### 2.2.3 Curing regimes

Sindutha et al. [62] reported that elevated temperature curing (30-75°C) helps to expand total pore volume and surface area which accelerates dissolution of precursor. They also observed that at lower temperature (below 30°C), binder is formed with precipitation of dissolved species instead of poly-condensation of silicate and aluminate. Kovalchuk et al. [69] reported that curing in covered moulds is more beneficial for strength development than dry curing and steam curing. Covered moulds stop water evaporation from geopolymer providing a water media to exchange silicon and aluminium ions within the synthesis. In the above study the specimen cured in sealed bags, achieved maximum strength of 102.1 MPa while, the dry cured specimen and steam cured specimen recorded 31.8 MPa and 71 MPa respectively.
Previous research has indicated several curing regimes for geopolymer. Perera et al. [70] reported that curing temperature should be maintained in between at 40-60°C temperature value to avoid cracks. In addition, Swanepoel et al. [71] found that combination of 60°C temperature and 48 hours curing time gives the optimum strength for the binder. Memon et al. [72] disclosed that samples cured at 70°C temperature have the maximum strength and stated that longer curing (more than 48hrs) is not beneficial to geopolymer. Thakur and Ghosh [73] stated that maximum strength is obtained when their geopolymer samples were cured at 85°C for 48 hours. Yunfen et al. [74] reported the effective curing temperature as 65°C. Bakharev [75] found that fly ash-based geopolymers benefit significantly from pre-curing storage at 23°C before heat curing at 75-95°C. A rest period of 24 hours increased the strength equivalent to one month of continuous curing at elevated temperature. Even though, heat curing is essential for setting of pure alumina-silicate based geopolymer (class F fly ash or metakaolin), calcium rich alumina-silicate source materials can be cured at room temperature (ambient curing).

Ismail et al. [63] researched on ambient cured class F fly ash and slag blended geopolymer concrete. The concrete samples show significantly higher compressive strength (65 MPa) compared to OPC concrete (60 MPa) in 90 days. Ismail et al. [63] also showed that ambient cured geopolymer concrete specimens have lower permeability. Nath and Saker [76] blended class F fly ash and OPC to achieve ambient cured geopolymer concrete. The authors reported that the concrete shows 40-45 MPa compressive strength after 28 days. Guo et al. [77] showed that compressive strength of geopolymer cured at room temperature increases with the slag content in the mix. Reaction mechanisms of fly ash and slag blended geopolymer systems are discussed in chapter 4, chapter 5 and chapter 6.

2.3 Properties of geopolymer binders

2.3.1 Properties of fresh geopolymer binders

Geopolymer concrete produced with low water to binder ratio can be very stiff and would not have the increased flow required for better workability and ease of placement. A number of super plasticisers, water reducer and set retarders have been used in geopolymer systems to increase workability with varying extents of success [78]. Previously it was reported that traditional (designed for OPC) super plasticizers,
setting accelerators and setting retarders are not affective in adjusting the workability and setting of geopolymer systems [79]. Kong and Sanjayan [80] studied mixes with 8.4 kg of fly ash, 2 kg of water glass (modulus SiO$_2$/Na$_2$O=2) and 0.8 kg of KOH (7M). They showed that the improvement of workability due to the use of super-plasticiser (Glenium 27 at 3% by mass of fly ash; or Rheobuild 1000 at 1% by mass of fly ash), was marginal while it caused significant strength reduction (the more the worse).

However, few alternative methods have been tried to change the fresh properties of geopolymers. Lee et al. [81] tried phosphoric acid to retard the setting of fly ash and slag blended geopolymers with liquid sodium hydroxide and sodium silicate solutions. They concluded that the acid did not significantly change the initial setting time of the binder. However, they observed that adjusting alkalinity and modulus (SiO$_2$/Na$_2$O mass ratio) of the liquid activator solution can change the setting of geopolymers. These observations were in agreement with the results [82]. Balczár et al. [83] also stated that increasing soluble silica in the geopolymer systems has a higher impact on setting than increasing the alkali contents. The above studies were carried out for liquid alkali activators hence they are not directly relevant for solid activator based geopolymers. Ravikumar et al. [84] used sodium silicate (D-grade) and sodium hydroxide both in powder form as alkali activators in their slag binders. The authors stated that, fresh slag mixes containing powder activators shows quick setting (with an initial setting below 30 minutes and a final setting below 60 minutes). Nath et al. [82] also observed that the setting time and workability of the binder reduced significantly when the GGBS content was increased in the geopolymer binder, which was in agreement with other studies [81, 85, 86]. This shows that slag reduces the setting of geopolymer binder but due to the effect of slag on the mechanical properties, slag alone is not adequate to control the setting characteristics of geopolymer.

### 2.3.2 Properties of harden geopolymer binders

**Compressive strength and flexural strength of geopolymer concrete**

Engineering properties of geopolymers varies according to factors including source materials, alkali activator type and alkali activator content, curing parameters, water content and mixing parameters. Research has indicated that, geopolymer concrete can have comparable mechanical properties to those achieved by OPC binders. Diaz et al. [19] used a variety of class F and class C fly ashes to prepare geopolymer concrete.
Their results showed that class C fly ash based geopolymers achieved compressive strengths in the range 50-80 MPa while the compressive strength achieved by class F fly ash based geopolymer was 45-50 MPa (except one group of class F fly ash which has lower than 20 MPa strength). Hardjito et al. [87] reported that 100% Australian class F fly ash based geopolymer concrete can have compressive strength similar or slightly higher than that of OPC concrete. Sofi et al. [88] prepared geopolymer concrete using four types of Australian class F fly ashes and slag which achieved compressive strengths around 45-60 MPa. Geopolymers with higher alkali content, higher curing temperature and low water content can result in high strength concrete (80MPa or more). The maximum compressive strength of geopolymer binders is achieved when samples are cured at elevated temperature [89].

Previously research has reported that compressive strength of geopolymer concrete containing calcium rich source materials cured at ambient temperature is comparable with elevated temperature cured fly ash geopolymer. Ismail et al. [63] showed that addition of slag into geopolymer mix enhanced mechanical strength significantly at ambient temperature. There geopolymer concretes prepared with 50/50 fly ash/slag blends gained 45 MPa in 28 day while reaching 65 MPa in 90 days. These results are in agreement with the work done by Guerrieri and Sanjayan [90]. Deb et al. [91] reported a 28 day compressive strength of around 51 MPa for geopolymer systems with 80/20 fly ash/slag at ambient curing temperature. The above experiments were only conducted for geopolymer concrete specimens that are less than one year old.

Flexural strength of concrete is an important parameter to evaluate which relate the behaviour of structures under service load. The flexure strength of geopolymer concrete specimens with higher compressive strength varied in the range 4-6 MPa. Sofi et al. [88] reported that the flexural capacity of geopolymer concrete is higher than OPC concrete. Geopolymer concrete prepared by Diaz et al. [19] showed flexural strengths around 10.5% of compressive strength which is slightly higher than that of OPC concrete.

**Stress-strain behaviour**

Stress-strain behaviour of a concrete provides insight into its ability to ensure adequate degree of safety and serviceability in structural applications. Hardjito [92] studied
stress-strain behaviour of elevated temperature cured pure class F fly ash based geopolymers with compressive strength in the range of 44-89 MPa. They found that the modulus of elasticity of geopolymers was similar to the value obtained for OPC concrete in the same strength range i.e. 23-30.8 GPa. These results were recently confirmed by Yost et al. [93]. Diaz et al. [19] prepared geopolymer concrete using several class F and class C fly ash types and the measured modulus of elasticity were similar to OPC concrete. There are many techniques proposed in literature that can be used to predict the modulus of elasticity of a concrete using the compressive strength values and other parameters. As these techniques are designed for OPC based concrete and they can be used to evaluate how close the results are to that of OPC based concrete. Fernández-Jiménez et al. [94] and Sofi et al. [88] reported geopolymer concrete showed lower modulus of elasticity than predicted values from the existing equations from AS 3600 [95]. Similarly, Lee and Lee [96] reported geopolymer concrete synthesised using fly ash and slag had lower modulus of elasticity than the predicted values from ACI 318 [97]. Yang et al. [98] researched on stress-strain behaviour of alkali-activated slag concrete. They also found that the modulus of elasticity of slag based geopolymer is lower than the values predicted with standards. Douglas et al. [99] reported that elastic modulus of alkali activated slag concrete is increased with age (28 days to 90 days).

**Drying shrinkage**

Shrinkage of concrete can occur due to drying of concrete or chemical reorganization of the structure. Shrinkage increases the internal tensile stresses of concrete which leads to concrete cracking and shrinkage warping [100]. Understanding of volume change due to shrinkage in concrete is highly important in designing concrete structures with adequate degree of serviceability. Shrinkage of OPC concrete is known to depend on the various factors including mix proportions, water to cement ratio, mixing and curing regimes and humidity of the environment.

While it is still not very clear how different feedstock affect the drying shrinkage of geopolymers, a geopolymer concrete can be subjected to high drying shrinkage in absence of appropriate curing, due to exposure to drying environment in early stage and high water content [101]. Kukko and Mannonen [102] reported that alkali activated blast furnace slag has 10% less shrinkage compared to OPC concrete. Furthermore, they
stated that high water to binder ratio results in high shrinkage of the concrete. Neto et al. [103] activated blast furnace slag with sodium silicate solutions at varying SiO₂ and Na₂O composition. They concluded that increase of sodium silicate in the binder results in higher shrinkage. Furthermore, the same authors stated that autogenous shrinkage is higher in alkali activated slag mortar compared to the drying shrinkage. Duglous et al. [104] and Cincotto et al. [105] observed that drying shrinkage increases with alkali activator content in slag based geopolymer. They stated that increase amount of activator causes an increase in C-S-H volume and this decrease the porosity at latter stages. Collins and Sanjayan [106] investigated the shrinkage of alkali activated slag compared to OPC and found that alkali activated slag has higher shrinkage. Moreover, they concluded that the mass loss does not correlate with the shrinkage values for slag based binders.

Shrinkage of alkali activated fly ash and slag blended geopolymer were studied by Yong [107]. The author prepared geopolymer concrete using sodium silicate and 60/40 fly ash/slag blend and reported 6000 μstrain drying shrinkage after 6 months. The same author observed that the drying shrinkage of geopolymer binder increases with the water content. The above observation is in line with other study which is mainly caused by increase of porosity [108]. In the same study, Yong [107] found that drying shrinkage depends on the alkali activator type used in the binder. The shrinkage values observed in the above studies were higher than OPC concrete. Domroksi et al. [45] reported that addition of high amount of calcium content result in a significant increase of shrinkage and cracking which ultimately leads to a weaker structure. Deb et al. [109] showed that fly ash/slag blended geopolymer concrete has similar drying shrinkage value in 180 days compared to OPC concrete. They showed that drying shrinkage of geopolymer concrete can vary slightly according to the alkali activator and precursor material used.

**Abrasion resistance**

Cyclic mechanical action (or abrasion of concrete) that takes place over a long period of time is a cause of concrete degradation. Abrasion removes the surface layer of concrete, and exposes the inner part of the structure to the environment. This action can accelerate other durability problems like corrosion and sulphate attacks. Abrasion of concrete pavers has shown to be influenced by factors like concrete compressive strength, binder
content and type, aggregate characteristics, curing, surface finishing and bond between aggregate and cement paste [110].

Several studies have been conducted on abrasion of OPC and blended cement based concrete. Sadegzadeh et al. [111] showed that percentage of permeable voids in the surface layer of concrete has significant influence on the abrasion resistance. Atiş [112] researched on abrasion of high volume fly ash based concrete. The author stated that concrete contained fly ash showed higher abrasion than OPC concrete. Naik et al. [113] studied about abrasion resistance of class C fly ash blended cement based concrete. They concluded that abrasion resistance of pure OPC based concrete is high relative to the blended cement based concrete. In another study, Naik et al. [114] reported that up to 40% inclusion of fly ash in concrete has no adverse influence on the abrasion resistance. The authors reported that abrasion resistance was primarily controlled by the compressive strength of concrete.

Yen et al. [110] reported that inclusion of less than 15% of class F fly in to OPC does not have any adverse effects in terms of abrasion resistance. However, increasing the class F fly percentages beyond 15% decreases the resistance to abrasion in resulting concrete. Alaa et al. [115] reported that when OPC is blended with granulated blast furnace slag, the concrete has lower resistance to abrasion compared to pure OPC concrete.

Even though, abrasion resistance of OPC and blended cement based concrete has been extensively researched, abrasion resistance of geopolymer concrete has only been covered in [116]. Ramujee et al. [116] analysed the abrasion resistance of pure fly ash based geopolymer concrete and found that geopolymer concrete has better abrasion resistance compared to OPC concrete. However, they used elevated temperature (60°C) to cure geopolymer concrete and the quality of the surface used in the analysis was not reported.

2.4 Durability of geopolymers

While geopolymer bases systems can achieve initial advance mechanical properties, performance of geopolymer concrete can decay mainly due to carbonation, chloride penetration, sulphate attack and alkali aggregate reaction [117]. This section reviews
various types of durability problems encountered by concrete and the work done in identifying the durability properties of geopolymer systems.

2.4.1 Sulphate attack

Sulphate contaminated water or aggregates can cause sulphate attack in concrete. Sulphate attack on concrete form expansive compounds, e.g. gypsum (CaSO$_4$·2H$_2$O), ettringite (CaO·Al$_2$O$_3$·3CaSO$_4$·32H$_2$O) and thaumasite (Ca$_3$Si(OH)$_6$(CO$_3$)(SO$_4$)·12H$_2$O), between cement hydration products (the calcium silicate hydrates, or C-S-H phases) and the sulphate ions. In the process the cement hydration products would lose calcium and silicate ions, which changes the microstructure of cement paste leading to decay the mechanical performance of concrete [117]. Addition to this, highly expansive products can induce internal pressure to create concrete cracking. Wallah et al. [118] and Bakharev [14] analysed 100% fly ash based geopolymer concrete and identified that they show good sulphate resistance. Bakharev et al. [119] immersed alkali activated slag geopolymer samples in magnesium sulphate and sodium sulphate solutions separately. They observed cracks in the specimens which were intact with magnesium sulphate and samples immersed in sodium sulphate solution did not have any visible cracks. However, they found that geopolymer concrete performed well compared to OPC concrete.

Ariffin et al. [120] prepared geopolymers using pulverized fuel ash and palm oil fuel ash blends and samples were immersed in 2% Na$_2$SO$_4$ solution for 18 months. Geopolymers showed a mass loss about 8% after 18 months while OPC based binders showed a mass loss about 20% during the same period. The final geopolymer had about 35% compressive strength reduction (of the initial value) compared to 65% compressive strength found in OPC based binder after immersion. The authors stated that C-S-H phases in OPC binder can be attacked by sulphate ions and gypsum can be formed. On the other hand, since geopolymers have N-A-S-H as major phases, the structure of binder is not affected by sulphate ions. Dung et al. [121] showed that slag and fly ash blended geopolymers have better performance with respect to sulphate attack. The authors stated that after 143 days, geopolymer specimen immersed 5% Na$_2$SO$_4$ solution had strength loss between 5% and 15% respectively. The strength reduction is due to expansion of C$_6$AS$_3$H$_3$ and formation of gypsum. Komljenović, et al. [122] compared sulphate resistance of alkali activated slag to OPC based binder. Both samples were
immersed in a 5% \( \text{Na}_2\text{SO}_4 \). They stated that after 90 days of immersion period slag samples shows very low strength reduction compared to OPC. Ismail et al. [123] produced geopolymer binders using fly ash and slag blends and investigated the resistance to sulphate attack. The samples were exposed to \( \text{MgSO}_4 \) and \( \text{Na}_2\text{SO}_4 \) solution for three months. They observed magnesium sulphate is more aggressive environment compared to \( \text{Na}_2\text{SO}_4 \). Furthermore, they concluded that Mg can attack phase like C-S-H and C/N-A-S-H and decay the mechanical properties of the binders.

2.4.2 Alkali aggregate reaction (AAR)

Major structures have suffered due to AAR reducing their service life or requiring large repair costs [124-126]. One approach to reduce AAR is the use of non-reactive aggregate in the concrete. However, this method is not always possible due to practical difficulties in acquiring non-reactive aggregates locally.

In previous studies, It has already been identified that AAR expansion can be reduced using supplementary cementitious materials like low calcium fly ashes [125]. This is due to factors such as reduction in alkalinity of pore solution and lower availability of calcium in the binder [127]. Geopolymer has a silica based polymer structure which has shown superior durability compared to OPC. It has less CaO and higher Na\(_2\)O compared to OPC. Previous studies showed that the pH value of pore solution is above 11.5; which is adequate to attack reactive silica phases in aggregate [128]. However, AAR formation in geopolymer concrete is different from that of OPC concrete due to crossed link SiO\(_4\) and AlO\(_4\) in geopolymer matrix compared to C-S-H in OPC. Therefore, it is worthwhile to identify the susceptibility geopolymer binder to AAR expansion. Geopolymer binder which is formed after a series of chemical reactions between silicon, aluminum and alkali hydroxides does not have hydrated phases or free calcium, which is an important factor in the expansion problems. Instead geopolymer contains three dimensional silicon polymer networks which can resist most of the above durability issues of OPC concrete.

Davidovits [129] stated that geopolymer based mortar bars which contained high alkali content (Na\(_2\)O= 9.2%) have shown less expansion level compared to Portland cement binder based mortar bars. Kupwade-Patil and Allouche [130] reported that, mortar bars of alkali activated fly ash did not create any expansive gel due to absence of calcium.
Although, they did not provide initial curing condition used in their study, it is well known that 100% class F fly ash based geopolymer needs to be cured at elevated temperature (over 23°C) [75]. García- Lodeiro et al. [127] also compared alkali aggregate reaction of alkali activated 100% class F fly ash binder with Portland cement binder using accelerated mortar bar method (1M NaOH, 80°C). They reported that fly ash based geopolymer mortars showed less expansion compared to OPC mortars due to AAR. However, they cured samples initially at elevated temperature (85°C). More recently, Pouhet et al. [131] researched on AAR expansion of metakolin based geopolymer in the presence of reactive sand types. Expansion measurements after elevated curing are not ideal as expansion can occur before the zero measurement due to acceleration of AAR reaction at elevated temperature.

Although some aspects of AAR in class F fly ash based geopolymer has been studied so far, AAR in geopolymer mortars or concrete formulated with calcium rich material (i.e slag) and other alumino-silicate material has not been fully investigated. Bakharev et al. [132] and Puertas et al. [133], reported that concrete made with 100% alkali activated slag can show larger expansions than OPC concrete. However, addition of a calcium rich source into geopolymer systems is necessary as it enhances the setting behavior and mechanical properties of geopolymers [134]. Ground granulated blast furnace slag is mostly used as the calcium source in geopolymer systems due to its high reactivity in alkaline environment. The reaction product of slag contains calcium silicate hydrate (C-S-H) as well as geopolymer network. Despite the fact that slag improves the engineering properties of geopolymer binder excess Ca in geopolymer system can create phases like portlandite Ca(OH)₂ which may facilitate AAR. Fly ash and slag blended geopolymer binders contain less Ca, but their AAR susceptibility has not been thoroughly studied in the past.

2.4.3 Carbonation

Carbon dioxide in the atmosphere can diffuse into concrete through the permeable voids leading to reduction of pH in concrete pore water. Corrosion in the embedded reinforcement is initiated when the pH of concrete pore water is reduced below eight [117]. It is important to understand the carbonation of geopolymer concrete containing different binder compositions.
Bakharev [135] studied the resistance for the carbonation in alkali activated slag based geopolymer and OPC binder. They found that alkali activated slag has less resistance to carbonation and the compressive strength of the concrete decays when exposed to carbonating environment. They also mentioned that alkali activated slag has comparably lower Ca content (compared to OPC) and decomposition of CaCO₃ is lower. This may have led to higher porosity which results in high carbon dioxide diffusion into the binder. Ul Haq et al. [136] explored the effect of internal carbonates in fly ash based systems on geopolymer network formation and mechanical properties. They blended sodium bicarbonate with the geopolymer source materials. Authors observed faster geopolymer reaction in geopolymer with NaHCO₃ and they stated that CO₂ formation due to decomposition of sodium carbonate help leaching of Si and Al ions from precursor leading to higher reaction rate. However, addition of NaHCO₃ more than 5% affects negatively decaying mechanical properties of geopolymer binders. Badar et al. [137] used fly ash based geopolymer binders and the samples were exposed to 5% CO₂ environment. They observed a higher reduction of pH in geopolymer samples made using fly ash containing significant level of CaO (12.9%) compared to other geopolymers with lower CaO content. The researchers also measured splitting tensile strength in both carbonated samples and control samples. After 450 days of CO₂ exposure, geopolymer samples with high CaO level reduced the strength by about 35% compared to 3% and 17% strength reduction observed in other low CaO based geopolymers. Moreover, they observed carbonated high calcium fly ash based geopolymer had total porosity about 28% and this value was double the value that obtained for low calcium fly ash based systems.

Bernal et al. [138] compared the performance of alkali activated slag concrete and OPC concrete with binder contents of 300, 400 and 500 kg/m³ and found that, regardless of the binder content, the activated slag concrete performed similar or better than the corresponding OPC concrete with respect to strength, water absorption, permeability and porosity. However, the carbonation resistance of the activated slag concrete was inferior to the OPC concrete. Bernal et al. [139] investigated the pore solution chemistry of alkali activated binders and found different behaviours under normal carbonation and accelerated carbonation. They found that under normal exposure to the atmosphere, the pore solution develops sodium carbonate develops, whereas under accelerated curing
sodium bicarbonate is developed rapidly. Therefore, they concluded that the predicted carbonation time would be shorter than it would be under normal exposure condition.

### 2.4.4 Corrosion due to chloride ingestion

Corrosion is one of the main durability problems in the concrete structures. However, only a few studies have been conducted on corrosion activity in embedded rebar in geopolymer concrete.

Corrosion due to chloride ingestion is associated with chloride transport rate into concrete. Ganesan et al. [140] reported that chloride diffusion for fly ash based geopolymer and OPC based binder is almost the same. Authors used AgNO₃ spraying to identify the depth of chloride penetration (ASTM C1556 [141]). However, according to the study of Olivia et al. [142], the rate of chloride penetration in 100% fly ash based geopolymer concrete is higher than that of OPC concrete. More recently, Ma et al. [143] found that slag based geopolymer concrete has lower chloride diffusion coefficient compared to OPC concrete. And they suggested that alkali activated slag has denser pore structure compared to OPC binder, in turn; it reduces the rate of chloride ingression. In the same study, the authors found that the corrosion rate of rebar inside alkali activated slag is not significantly lower than that of the rebar in OPC.

Malolepszy and Deja [144] compared the corrosion activity of steel embedded in OPC mortar to alkali-activated slag mortar, using a variety of techniques. They found that there was no difference between the two systems up to 336 days. However, they recommended that long-term studies be undertaken to ascertain whether the situation would remain the same. Pacheco-Torgal et al. [145] reviewed the various durability-related issues of geopolymers, including steel corrosion, AAR, acid resistance and freezing/thawing. Some of the issues, such as acid resistance clearly depend on the composition of the geopolymer, and whether they are Al-Si rich or calcium rich. However, resistance to corrosion also depends on the microstructure and the environment. They state that such issues still remain to be resolved. Reddy et al. [146] evaluated the durability characteristics of low calcium, fly ash based geopolymer concrete subjected to aggressive marine environment. They tested a series of geopolymer concrete beams, containing fly ash activated with 8M and 14M concentrations of NaOH and SiO₂/Na₂O solutions, and centrally reinforced with 1/2"Ø
rebar, for accelerated corrosion exposure, with wet and dry cycling in artificial seawater together with induced corrosion current. The specimens were monitored for sudden rise in the current intensity due to specimen cracking, which was considered a durability issue. The test results indicated that the geopolymer concrete had excellent resistance to chloride-induced corrosion. Time taken for corrosion cracking was longer for geopolymer concrete compared to OPC concrete. Miranda et al. [147] observed that the pure fly ash based geopolymer mix containing 2% chloride, steel does not have protective passive layer showing similar corrosion behaviour to OPC concrete. More recently, Monticelli et al. [148] reported that fly ash based geopolymer concrete has slightly better resistance for corrosion compared to OPC. Moreover, they stated that embedded rebar in geopolymer concrete had surface layer consists of akaganeite which lead to non-uniform corrosion. Bastidas et al. [149] research work is in agreement with the later work. Additionally, the authors observed that in the presence of 0.2 and 0.4% CaCl₂, the embedded rebar had passive film layer. Kriven et al. [150] used metakaoline based geopolymer coating in rebar and identified that rebar corrosion was reduced greatly compared un-coated rebar.

2.5 Behaviour of large scale reinforced geopolymer concrete elements

There are very few studies in literature on identifying the characteristics of geopolymer based structural elements. Sumajouw and Rangan [151] studied the behaviour of class F fly ash based geopolymer concrete beams and columns with different tensile reinforcement ratios. They identified that the load carrying capacity and failure modes of under-reinforced geopolymer concrete beams are in line with that of the OPC beams. More recently, Yost et al. [152] studied class F fly ash based geopolymer concrete beams with three different reinforcement designs (under-reinforcement, over reinforcement and shear critical). Authors reported that under flexure failure mode, geopolymer concrete beams are more brittle than their OPC counterparts. Yost et al. [152] also observed that maximum load of the geopolymer beams dropped quickly at failure resulting in sudden and complete collapse of the compression zone in the inner span which was different to OPC. However, they did not provide an explanation of this sudden failure in geopolymer beams. Cross et al. [153] studied the structural behaviour of class C fly ash based geopolymer concrete beams. Authors stated that crack propagations, failure modes and ductility were analogous with OPC beams. The post-
yield deflection/ductility of geopolymer concrete has not been discussed in the previous work.

2.2. References for chapter 2


[20] C. Li, H. Sun, L. Li, A review: The comparison between alkali-activated slag (Si +Ca) and metakaolin (Si + Al) cements, Cement and Concrete Research, 40 (2010) 1341-1349.


[92] D. Hardjito, Studies on fly ash based geopolymer concrete, Department of civil Engineering, Curtin University of Technology, 2005.


3. Fly ashes in Australia for geopolymer production

3.1 Introduction

Precursor material for geopolymer can be a by-product from industrial processes such as coal fly ash, slag, red mud and rice husk ash (RHA) or a geological resource like metakaoline. According to Heidrich [1] study, coal fly ash production in Australia is 12 million tonnes/year, of which 5.5 million tonnes were utilised effectively. Majority of coal fly ash produced in Australia is from black coal which is classified as ASTM class F type. Despite the fact that, class F fly ashes have been identified as the preferred source material for geopolymer binders, the fly is not fully utilized due to limited knowledge of fly ash characteristics [2, 3]. Significant level of brown coal fly ash (1.13 million tons annually) is also produced in the state of Victoria, Australia as a result of burning brown coal (younger sub-bituminous coal sources). Fly ash produced from Brown coal has different chemical and physical characteristics to that of class F fly ash. Therefore, current usage of this material as a supplementary cementitious material is restricted resulting in high amount of fly ash deposits with environment consequences [4].

The most important characteristics of coal fly ash that influence the mechanical properties of geopolymers are particle size distribution of fly ash, Al₂O₃, SiO₂ and amorphous content of fly ash. Rickard et al. [5] analysed five Australian fly ashes and showed that geopolymer amorphous SiO₂/Al₂O₃ ratio is the most important factor where when the ratio is greater than 5 the strength of geopolymer is high. Williams and Van Riessen [6] reported that Australian class F fly ash geopolymers result in better strength properties when synthesised based on the fly ash’s amorphous silica content of fly ash. More recently, Gunasekara et al. [7] used Australian class F fly ashes and showed that zeta potential of fly ash particle is the factor that controls the reactivity in geopolymerisation. Even though these studies give some knowledge about the Australian class F fly ash, more studies are needed to understand characteristics of the fly ashes in Australia and their suitability in geopolymers.

Above mentioned studies are on Australian class F fly ash based geopolymers and only limited work has been done on geopolymer binder synthesis using brown coal fly ash [8]. Bankowski et al. [9] investigated the use of brown coal fly ash geopolymer binders as containment matrices to reduce the leaching of heavy metals in land fill applications.
Metakaolin was incorporated in their geopolymer synthesis because the brown coal fly ash has limited amounts of reactive aluminium and silicon. This study however, did not provide data on engineering properties of brown coal fly ash based geopolymer binders. The authors stated that utilisation of 100% Victoria, Australia brown coal fly ash in geopolymer systems remained unsatisfactory. More recently, Law et al. [10] prepared geopolymer mortars based on Australian brown coal dry precipitator fly ash. Their binders attained compressive strengths of 50 MPa in 7 days demonstrating potential for use of this material in geopolymer systems. However, geopolymer binders in the previous study were produced using high alkaline systems (15 M) and high curing temperatures (90°C), representing processing conditions over and above general concreting practise. The researchers also did not analyse the phase evolution and reaction mechanisms of brown coal fly ash based geopolymers deemed essential to understanding key requirements for binder mix design for better mechanical properties.

This chapter is segmented into two key parts. In the first part the author investigate the mineralogical and chemical suitability of four types of brown coal fly ashes (class C fly ash), for geopolymer matrix formation. Based on the results the author formulated several geopolymer binders and evaluated their mechanical properties. In the second part of the chapter, six types of Australian class F fly ash are analysed in order to identify the relationship between the fly ash characteristics and properties of geopolymers synthesised with the fly ash.

### 3.2 Analysis of brown coal fly ash based geopolymers

#### 3.2.1 Materials and methods

**Materials and Methods**

Brown coal fly ash types used in this work were sourced from, the La-Trobe Valley, Victoria Australia. Loy Yang, Hazelwood and Yallourn were collected directly from the precipitators in dry condition while Loy Yang lagoon fly ash was collected from the ash ponds in a wet state. Class F fly ash was obtained from Gladstone power station Queensland, Australia. Ground granulated blast furnace slag was supplied by Independent Cement Australia Pty Ltd. Table 3-1 provides detailed chemical composition and source origin of each fly ash type. The notations are used thereafter in this chapter for the fly ashes and slag is as shown in Table 3-1 (example: Loy Yang Lagoon ash-LYLG).
Table 3-1: Bulk chemical composition of source materials

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Loy Yang dry precipitator ash (%)</th>
<th>Loy Yang lagoon ash (%)</th>
<th>Hazelwood dry precipitator ash (%)</th>
<th>Yallourn dry precipitator ash (%)</th>
<th>Granulated blast furnace slag (%)</th>
<th>Class F fly ash (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>48.90</td>
<td>41.51</td>
<td>2.18</td>
<td>0.81</td>
<td>32.38</td>
<td>51.88</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>15.16</td>
<td>31.61</td>
<td>1.21</td>
<td>1.27</td>
<td>12.24</td>
<td>25.92</td>
</tr>
<tr>
<td>CaO</td>
<td>2.44</td>
<td>2.12</td>
<td>25.01</td>
<td>6.81</td>
<td>44.04</td>
<td>4.35</td>
</tr>
<tr>
<td>MgO</td>
<td>5.38</td>
<td>7.27</td>
<td>20.26</td>
<td>19.53</td>
<td>5.13</td>
<td>1.54</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>9.68</td>
<td>5.87</td>
<td>13.30</td>
<td>39.35</td>
<td>0.49</td>
<td>12.66</td>
</tr>
<tr>
<td>MnO</td>
<td>0.05</td>
<td>0.04</td>
<td>0.34</td>
<td>0.45</td>
<td>0.37</td>
<td>0.15</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.41</td>
<td>0.56</td>
<td>0.34</td>
<td>0.72</td>
<td>0.33</td>
<td>0.71</td>
</tr>
<tr>
<td>Na₂O</td>
<td>4.86</td>
<td>3.19</td>
<td>4.08</td>
<td>9.37</td>
<td>0.22</td>
<td>0.78</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.58</td>
<td>2.12</td>
<td>0.17</td>
<td>0.06</td>
<td>0.51</td>
<td>1.30</td>
</tr>
<tr>
<td>SO₃</td>
<td>7.48</td>
<td>0.46</td>
<td>13.37</td>
<td>19.82</td>
<td>4.21</td>
<td>0.24</td>
</tr>
<tr>
<td>LOI</td>
<td>4.04</td>
<td>5.05</td>
<td>19.76</td>
<td>1.81</td>
<td>0.08</td>
<td>0.55</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

A commercial D grade sodium silicate solution (29.4% SiO₂ and 14.7% Na₂O by weight) from PQ Australia and 8M sodium hydroxide solution was used throughout this study. The mass ratio between Na₂SiO₃ and NaOH was kept constant at unity. NaOH and Na₂SiO₃ solutions are added separately into fly ash dry mix. Feedstock blending was employed in order to achieve target oxide compositions (SiO₂, Na₂O, CaO and Al₂O₃) and target oxide ratios (SiO₂ /Al₂O₃ (2.5-4.5 molar ratio) and Na₂O/Al₂O₃ (1.5-2.5 molar ratio)) by mixing brown coal fly ash with class F fly ash and slag according to blending formulations given in Table 3-2. The water content was calculated (i.e. the water in 8M NaOH concentrated solution has 73.8% water and D-grade sodium silicate solution has 55.5% water). The blends were mixed with alkali activator solutions in a small mortar mixer. It should be noted that LYLG ash was dried in an oven prior to synthesis in order to remove moisture.

Table 3-2: Mix proportions of the alkali-activated fly ash pastes blends

<table>
<thead>
<tr>
<th>Mix number</th>
<th>Brown coal fly ash (g)</th>
<th>Brown coal fly ash type</th>
<th>Class F fly ash (g)</th>
<th>Slag (g)</th>
<th>NaOH (8M) (g)</th>
<th>Na₂SiO₃ (g)</th>
<th>water to solid ratio (W/S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GP1</td>
<td>1000</td>
<td>LYDP</td>
<td>-</td>
<td>-</td>
<td>382</td>
<td>382</td>
<td>0.495</td>
</tr>
</tbody>
</table>
Alkali activated paste specimens prepared on equal flow basis were cast in 50 mm cube moulds. All specimens were cured for 24 hours at 60°C (100% RH) and kept thereafter in air tight containers under ambient condition (at 23°C temperature) before compressive strength tests in 7 days. The specimens which showed better compressive strength were prepared again and cured at 60°C for 8 hours (100% RH). The set of specimens were used to measure compressive strength up to 120 days. Compressive strength test was conducted using an ELE International Universal Tester, at a loading rate of 1.0 kN/s for the 50 mm cubes according to ASTM C109 [36].

**Analytical techniques**

Microstructural and chemical analyses were performed on raw materials or pastes samples through:

- The XRD analysis was carried out using a Bruker D8 Advance X-ray diffractometer. Scans were collected between 5-70° (2θ) with a step size of 0.02° and a scan rate of 5s per step. An internal standard (10%wt corundum, Al₂O₃) was added to allow quantitative analysis using Rietveld refinement. Phase identification was completed using Materials Data, Inc., Jade 9.3 software and Quantitative Rietveld analysis using Bruker Diffracplus Topas software.

- Particle size of the materials was obtained using Cilas laser diffraction particle analyser. The samples were prepared by dispersing 1-10g of fly ash in water.

- Isothermal calorimetric experiments were conducted using a TAM Air isothermal calorimeter, at a base temperature of 25 ± 0.02°C. Fresh pastes were mixed externally, weighed into an ampoule, and immediately placed in the

<p>| | | | | | |</p>
<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>GP2</td>
<td>1000</td>
<td>LYLG</td>
<td>-</td>
<td>-</td>
<td>600</td>
</tr>
<tr>
<td>GP3</td>
<td>1000</td>
<td>HZDP</td>
<td>-</td>
<td>-</td>
<td>400</td>
</tr>
<tr>
<td>GP4</td>
<td>1000</td>
<td>YLD</td>
<td>-</td>
<td>-</td>
<td>400</td>
</tr>
<tr>
<td>GP5</td>
<td>700</td>
<td>LYL</td>
<td>150</td>
<td>150</td>
<td>375</td>
</tr>
<tr>
<td>GP6</td>
<td>700</td>
<td>LYLG</td>
<td>150</td>
<td>150</td>
<td>550</td>
</tr>
<tr>
<td>GP7</td>
<td>700</td>
<td>LYLDP</td>
<td>100</td>
<td>200</td>
<td>350</td>
</tr>
<tr>
<td>GP8</td>
<td>700</td>
<td>LYL</td>
<td>100</td>
<td>200</td>
<td>550</td>
</tr>
<tr>
<td>GP9</td>
<td>600</td>
<td>LYLDP</td>
<td>200</td>
<td>200</td>
<td>350</td>
</tr>
<tr>
<td>GP10</td>
<td>600</td>
<td>LYLG</td>
<td>200</td>
<td>200</td>
<td>550</td>
</tr>
<tr>
<td>GP11</td>
<td>400</td>
<td>LYLDP</td>
<td>300</td>
<td>300</td>
<td>350</td>
</tr>
<tr>
<td>GP12</td>
<td>400</td>
<td>LYLG</td>
<td>300</td>
<td>300</td>
<td>414</td>
</tr>
<tr>
<td>GP13</td>
<td>400</td>
<td>HZDP</td>
<td>300</td>
<td>300</td>
<td>375</td>
</tr>
<tr>
<td>GP14</td>
<td>400</td>
<td>YLD</td>
<td>300</td>
<td>300</td>
<td>325</td>
</tr>
</tbody>
</table>
calorimeter, and the heat flow was recorded for the first 140 h of reaction. All values of heat release rate are normalised by total weight of paste.

- Environmental scanning electron microscopy (ESEM) with energy dispersive X-ray (EDX) analysis was carried out (at an accelerating voltage of 15 kV) using an FEI Quanta ESEM instrument. For this test, the paste samples were sectioned, and polished up to 1μm surface fineness using diamond paste.

3.2.2 Results and Discussion

Characterisation of the raw materials

X-ray diffraction analyses

The bulk chemical composition and reactive phases were quantified using X-ray fluorescence (XRF) and quantitative X-ray diffraction (XRD) techniques respectively. The chemical composition of the fly ashes is shown in Table 3-1 while Table 3-3 shows the mineralogical phases of the materials. Furthermore, Figure 3-1 shows x-ray diffraction pattern and crystalline phases of precursor materials used in this study. Comparison of Figure 3-1(a) and (b) shows that GFA and slag have significant humps at around 25 and 30 degrees respectively while brown coal fly ashes do not have that kind of hump in their diffraction patterns indicating that brown coal fly ashes have less amorphous content compared to GFA and slag. Moreover, Figure 3-1 shows that LYDP has significant mullite content which is absent in LYLG specimens. Additionally, gehlenite (Ca₂Al(AlSi)O₇), srebrodolskite (Ca₂FeO₅) and periclase (MgO) crystalline phases are observed in HZDP and YLDP. Even though, original LYDP has higher SO₃ content (7.48%) than LYLG (0.46%), thenardite (Na₂SO₄) crystalline phases which associate with sulphate ions are only observed in LYLG. SO₃ in LYDP may be in amorphous form which is not detected by XRD.

Table 3-3: Mineralogical phase percentages of source materials

<table>
<thead>
<tr>
<th>Phase Name</th>
<th>LYDP</th>
<th>LYLG</th>
<th>HZDP</th>
<th>YLDP</th>
<th>Slag</th>
<th>GFA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>8.56</td>
<td>7.97</td>
<td>3.54</td>
<td>-</td>
<td>-</td>
<td>12.98</td>
</tr>
<tr>
<td>Mullite</td>
<td>10.62</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>14.57</td>
</tr>
<tr>
<td>Calcite</td>
<td>-</td>
<td>3.23</td>
<td>-</td>
<td>-</td>
<td>6.22</td>
<td>-</td>
</tr>
<tr>
<td>Magnetite</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.82</td>
<td>-</td>
<td>1.88</td>
</tr>
<tr>
<td>Hematite</td>
<td>-</td>
<td>7.92</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.18</td>
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<tr>
<td>Anorthite</td>
<td>9.71</td>
<td>-</td>
<td>-</td>
<td>11.36</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Rutile</td>
<td>-</td>
<td>3.08</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Thenardite</td>
<td>-</td>
<td>4.35</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Srebrodolskite</td>
<td>-</td>
<td>-</td>
<td>14.47</td>
<td>6.36</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Gypsum</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7.42</td>
<td>-</td>
</tr>
<tr>
<td>Periclase</td>
<td>-</td>
<td>-</td>
<td>12.73</td>
<td>4.25</td>
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<td>-</td>
</tr>
<tr>
<td>Lime</td>
<td>-</td>
<td>-</td>
<td>2.18</td>
<td>-</td>
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<tr>
<td>Gehlenite</td>
<td>-</td>
<td>-</td>
<td>12.73</td>
<td>2.63</td>
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<tr>
<td>Amorphous</td>
<td>71.11</td>
<td>73.45</td>
<td>54.35</td>
<td>72.58</td>
<td>86.36</td>
<td>66.39</td>
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<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

(a)
Figure 3-1: X-ray diffraction analysis of raw materials (a) brown coal fly ashes (b) slag and GFA

**Particle size distribution**

Figure 3-2 shows the particle size distribution of fly ashes while Table 3-4 shows the summarized particle size distribution results. As seen in the Figure 3-2, 90% of particles of the brown coal fly ashes are less than 50 $\mu$m which makes it appropriate in the geopolymer feedstock. GFA has 30% particles less than 2 $\mu$m while LYDP and LYLG have corresponding percentage values are 20 and 10 respectively. LYLG was deposited in ash ponds for few months and fly ash particles can be broken into smaller particles down during in the ash pond. Chindaprasirt et al. [11] observed that fly ash based geopolymer binder is accelerated the setting when particle size of the fly ash is decreased. Variations in particle size lead to different reaction rates therefore the optimal particle size distribution remains an important parameter in overall reactivity of fly ashes for geopolymer synthesis [12].
Figure 3-2: Particle size distribution of fly ashes

Table 3-4: Particle size distribution (Passing percentage)

<table>
<thead>
<tr>
<th></th>
<th>90% (μm)</th>
<th>50% (μm)</th>
<th>10% (μm)</th>
<th>Mean (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LYDP</td>
<td>44.23</td>
<td>21.28</td>
<td>7.61</td>
<td>23.95</td>
</tr>
<tr>
<td>LYLG</td>
<td>33.64</td>
<td>14.15</td>
<td>4.24</td>
<td>16.92</td>
</tr>
<tr>
<td>HZDP</td>
<td>38.69</td>
<td>16.02</td>
<td>6.28</td>
<td>19.87</td>
</tr>
<tr>
<td>YLDP</td>
<td>18.23</td>
<td>10.23</td>
<td>3.45</td>
<td>10.63</td>
</tr>
<tr>
<td>GFA</td>
<td>24.40</td>
<td>5.54</td>
<td>1.10</td>
<td>9.32</td>
</tr>
</tbody>
</table>

Short term compressive strength of geopolymer fly ashes blends

Table 3-5 shows the amorphous SiO$_2$/Al$_2$O$_3$ and Na$_2$O/Al$_2$O$_3$ molar ratios in the blends of materials. The method used for calculating the reactive (or amorphous) molar content of source materials is described in the section 0. Ross et al. [6] used a similar method to calculate such ratios in their study.

Table 3-5 shows that 100% LYDP has high SiO$_2$/Al$_2$O$_3$ (10.4) and Na$_2$O/Al$_2$O$_3$ (4.1%) compared to the corresponding ratios of 100% LYLG fly ash (1.80 and 1.12). Additionally, GP5 and GP7 (LYDP blended geopolymer) mixes also have higher SiO$_2$/Al$_2$O$_3$ and Na$_2$O/Al$_2$O$_3$ molar ratios compared to their corresponding LYLG blends (GP6 and GP8). This is due to LYDP has lower aluminium content (15.36%) compared to aluminium in LYLG (31.61%). Additionally, YLDP has higher percentage of Fe$_2$O$_3$ content (39.35%) than Fe$_2$O$_3$ in other fly ashes used in this study. Influence of iron content in geopolymerisation was discussed in the work by Redmond et al. [13]. They
observed that fly ash particles with high iron content were remained largely unreacted. HZDP and YLDP have very low SiO₂ and Al₂O₃ content (less than 3% for each) making SiO₂ /Al₂O₃ ratio equal to zero. However, when HZDP and YLDP were blended with GFA and slag the oxide ratios were also changed thereby the seven day was increased compressive strength. Early age (i.e. 7day) compressive strength results of 100% brown coal fly ash geopolymer (GP1-GP4) given in Table 3-5 shows very low compressive strength (typically lower than 5MPa).

Table 3-5: Oxide ratios and seven day compressive strength of geopolymer binder pastes (Oxide ratios are calculated including alkali activator compositions).

<table>
<thead>
<tr>
<th>Mix No</th>
<th>Blend formulations</th>
<th>Amorphous SiO₂/Al₂O₃ molar ratio</th>
<th>Na₂O/Al₂O₃ molar ratio</th>
<th>H₂O molar</th>
<th>Average 7 day strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GP1</td>
<td>100% LYDP</td>
<td>10.40</td>
<td>4.06</td>
<td>27.5</td>
<td>4.0</td>
</tr>
<tr>
<td>GP2</td>
<td>100% LYLG</td>
<td>1.80</td>
<td>1.12</td>
<td>43.9</td>
<td>4.5</td>
</tr>
<tr>
<td>GP3</td>
<td>100% HZDP</td>
<td>0.01</td>
<td></td>
<td>28.8</td>
<td>3.5</td>
</tr>
<tr>
<td>GP4</td>
<td>100% YLDP</td>
<td>0.01</td>
<td></td>
<td>28.8</td>
<td>2.0</td>
</tr>
<tr>
<td>GP5</td>
<td>70%LYDP/15%SL/15%GFA</td>
<td>6.90</td>
<td>3.60</td>
<td>27.0</td>
<td>17.5</td>
</tr>
<tr>
<td>GP6</td>
<td>70%LYLG/15%SL/15%GFA</td>
<td>2.10</td>
<td>1.23</td>
<td>39.6</td>
<td>17.0</td>
</tr>
<tr>
<td>GP7</td>
<td>70%LYDP/10%SL/20%GFA</td>
<td>6.00</td>
<td>3.75</td>
<td>25.2</td>
<td>14.0</td>
</tr>
<tr>
<td>GP8</td>
<td>70%LYLG/10%SL/20%GFA</td>
<td>1.90</td>
<td>1.36</td>
<td>39.6</td>
<td>15.0</td>
</tr>
<tr>
<td>GP9</td>
<td>60%LYDP/20%SL/20%GFA</td>
<td>6.10</td>
<td>3.46</td>
<td>25.2</td>
<td>11.0</td>
</tr>
<tr>
<td>GP10</td>
<td>60%LYLG/20%SL/20%GFA</td>
<td>2.20</td>
<td>0.81</td>
<td>39.6</td>
<td>17.0</td>
</tr>
<tr>
<td>GP11</td>
<td>40%LYDP/30%SL/30%GFA</td>
<td>5.10</td>
<td>1.84</td>
<td>25.2</td>
<td>32.0</td>
</tr>
<tr>
<td>GP12</td>
<td>40%LYLG/30%SL/30%GFA</td>
<td>2.60</td>
<td>1.12</td>
<td>29.8</td>
<td>32.0</td>
</tr>
<tr>
<td>GP13</td>
<td>40%HZDP/30%SL/30%GFA</td>
<td>3.76</td>
<td>2.45</td>
<td>27.0</td>
<td>27.0</td>
</tr>
<tr>
<td>GP14</td>
<td>40%YLD/30%SL/30%GFA</td>
<td>3.76</td>
<td>2.12</td>
<td>23.4</td>
<td>32.5</td>
</tr>
</tbody>
</table>

As mentioned previously, GP 1 has very high SiO₂/Al₂O₃ ratio (10.40). De Silva et al. [14] stated that amorphous gel phases in Na₂O-SiO₂-Al₂O₃-H₂O geopolymer matrix systems with high SiO₂/Al₂O₃ (> 3.8) and Na₂O tend to convert to a crystalline phases easily, potentially leading to a decrease of mechanical strength. GP2 to GP4 has very low amorphous SiO₂/Al₂O₃ ratio (according to the XRD analysis) in turn the compressive strength values were also very low. Fletcher et al. [15] investigated metakaolin based geopolymer systems with different SiO₂/Al₂O₃ ratios ranging from 0.5 to 300. They observed that geopolymer binder phases with lower SiO₂/Al₂O₃ (< 2) ratio or high aluminium content showed a weak structure with several discrete compounds. This suggests lower SiO₂/Al₂O₃ (< 2) ratio may also be a plausible reason for observed low compressive strength. Even though, 100% YLDP (GP4) has the smallest particle
size among the four brown coal fly ash types, 100% YLDP samples have lowest compressive strength in seven days ~2 MPa, (100% LYDP has very low silica (0.81%) and aluminium content (1.27%) that are essential to geopolymer network formation). In addition, fly ash types HZDP (GP3) and YLDP (GP4) with high SO₃ and MgO content appear to adversely affect the geopolymerization reaction given that the presence of sulphate tends to reduce reaction rates while by favouring conversion of network structures into more crystalline analogues [4, 16].

100% brown coal fly ash and blended fly ash mixes consume high level of alkali activator solution compared to class F fly ash (pure class F fly ash (GFA) based geopolymer can be formulated using lower water content w/s = 0.2 (see section 0)). Mcphee et al. [4] reported that brown coal by products contain low volatile char from unburned wood particles. These particles of char can also absorb alkaline liquid during geopolymer process because of their high porosity [17]. Excessive alkali solution in geopolymer binders due to high water content can cause high porosity, drying shrinkage and later durability issues like alkali aggregate reactions [18]. Since the usage of 100% brown coal fly ash in geopolymer synthesis is unsatisfactory (low compressive strength), blending of brown coal fly ash with another alumina-silicate source material is required. When brown coal fly ash content is reduced in the geopolymers, the compressive strength of the geopolymer binders are significantly improved in particular mixes GP8, GP10 and GP12 (the compressive strengths are 15, 17 and 32 MPa, respectively). This may be due to high availability of Al, Si and Ca ions in the presence of slag and GFA which improves the reaction mechanism (the author later show that in these mixes brown coal fly ash particles participate in geopolymer reaction and does not merely act as a filler material). It was observed in Figure 3-1 that, slag and GFA have high amorphous (86 and 66% amorphous content respectively) content thereby Al, Si and Ca ions can be leached faster. Even though, GP6 and GP8 have the same LYLG content, the compressive strength of GP6 (17 MPa) was slightly higher than GP8 (14 MPa). It is worthwhile noting that, GP6 had 5% higher slag content than GP8. This shows that slag contributes to achieve high strength in early stage of the binder. LYDP blended geopolymer showed scattered strength pattern when more than 40% fly ash was used. GP5, GP7, GP9 and GP11 had compressive strength 17.5, 14.0, 11.0 and 32.0 MPa respectively. Among all binders, GP11 - GP14 achieved compressive strength which is higher than 25 MPa at seven days.
Not only 100% brown coal fly ash based geopolymers had lower strength gain but also the binders showed cracks when water was sprayed to the specimens. Figure 3-3(a) shows the decomposition of GP4 geopolymer samples after 2 hours in the water. Figure 3-3(b) illustrates the crystalline phases formed in the geopolymer (GP4) sample. XRD analysis revealed that, significant amount of sulphate related crystalline phases are formed in the geopolymer. Magnesium sulphate, sodium sulphate, magnesium sulphate hydrate and sodium sulphate hydrate are the main crystalline phases that formed in the binder. These phases can hinder the geopolymer formation and create durability problems like decomposition in high moist environment.

Figure 3-3: (a) GP4 deterioration after immersed in the water (b) XRD patterns of GP4 geopolymer binder

The results (Table 3-5) indicated that the maximum brown coal fly ash content that may be used in geopolymer synthesis is 40% to obtain compressive strength>25 MPa. Even though GP11 to GP14 achieved high compressive strength, GP13 and GP14 showed the cracks (Figure 3-4) in 7-days particularly when the samples were exposed to high moist environments. This type of deterioration is generally attributed the high SO$_3$ content, which appears to characterise in HZDP and YLDP. Brown coal fly ash systems typically have high Na$^{2+}$, SO$_4^{2-}$ and Mg$^{2+}$ contents which can produce NaSO$_4$ and MgSO$_4$ salt in geopolymer to form crystals that destroy the geopolymer bonds. In the presence of water, the reaction may be accelerated by dissolving the sodium/magnesium and sulphate followed by re-crystallisation. Criado et al. [16] observed than in the
presence of $\text{SO}_4^{2-}$ geopolymer gel tends to convert into crystalline phases. Moreover, they observed that sodium aluminate silicate hydrate formation (N-A-S-H) is retarded due to sulphate ions.

(a) GP13
(b) GP14
Figure 3-4: De-composition of GP13 and GP14 after water immersion

Calorimetric measurements

Figure 3-5(a) shows the heat generation during initial stage (0-120 mins) of the geopolymer reaction for mixes GP11 and GP12 (these two mixes showed the highest strength). Here the heat generation of GFA, slag geopolymers and OPC binders are also plotted for the comparison. The initial heat generation (first hour of the reaction) is mainly caused by dissolution and wetting of fly ash or slag particles [19]. It shows that, 100% slag binder generated the maximum heat during the dissolution stage, indicating high reactivity with alkali. The calorimetric curve of 100% slag has the maximum peak (18 MW/g) at about 30 minutes of time the peak corresponds for dissolution of slag particles. The corresponding dissolution curve for GFA binder peaked at (2 MW/g) during the reaction within approximately 15 minutes indicating less heat production during dissolution. Even though GP11, GP12 and GFA binder have the maximum heat peaks at the same time intervals during dissolution process, GP11 and GP12 showed high magnitude of heat flow. This shows that slag addition and high alkali content improve the dissolution of brown coal fly ash blends compared to GFA binder. OPC binder does not shown any peak during 0-120 mins time interval.

The amount of heat flow at maxima during dissolution process can be ordered as slag>GP12>GP11> GFA >OPC which can be due to two main factors. This shows that leaching of Al, Si and Ca ions in slag particles is higher than leaching in fly ash. The work done by Panagiotopoulou et al. [20] also showed that, in the presence of alkali, leaching ability of Al and Si ions in slag is higher than fly ash. It should be noted that
alkali liquid consumption in GP11 and GP12 was higher compared to slag and GFA, thereby, GP11 and GP12 syntheses contained high alkali (Na₂O) and soluble silica content. This high alkalinity may cause rapid leaching rates and, hence, higher heat flow is observed in GP11 and GP12 curves than slag.

Figure 3-5(b) shows the heat generation involved with dissolution and reaction product formation together (0-720 mins time interval). Slag, GP11 and GP12 samples again show high heat generation compared to GFA binder. While GP11 and GP12 indicate high heat production in within a shorter time period (main peak at 15 mins, secondary peak at 100mins) compared to slag binder (main peak at 30 mins, secondary peak at 150 mins). Portland cement based binder (OPC) was used in the experiment as a control and the calorimetric curve show that OPC hydration reaction is relatively slow compared to geopolymers. OPC showed the main peak (4MW/g) at about 120 mins reaction time and secondary peak at about 240 mins. Previous results show that alkali activated slag has low hydration activation energy compared OPC [21]. All this is consistent with Z.Yunsheng et al. [22] who reported C-S-H formation with low Ca/Si ratio could lead to low heat generation in alkali activated slag systems.

![Figure 3-5](image)

Figure 3-5: Calorimetric measurements for brown coal fly ash blended geopolymer binders (a) initial reaction (0-120 mins) (b) total reaction time (0-700mins)

**Long term compressive strength measurements**

Figure 3-6 shows the average compressive strength development of GP11 and GP12 geopolymers until 120 days. GP11 and GP12 reached up to 40 and 35 MPa compressive strength respectively in 120 days. However, both binders did not show significant improvement in the compressive strength after 28 days. The reason could be, the
presence of slag, for which the reaction process completes in very early stage (in 28 days) at elevated temperature [3]. In 56 days, there is slight reduction in strength (about 1MPa). However, strength difference between 28 days and 56 days may be reasonably considered to be well within experimental errors and therefore does not appear to alter overall trends in observed strength development. As seen in the Figure 3-6, GP12 shows higher compressive strength (increase of approximately 5 MPa) than GP11. Given that GP12 has higher alkali content than GP11 (usage of alkali solution is higher in GP12 (830g) than in GP11 (700g)), the high activator loading, hence high overall water content, could lead to a more porous structure in GP12 binder and eventually lower compressive strength.

Figure 3-6: Compressive strength development of blended brown coal fly ash geopolymers

To assess observed trends in strength development relative to mix composition, the author have plotted the blend compositions and strength in ternary diagram as shown Figure 3-7. This approach enables to correlate the amorphous molar ratio of precursor materials in the geopolymer mix with measured 28 days compressive strength of corresponding geopolymer pastes. Only the amorphous mass of SiO₂, Al₂O₃ and CaO of source material blends were used in the ternary plot which was derived according to the procedure given below.

- \( X = \text{mass of amorphous SiO}_2 \in \text{GFA} = \text{mass of GFA in blend} \times (\text{Total SiO}_2 \text{ percentage (51.88%)} - \text{crystalline SiO}_2 \text{ from quartz (12.68%)} - \text{crystalline SiO}_2 \text{ from mullite (14.57%×0.4))} \)
Y = mass of amorphous Al_2O_3 in GFA = mass of GFA in blend × (Total Al_2O_3 percentage (25.92%) – crystalline SiO_2 from mullite (14.57% × 0.6))

Z = mass of amorphous CaO in GFA = mass of GFA in blend × Total CaO percentage (No calcium based crystalline phases were identified)

The similar calculation is conducted for slag and brown coal fly ashes to calculate the amorphous SiO_2, Al_2O_3 and CaO. The reactive mass (amorphous) contents was then normalized (i.e. SiO_2/ (CaO + Al_2O_3 + SiO_2) as shown below; with “A”, “B” and “C” designations for amorphous mass SiO_2, Al_2O_3, and CaO respectively.

- A = SiO_2 mass from fly ashes (GFA and brown coal fly ash) amorphous phases + SiO_2 mass from slag amorphous phases
- B = Al_2O_3 mass from fly ashes (GFA and brown coal fly ash) amorphous phases + Al_2O_3 mass from slag amorphous phases
- C = CaO mass from fly ashes (GFA and brown coal fly ash) amorphous phases + CaO mass from slag amorphous phases

The respective mass fractions of each amorphous oxide constituents were determined by the following ratios:

- Reactive SiO_2 fraction = A/(A+B+C)
- Reactive Al_2O_3 fraction = B/(A+B+C)
- Reactive CaO fraction = C/(A+B+C)

Using these fractions of each blend and the compressive strength of resulting binder, ternary diagram was obtained as shown in Figure 3-7. Other commonly used construction materials (based on Scrivener et al. [23]) were also included into the ternary diagram to compare the characteristics of brown coal fly ash/fly ash blends.

As seen in the ternary diagram (Figure 3-7), 100% Brown coal fly ash HZLD and YLDP with high calcium oxide fraction (calcium oxide fraction =1), and very low SiO_2 and Al_2O_3, yield low strength of these fly ashes based geopolymers. On the other hand 100% LYDP showed very high SiO_2 fraction of 0.8 compared to LYLG. It was also observed that, brown coal fly ash blended types (GP11-GP14) which achieved high compressive strength (>25 MPa) have SiO_2, Al_2O_3 and CaO oxides within following ranges respectively, 35- 45 % (or 0.45 to 0.65 fraction), 15 – 25 % and 35- 55 %. The latter range is similar to the weight composition found in different slag types. Even though, some of the fly ash blends show chemical composition similar to class C fly ash
types, the resulting geopolymer had lower compressive strength (<25 MPa). It was observed that, LYG chemical composition is similar to metakaolin, but the geopolymer made with LYG shows very low strength.

Van Deventer et al. [24] presented a ternary diagram that contained the binder gel composition in different alkali activated binders. They observed that slag blended fly ash based binders can form C-(N)-A-S-H phases and their SiO$_2$, CaO and Al$_2$O$_3$ fractions also coincides with compositional ranges obtained for GP11-GP14. This may partly be the reason that GP11-GP14 binders show high compressive strength compared to other brown coal blends. Garcia-Lodeiro et al. [25] also demonstrated that the availability of calcium in geopolymer systems may lead to partial replacement of Na in (N-A-S-H gel) by using alkali systems with compositions CaO/ SiO$_2$ ratio =0.24 and SiO$_2$ /Al$_2$O$_3$ ratio = 3 and C-(N)-A-S-H phases. GP11 and GP12 have CaO/ SiO$_2$ ratio 0.42 and 0.43 respectively and SiO$_2$ /Al$_2$O$_3$ ratio 5.2 and 2.5 respectively. Since GP11 has high SiO$_2$ /Al$_2$O$_3$ ratio in the solid material, C-(N)-A-S-H phases should have less aluminium percentage (C$_{0.095}$A$_{0.06}$SHX). Garcia-Lodeiro et al. [25] further explained that when CaO/ Al$_2$O$_3$ ratio is reduced, the C-(N)-A-S-H phases can have saturated aluminium percentage (C$_{0.72}$A$_{0.1}$SHX). Therefore, GP12 may have saturated aluminium level in the phases and show compressive strength higher than 25 MPa. On the other hand, GP13 and GP14 have CaO/ SiO$_2$ ratio 0.66 and 0.77 respectively and SiO$_2$ /Al$_2$O$_3$ ratio 3.75 and 3.75 respectively these binders may also produce C-(N)-A-S-H phases with lower aluminium content. Other brown coal blends which achieve less than 25 MPa have SiO$_2$ /Al$_2$O$_3$ and CaO/ SiO$_2$ ratios favour C-(N)-A-S-H phases with very little aluminium content [26].
Long term water stability of geopolymers

The extent of decomposition of 28 days geopolymer samples after full immersion in water is shown in Figure 3-8. The deterioration was most severe in blended GP11 pastes after 3 days exposure while GP12 binders display good water stability. The main reason for deterioration could be the high SO$_3$ content present in LYDP fly ash triggering possible geopolymer network can be attacked by SO$_4^{2-}$. The SO$_3$ content of LYDP type is 7% while LYLG has about 0.4% SO$_3$ level.

Another reason might be that the MgO present in fly ash can react with alkaline NaOH to create-Mg(OH)$_2$ which has high solubility in water [27]. However, XRF results show that LYDP and LYLG have the same level of MgO content therefore further investigation is necessary to identify the role of MgO in geopolymer reaction. Partly to offset durability concerns, Brown et al. [28] used washed brown coal ash as concrete additive and observed that removal of water soluble compounds and char content can improve mechanical properties of the binder.
The other key difference in LYLG ash and LYDP is the aluminium content in the fly ash. LYLG has 31.3% total aluminium while LYDP fly ash has 15.5% aluminium. GP12 has higher aluminium ratio than aluminium in other fly ash blends. In general, the aluminium content in the alumina-silicate source material controls large number of geopolymer properties including stability of geopolymer network which affects compressive strength and durability. Fernández-Jiménez et al. [29] showed that there should be a minimum amount of reactive aluminium in source materials for binder formation and 75% of this aluminium is saved to be consumed within the first stage of reaction. As seen in the Table 3-6, GP12 has about 28% reactive aluminium compared to 16% in GP11, 11% in both GP13 and GP14. Therefore, for GP12, a continuous gel phase reaction mechanism due to its high reactive aluminium may be envisaged. GP11 has the highest SiO₂ ratio compared to other binders. GP11 and GP12 have the same CaO content obtained from 30% slag blending, but for GP13 and GP14 the high CaO content is due to their high calcium inside the fly ash particles. GP12 expected to have different microstructure compared to GP11 which will be discussed in the next section.

Table 3-6: Total reactive Al₂O₃ and SiO₂ molar ratios of brown coal fly ash blends

<table>
<thead>
<tr>
<th>Mix</th>
<th>Reactive Al (%)</th>
<th>SiO₂/ (SiO₂+Al₂O₃+CaO)</th>
<th>Al₂O₃/ (SiO₂+Al₂O₃+CaO)</th>
<th>CaO/(SiO₂+Al₂O₃+CaO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GP11</td>
<td>16</td>
<td>0.62</td>
<td>0.12</td>
<td>0.26</td>
</tr>
<tr>
<td>GP12</td>
<td>28</td>
<td>0.55</td>
<td>0.22</td>
<td>0.24</td>
</tr>
<tr>
<td>GP13</td>
<td>11</td>
<td>0.45</td>
<td>0.12</td>
<td>0.43</td>
</tr>
<tr>
<td>GP14</td>
<td>11</td>
<td>0.49</td>
<td>0.13</td>
<td>0.38</td>
</tr>
</tbody>
</table>
Microstructure analysis

X-ray diffraction analysis

Figure 3-9 illustrates the phase development of GP11 and GP12 up to one month. Both LYDP and LYLG fly ash types show the presence of crystalline quartz, mullite and calcite phases which were also detected in the original ashes (Figure 3-1). GP12 binder displays a clear hump around 30° (2θ) which is characteristic of Na₂O-Al₂O₃-SiO₂-H₂O geopolymer matrix whereas the corresponding hump in GP11 blended geopolymer mixtures is weak which may indicate limited geopolymer gel phase formation in the binder. High content of mullite in the initial GP11 mix remained in the geopolymer at 28 days while GP12 does not contain mullite phases. The sodium aluminium silicate hydrate (N-A-S-H) crystalline phases in GP11 appear to have increased in 28 days compared to 7 days. The intensity of quartz phases have also increased in samples with longer curing. The calcite phases in GP12 remained the same as observed in the initial fly ash and amorphous content of geopolymer increased over 28 days (due to formation of new N-A-S-H phases are formed which are not observable at one day). It is also noteworthy, that geopolymer reaction in GP12 may be more efficient due to its high alkali content allowing faster leaching process of main precursor materials and high reactivity of GP12 which is consistent with calorimetric results.

Apart from geopolymer gel, GP12 and GP11 pastes also contain calcium aluminate silicate hydrate (Na/Ca)-A-S-H and calcium silicate hydrate (C-S-H). The corresponding peaks are at around 30 and 50 2θ degrees respectively [30]. Previous research work also reported that at 60°C curing, fly ash with slag geopolymer binders form the following products: (Na/Ca)-A-S-H when Si/Al ratio is around 2 and C-S-H when Si/Al ratio is 2.5 and Ca/Si ratio is 0.8 [30]. Addition to this, the coexistence of these products enhances compactness of the binder. Li et al. [31] disclosed that in the presence of slag Si and Al binding energies are decreased and that the new energy level which is closer to zeolite phases. The results, also in-line with this observation, shows that slag blended brown coal fly ash based geopolymers (GP11 and GP12) have started to transform into zeolites. However, the XRD analysis shows that the brown coal fly ash in the blend have participated in the geopolymer matrix rather than acting as a filler material.
Figure 3-9: XRD patterns for geopolymers (a) GP11 (b) GP12 (each pattern corresponds to 1 day, 7 day, and 28 days as shown)

**Scanning electron microscopy**

Backscattered electron (BSE) images of the two pastes specimens (GP11 and GP12) evaluated at three different magnifications after 1 year are shown in Figure 3-10. In these images, different shades of grey circled particles are the reacted and unreacted...
particle of fly ash. Light grey angular particles surrounded by dark grey line are corresponding to the remnant of unreacted slag grains. The analysis (Figure 3-10) shows several distinctive features in GP11 and GP 12 (identified with varying greyscale intensities). At high magnification, (Figure 3-10 A3 and B3) larger amount of cracks is identified in GP12 compared to GP11. The reason for that is in the preparation of GP12 consumed higher alkali activator solution than GP12. The excess water in the geopolymer binder may leave inducing high porous structure and these pores are interconnected to create cracks [32].

Another notable difference between GP11 and GP12 is that unreacted particle found in slag in GP12 (Figure 3-10 (B1, B2, B3)) is minimal compared to GP11 (Figure 3-11 (A1, A2, A3)). During SEM analysis, only larger unreacted slag particles are detected (as shown Figure 3-11). As mentioned in the previous section, GP12 has very high reactive aluminium content (31%) compared to the aluminium in GP11. Binder containing high aluminium may help to improve geopolymer reaction. In the presence of aluminium rich environment, slag particles may be consumed geopolymerisation continuously up to one year. San Nicolas et al. [33] stated that slag particles of the binder and alkali ions in the pore continuously react over a period of time to form homogeneous matrix. They proposed that slag based systems with sufficient aluminium lead advance reaction mechanisms in both early and later stages of binder development.
The EDX analysis of GP12 shows in Figure 3-11 indicates that a light grey unreacted particle of slag remains, showing a high content of calcium [33]. The unreacted slag particle showed typical slag composition. The surrounded gel also has higher calcium and silicon than the gel further away from the slag particle. The calcium in slag can propagate into near gel leading to high calcium based composition [33]. Figure 3-12 shows the chemical composition of GP11 and GP12 gel phases. Both GP11 and GP12 show similar silicon, calcium and aluminium level in the gel. Furthermore, the chemical compositions of the two binders were compared in Figure 3-13 using the element ratios (Si/Al and Al/Na) obtained at different locations in the binders. At given Na/Al ratio, Si/Al ratio is higher in GP11 than the ratios in GP12. It should be noted that the initial GP11 blend had high Si/Al ratio (SiO₂/Al₂O₃=5.1 or Si/Al= 2.55) compared GP12 blend.
(Si/Al= 1.30). Therefore, the resulting gel (GP11) also has higher Si/Al ratio than the ratio of the gel formed in GP12.

Figure 3-11: BSE image of GP12 with EDX analyses (a) unreacted particle of slag, (b) reacted binder near the unreacted particle of slag (c) binder further away from the unreacted particle of slag

Figure 3-12: BSE image of blended geopolymer binders with EDX analyses, top- GP11, and bottom-GP12

Despite the fact that initial GP11 and GP12 solid blends had similar Na/Al ratios (Table 3-5, Na2O/Al2O3= Na/Al, 1.84 and 1.12 respectively), the end geopolymer product GP12 has scattered Na/Al ratios (in a wide range 1-2.5) (refer to Figure 3-13). GP11 has
this ratio in the range of 1-1.5. The GP12 synthesis has high Al content and high alkali content initially which can lead to reactions in different level in the pastes. This trend indicates that most of alkali added to the system participated in geopolymer gel formation.

![Figure 3-13: Atomic ratios of GP11 and GP12 of paste (EDX analysis data)](image)

Figure 3-14 and Figure 3-15 show the maps obtained from the elemental mapping for GP11 and GP12 binder. GP12 binder shows consistent distribution of aluminium throughout the gel while GP11 shows aluminium mainly in the unreacted slag and fly ash particles. Since condensation rate in geopolymer largely depend on the aluminate content, the geopolymer reaction in GP12 has been accelerated forming C-A-S-H homogeneous matrix [34]. Weng et al. [34] reported that Al atom has higher positive charge than Si atom in the same alkaline environment. Therefore, [Al(OH)₄]⁻ tetrahedral tend to attract more hydroxyl ions which will encourage more aluminate species to participate for condensation reaction.

Both GP11 and GP12 binders show silicon in isolated patches which are mainly from the crystalline phases (quartz and mullite) of fly ash and slag. GP11 also shows magnesium spots which may remain from brown coal fly ash and slag particles (Figure 3-14) while GP12 does not show noticeable magnesium elements left in the binder (Figure 3-15). High reactivity in GP12 may incorporate magnesium into geopolymer gel. Previously it has been shown that magnesium can participate into geopolymer matrix similar to calcium [35].
Even though, significant level of sulphate was identified in brown coal fly ash LYDP and LYLG (XRF analysis), the corresponding element mapping for sulphur did not detect sulphur in the binder. Criado et al. [16] prepared geopolymer mixing sodium sulphate into geopolymer synthesis, they did not observed sulphate related phases in their XRD study. Mcphee at al.[4] also stated that brown coal fly ash blended cement did not show any sulphate related phases or unreacted MgO after hydration.

Figure 3-14: BSE image and corresponding elemental maps of 1 year old GP11 blended geopolymer binder
3.3 Analysis of Australian class F fly ash based Geopolymer

3.3.1 Experimental analysis

Precursor Materials

Six types of Australian class F fly ashes (obtained from Gladstone, Collie, Mt Piper, Eraring, Tarong and Bayswater power stations) were used as the main alumino-silicate source materials in this study. D-Grade sodium silicate solution (29.4% SiO$_2$ and 14.7% Na$_2$O by weight) from PQ Australia Pty Ltd. and analytical grade NaOH solid from Sigma Aldrich Pty Ltd were used as alkaline activators.
**Characterisation of fly ashes**

The bulk chemical composition, mineralogical phases, particle size distribution and summarized particle sizes, of the six fly ash types used in this study are given in Table 3-7, Table 3-8, Figure 3-16 and Table 3-9 respectively (the procedure used in obtaining these results was similar to the one described in section 3.2.2).

Table 3-7: Bulk chemical composition of the class F fly ashes

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Gladstone</th>
<th>Collie</th>
<th>Mt Piper</th>
<th>Eraring</th>
<th>Tarong</th>
<th>Bayswater</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>51.1</td>
<td>60.0</td>
<td>65.8</td>
<td>63.2</td>
<td>73.1</td>
<td>80.4</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>25.6</td>
<td>24.6</td>
<td>26.7</td>
<td>25.2</td>
<td>23.2</td>
<td>14.0</td>
</tr>
<tr>
<td>CaO</td>
<td>4.30</td>
<td>0.15</td>
<td>0.05</td>
<td>0.07</td>
<td>0.07</td>
<td>0.04</td>
</tr>
<tr>
<td>MgO</td>
<td>1.45</td>
<td>0.99</td>
<td>0.25</td>
<td>0.57</td>
<td>0.14</td>
<td>0.31</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>12.5</td>
<td>8.56</td>
<td>1.32</td>
<td>3.36</td>
<td>0.89</td>
<td>3.57</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.77</td>
<td>0.36</td>
<td>0.32</td>
<td>0.72</td>
<td>0.06</td>
<td>0.10</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.89</td>
<td>0.22</td>
<td>0.14</td>
<td>0.25</td>
<td>0.05</td>
<td>0.09</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>-</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.70</td>
<td>0.36</td>
<td>2.69</td>
<td>1.81</td>
<td>0.52</td>
<td>0.85</td>
</tr>
<tr>
<td>MnO</td>
<td>0.15</td>
<td>0.04</td>
<td>0.02</td>
<td>0.07</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>0.24</td>
<td>0.18</td>
<td>0.11</td>
<td>0.18</td>
<td>0.06</td>
<td>0.08</td>
</tr>
<tr>
<td>LOI</td>
<td>0.57</td>
<td>1.49</td>
<td>1.44</td>
<td>1.31</td>
<td>0.75</td>
<td>0.54</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>1.32</td>
<td>1.53</td>
<td>1.11</td>
<td>0.99</td>
<td>1.31</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Table 3-8: Mineralogical phases of fly ashes

<table>
<thead>
<tr>
<th>Crystalline phase</th>
<th>Gladstone</th>
<th>Collie</th>
<th>Mt Piper</th>
<th>Eraring</th>
<th>Tarong</th>
<th>Bayswater</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>13.0</td>
<td>8.42</td>
<td>5.58</td>
<td>8.12</td>
<td>5.88</td>
<td>8.75</td>
</tr>
<tr>
<td>Mullite</td>
<td>14.6</td>
<td>7.76</td>
<td>9.15</td>
<td>13.1</td>
<td>7.11</td>
<td>8.56</td>
</tr>
<tr>
<td>Hematite</td>
<td>4.17</td>
<td>1.87</td>
<td>1.88</td>
<td>-</td>
<td>-</td>
<td>2.21</td>
</tr>
<tr>
<td>Magnetite</td>
<td>1.83</td>
<td>1.71</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.52</td>
</tr>
<tr>
<td>Amorphous SiO$_2$</td>
<td>32.00</td>
<td>48.50</td>
<td>56.60</td>
<td>49.80</td>
<td>64.60</td>
<td>68.20</td>
</tr>
<tr>
<td>Amorphous Al$_2$O$_3$</td>
<td>16.80</td>
<td>19.90</td>
<td>21.20</td>
<td>17.40</td>
<td>18.90</td>
<td>8.90</td>
</tr>
<tr>
<td>Amorphous CaO</td>
<td>4.30</td>
<td>0.15</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.04</td>
</tr>
<tr>
<td>Total Amorphous</td>
<td>66.00</td>
<td>81.00</td>
<td>84.10</td>
<td>76.70</td>
<td>86.50</td>
<td>81.7</td>
</tr>
</tbody>
</table>

Remaining amorphous content coming from other oxides were not listed here.
Table 3-9: Particle size distribution (passing percentage)

<table>
<thead>
<tr>
<th>Fly ash type</th>
<th>90% (μm)</th>
<th>50% (μm)</th>
<th>10% (μm)</th>
<th>Mean (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gladstone</td>
<td>24.4</td>
<td>5.54</td>
<td>1.10</td>
<td>9.32</td>
</tr>
<tr>
<td>Collie</td>
<td>43.3</td>
<td>11.6</td>
<td>1.61</td>
<td>17.4</td>
</tr>
<tr>
<td>Mt Piper</td>
<td>41.8</td>
<td>12.9</td>
<td>2.23</td>
<td>18.0</td>
</tr>
<tr>
<td>Eraring</td>
<td>55.9</td>
<td>18.2</td>
<td>3.02</td>
<td>24.6</td>
</tr>
<tr>
<td>Tarong</td>
<td>40.1</td>
<td>12.3</td>
<td>2.71</td>
<td>17.3</td>
</tr>
<tr>
<td>Bayswater</td>
<td>35.3</td>
<td>12.8</td>
<td>2.54</td>
<td>16.2</td>
</tr>
</tbody>
</table>

Figure 3-16: Particle size distribution of fly ashes

**Preparation of geopolymer samples**

The geopolymer samples were prepared according to the following procedure: solid NaOH was first dissolved in water to obtain 8 M sodium hydroxide solution. The sodium hydroxide was then mixed with sodium silicate solution (1:1 ratio). The solution was then added to the fly ash in a small motor mixer and mixed until a consistent flow of 20-40% flow is obtained (flow was measured using 100 mm flow table). Some fly ashes consumed higher amount of activator solution than others to get the similar flow. The actual quantities used in each geopolymer mix are listed in Table 3-10. The alkali
activated mixtures were cast into 50 mm cubes and cured at 60°C and 100% RH for 24 h in sealed condition. After that, the samples were removed from the moulds and placed in sealed polythene bags. Compressive strength of cubic specimens in 1, 7 and 28 days was obtained according to the ASTM C109 [36].

Table 3-10: Mix designs for geopolymers

<table>
<thead>
<tr>
<th>Mix No</th>
<th>Mix formulation</th>
<th>Fly ash (g)</th>
<th>NaOH+ Na₂SiO₃ (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix1</td>
<td>Gladstone fly ash</td>
<td>3000</td>
<td>800</td>
</tr>
<tr>
<td>Mix2</td>
<td>Collie fly ash</td>
<td></td>
<td>1200</td>
</tr>
<tr>
<td>Mix3</td>
<td>Mt Piper fly ash</td>
<td></td>
<td>1300</td>
</tr>
<tr>
<td>Mix4</td>
<td>Eraring fly ash</td>
<td></td>
<td>1650</td>
</tr>
<tr>
<td>Mix5</td>
<td>Tarong fly ash</td>
<td></td>
<td>1900</td>
</tr>
<tr>
<td>Mix6</td>
<td>Bayswater fly ash</td>
<td></td>
<td>1850</td>
</tr>
<tr>
<td>Mix7</td>
<td>50%Gladstone/50%Tarong fly ash</td>
<td>1272</td>
<td></td>
</tr>
<tr>
<td>Mix8</td>
<td>30%Gladstone/70%Tarong fly ash</td>
<td></td>
<td>1440</td>
</tr>
</tbody>
</table>

3.3.2 Results and Discussion

Strength development

The results show that the geopolymer made using Gladstone fly ash achieved the highest overall compressive strength followed by Collie fly ash based geopolymer.

In Figure 3-16, Gladstone fly ash (with the highest compressive strength) has the lowest mean particle size (9.32 μm) among all the fly ashes whereas the fly ashes Bayswater, Tarong, Collie and Mt Piper, have approximately the same mean particle size (approximately doubled the size of Gladstone fly ash). LOI content of collie fly ash did not adversely affect the alkali consumption of geopolymer. This attributes the low particle size of collie fly ash.

Geopolymers based on Eraring fly with the largest mean particle size (24.6 μm) has the lowest strength in 28 days (15 MPa) (Eraring fly based geopolymer showed high one day compressive strength compared to Bayswater and Tarong based geopolymers). While the above results show that lower mean particle size leads to high compressive strengths. Collie fly ash based geopolymer with similar size particles to Bayswater, Tarong and Mt Piper fly ash (16-18 micron) showed significantly high 28 day compressive strengths. This is because collie fly ash contains higher percentage of very
fine particles (<2 μm) than other three fly ash types and the smaller particles (due to the high surface area) leads to higher reactivity with alkali.
It can also be observed that age of curing resulted high compressive strength of geopolymer. Geopolymer reaction is continual process where microstructure is more condensed with age; in turn the compressive strength is increased. This analysis confirms that particle size is an important parameter in determining the properties of geopolymers.

![Figure 3-17: Compressive strength of six types of fly ash based geopolymers; fly ash particle size increases from left to right](image)

Oxide ratios and water to solid ration of the geopolymer mixes (calculated according to procedure given in section 3.2.2) which are given in Table 3-11. The variation of compressive strength with water to solid ration and the age of curing is shown in Figure 3-18(b). This illustrates that high strengths (>30 MPa) can be achieved by using a liquid to solid ratio of less than 0.4. However it should be noted that the water to solid ratio is dependent on the, the amount of alkali activator added which was determined such that the flow of all mixtures remains constant this shows that water to solid ratio is not directly comparable. Although Collie geopolymer has a high ratio of liquid to solid (0.55), its strength is relatively high and falls into high strength range (>30 MPa).

![Figure 3-17: Compressive strength of six types of fly ash based geopolymers; fly ash particle size increases from left to right](image)
Figure 3-18: Effect of fly ash (a) particle size (b) Liquid to solid ratio on compressive strength of geopolymer pastes at different ages of curing

Table 3-11: Oxide ratios and 28 day compressive strength

<table>
<thead>
<tr>
<th>Mix No</th>
<th>Total reactive SiO$_2$/Al$_2$O$_3$ molar ratio</th>
<th>Amorphous SiO$_2$/Al$_2$O$_3$ molar ratio of fly ash</th>
<th>Water/Solid (mass ratio)</th>
<th>Na$_2$O/(SiO$_2$+Al$_2$O$_3$) reactive molar ratio</th>
<th>Compressive strength at 28 days (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix1</td>
<td>3.7</td>
<td>3.28</td>
<td>0.16</td>
<td>0.098</td>
<td>48</td>
</tr>
<tr>
<td>Mix2</td>
<td>4.6</td>
<td>4.13</td>
<td>0.23</td>
<td>0.102</td>
<td>37</td>
</tr>
<tr>
<td>Mix3</td>
<td>5.0</td>
<td>4.53</td>
<td>0.24</td>
<td>0.097</td>
<td>18</td>
</tr>
<tr>
<td>Mix4</td>
<td>5.7</td>
<td>4.87</td>
<td>0.30</td>
<td>0.136</td>
<td>15</td>
</tr>
<tr>
<td>Mix5</td>
<td>6.6</td>
<td>5.78</td>
<td>0.33</td>
<td>0.123</td>
<td>21</td>
</tr>
<tr>
<td>Mix6</td>
<td>14.8</td>
<td>13.1</td>
<td>0.34</td>
<td>0.129</td>
<td>20</td>
</tr>
<tr>
<td>Mix7</td>
<td>5.1</td>
<td>4.60</td>
<td>0.24</td>
<td>0.110</td>
<td>35</td>
</tr>
<tr>
<td>Mix8</td>
<td>5.7</td>
<td>5.10</td>
<td>0.27</td>
<td>0.112</td>
<td>32</td>
</tr>
</tbody>
</table>

To further evaluate possible pathways of phase evolution in the present system, it has to be recalled that materials of disordered (amorphous) nature generally dissolve quicker than the stable crystalline counterparts [37-39] in alkali. Moreover, the amorphous (reactive) alumina present in source materials dissolve more rapidly than the silica, producing an aluminium rich gel at initial stages of the reaction process [40]. It can be seen from Table 3-8 that Gladstone fly ash has the lowest amount of amorphous content. However, particle analysis results show that Gladstone fly ash has highest amount of fine particles which may increase the availability of amorphous elements for the reaction. Therefore, the strength of geopolymer is related to the amount of amorphous content in fine fly ash particles.

Next, the compressive strength of the geopolymer mixes is compared with the reactive SiO$_2$/Al$_2$O$_3$ ratio. In this analysis, addition to the results of the present study, the author also used the extensive data reported by Diaz et al [41] and Fernández-Jiménez et al [29]. The data reported in Diaz et al [41] is based on 16 different class F and class C fly ash geopolymer specimens while the data reported in Fernández-Jiménez et al [29] is based on three different geopolymer specimens.

Figure 3-19 illustrates the compressive strength variation with amorphous SiO$_2$/Al$_2$O$_3$ ratios. The plot the display is relatively clear that there is a correlation between amorphous SiO$_2$/Al$_2$O$_3$ molar ratio and the compressive strength. The strength remains consistently high (> 30 MPa) up to amorphous SiO$_2$/Al$_2$O$_3$ ratio = 4 beyond which a
noticeable strength reduction is observed. Mix 1 and Mix 2 geopolymers with lower reactive SiO$_2$/Al$_2$O$_3$ ratio (between 3.5 and 4.6) reached 28 days strength of over 30 MPa whereas Mix 3 to Mix 6 geopolymer with high reactive SiO$_2$/Al$_2$O$_3$ (>5) attained lower 28 days compressive strength value (< 25MPa).

Previously it was reported that geopolymer systems have SiO$_2$/Al$_2$O$_3$ ratio above 3.8 the pre-cursor phases tend to be transformed from amorphous to crystalline (zeolite forms) with such phase transformations resulting in relatively lower strength matrices [42]. Another study shows that Na$_2$O-Al$_2$O$_3$-SiO$_2$-H$_2$O gel compositions with higher or lower than SiO$_2$/Al$_2$O$_3$ $\approx$ 4 usually develop into zeolitic phases [14]. The formation of zeolitic phases is a common feature in geopolymer systems and the type of zeolite formed usually depend on the SiO$_2$/Al$_2$O$_3$ ratio of the system [14, 40, 43-45]. However, the final reaction product (Na$_2$O-Al$_2$O$_3$-SiO$_2$-H$_2$O gel) may evolve concurrently either into a crystalline zeolitic phase or to an amorphous geopolymer phase depending on the concentration of available aluminate and silicate species in solution. This possibly accounts for the presence of Si rich zeolitic phases such as faujasite. In general, crystalline Zeolitic phases are unstable than 3 dimensional geopolymer matrix.

Addition to that, Fletcher et al. [15] analysed for metakaoline based geopolymer systems with different SiO$_2$/Al$_2$O$_3$ ratios ranging from 0.5 to 300. They found that when SiO$_2$/Al$_2$O$_3$ ratio is greater than 24 geopolymer binder becomes more rubbery than brittleness. Moreover, geopolymer binder with lower SiO$_2$/Al$_2$O$_3$ (<2) ratio or high aluminium content shows weak structure with several discrete compounds. Based on these previous studies and the present work it is therefore suggested that the amorphous SiO$_2$/Al$_2$O$_3$ molar ratio of fly ash remains a key factor in controlling physical properties of geopolymer resulting in enhanced strength performance between SiO$_2$/Al$_2$O$_3$ ratios of 2-4.
Alkali content in the geopolymer systems is also an important parameter that controls the geopolymerization and the strength of the binder. Dissolution rate of SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} is mainly based on amorphous content and as well as alkalinity of the system. Figure 3-20 shows the variation of 28 day compressive strength with the molar ratio of available Na\textsubscript{2}O to reactive (SiO\textsubscript{2} + Al\textsubscript{2}O\textsubscript{3}) in the geopolymer systems. Even though Mix 1 and Mix 3 have almost equal alkalinity to amorphous (SiO\textsubscript{2} + Al\textsubscript{2}O\textsubscript{3}) molar ratio (i.e. 0.98), the strength value is high in Mix 1 (48 MPa) compared to Mix 3 (18 MPa). However, it should be noted that Mix 3 has higher reactive SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio than Mix 1. The strength of geopolymer has a combination effect from SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio and the Na\textsubscript{2}O/ (SiO\textsubscript{2}+Al\textsubscript{2}O\textsubscript{3}).
Above results show that Tarong, Eraring, Mt Piper and Bayswater fly ashes have the poor performance compared to Collie and Gladstone as a precursor material. The author further analysed Tarong fly ash based geopolymer. Figure 3-21 shows the compressive strength variation of geopolymers made with a combination of Gladstone fly ash and Tarong fly ash at several mixing ratios. As expected when Tarong fly ash content is increased in geopolymer synthesis, the compressive strength decreases. Possible reasons could be the initial 100% Tarong fly ash based synthesis had high SiO$_2$ contents and consumed high alkaline liquid to get consistent workability. It may be noted that those geopolymer systems have high water content and high Na$_2$O content. Similar to this study, Keyte [46] also reported that the lowest compressive strength is achieved for Tarong fly ash based geopolymer among other Australia class F fly ash based geopolymers. The author reported that that lower level of aluminium in Tarong fly ash would result the weak geopolymer network. Fletcher et al. [15] concluded that alumino-silicate systems with high silica, consume high water content than other systems. Nevertheless, addition of Gladstone fly ash appears to adjust the chemistry (increasing aluminium content) of the geopolymer mix, in turn, improved compressive strength can be obtained.
Figure 3-21: Average 28 days compressive strength variation with Tarong fly ash content in geopolymer mix

**Microstructure analysis**

Figure 3-22 illustrates fracture surfaces of Australian class F fly ash based geopolymers obtained using scanning electron microscopy. All of the specimens consist of unreacted fly ash particles (spherical shaped particles) and a certain amount of cracks. The cracks may associate with drying shrinkage of geopolymer binder. However, the crack formation in Gladstone fly ash based geopolymer is minimal compared to other binders (Figure 3-22a). As the Gladstone fly ash based geopolymer consumed the lowest amount of water content (alkali liquid content, L/S = 0.267) in turn; the binder should expected to have a lower drying shrinkage. Furthermore, Collie fly ash-based geopolymer was prepared using second lowest liquid to solid ratio (L/S=0.400) and specimen showed similar crack pattern (Figure 3-22(b)) as Gladstone fly ash-based geopolymer. The remaining binders showed significantly high amounts of cracks with large crack width and their compressive strength was considerably lower. In the previous studies it has been shown that excess water in geopolymer mix can lead to large pore structure which can interconnect later stage to form micro cracks [41]. On the other hand, lower water in geopolymer leads to a more condensed paste where cracks need to have high energies to propagate which the reason for lower cracks is observed in Gladstone based geopolymer. Furthermore, Figure 3-22 also illustrates, there is a significant amount of unreacted fly ash particles in all geopolymeric pastes. In general lower unreacted particles are an indication of good geopolymerisation. Even though,
Gladstone fly ash based geopolymer showed the largest strength gain among all geopolymers, the unreacted fly ash particles in the binder is almost similar to other binders.

Figure 3-22: Secondary electron SEM images of fracture surface of (a) Gladstone, (b) Collie, (c) Eraring, (d) Mt piper, (e) Bayswater and (f) Tarong fly ash-based geopolymers

3.4 Concluding remarks

1. The utilisation of unblended dry precipitator (LYDP) and lagoon fly (LYLG) ash as geopolymer alumino-silicate source material tends to be unsatisfactory due to their SiO$_2$/Al$_2$O$_3$ ratios of 10.4 and 1.8 which is far from the optimum SiO$_2$/Al$_2$O$_3$ values identified for geopolymer systems. However, it was observed
that Loy Yang dry precipitator and Loy Yang lagoon fly, after blending with other source materials such as class F fly ash and slag to adjust mixture oxide ratio ash, can be used as feedstock for geopolymer synthesis.

2. Geopolymer systems with Hazelwood and Yallourn fly ash type tend to undergo deterioration in the presence of water in the early stage (less than 7 days) because of availability of high sulphate (10-15%) content, while Loy Yang dry precipitator blended geopolymers also showed decomposition behaviour in high moist environment due to its 7.5% sulphate content in the source material.

3. Calorimetric results showed that Loy Yang lagoon and dry precipitator blended geopolymer synthesises have similar reaction rates. Dissolution of fly ashes generated the same amount of heat (heat during initial stage). The heat generation of brown coal fly ash blended geopolymers during dissolution phase and geopolymerisation reaction product formation phase is slightly higher than for GFA binders.

4. Microstructure of LYLG blended geopolymer (GP12) showed well reacted particles compared to LYDP blended mix (GP11). In elemental mapping of those binders, it was observed that in GP12, C-A-S-H type gel incorporated aluminium compared to isolated aluminium traces found in unreacted fly ash and slag particles for GP11. Elemental mapping revealed that almost all the aluminium and calcium of Loy Yang lagoon blends participated geopolymer network formation. The high reactive aluminium content (28%) of Lagoon fly ash blends appears to create a chemical pathway to development of a continuous geopolymer binder phase.

5. The critical factors for strong geopolymer network are reactive SiO₂/Al₂O₃ and Na₂O/(reactive SiO₂+Al₂O₃). Fly ashes containing high SiO₂/Al₂O₃ (> 5) leads to absorb higher solution content than other fly ashes.

6. Gladstone fly ash based geopolymer showed high compressive strength in 28 days (48 MPa). Particle analysis results showed that Gladstone fly ash has highest amount of fine particles which may help the distribution of the amorphous elements. It can be concluded that the strength of geopolymer is related to the amount of amorphous content in fine fly ash particles.
3.5. References for chapter 3


4. Thermal effects of activators on the setting time and rate of workability loss of geopolymers

4.1 Introduction

As mentioned in chapter 1, geopolymer can present challenges such as the requirement of elevated temperature curing, use of liquid alkali activator and difficulty in controlling workability or setting parameters [3, 4]. A number of parameters influence the properties of both fresh geopolymer concretes. Similar to the case of OPC concretes, fresh geopolymer concrete containing solid alkali activator must also exhibit desirable rheology and setting behaviours in order to be useful for field applications. These properties of in geopolymer concrete cannot be controlled using traditional super plasticisers, water reducer of set retarders [1-3]. Therefore, the significance of understanding of alternative methods to alter the properties of fresh geopolymer concrete is very high.

Class F fly-ash (FA) is commonly used in geopolymer as the alumino-silicate source material due to the availability, composition and low cost [4-6]. However, geopolymer based on FA alone requires elevated temperature curing for the hardening process to take place within an acceptable period of time [7]. According to the literature, the setting time of geopolymers can be modified by the alumino-silicate materials, the calcium content, the alkali content, the activator type and water content [4, 8-13]. Previous research has shown that the hardening process (at room temperature) can be accelerated by blending FA with calcium rich source materials like granulated blast furnace slag [9, 14]. According to Lee et al. [15], the double charged calcium ions introduced by slag combines with hydroxyl to form hydroxide precipitates. This causes a pH reduction around the hydroxide precipitates and helps to form silicate polymers which are comparatively large solid particle with lower surface energy. This enhances the nucleation and polymerisation between the soluble silicate and solid particles leading to an increase in the rate of hardening.

The blending of slag not only changes setting characteristics but also significantly alters the mechanical properties of the resulting geopolymer [16]. Chithiraputhiran et al. [7] reported an initial setting time of 6 hours and 28 day compressive strength of 20 MPa for a blend of 15% fly ash and 85% slag, designated 85/15 (FA/slag). They observed
that, when slag content was increased up to 50%, the setting time decreased to 1 hour and the strength increased to 40 MPa. In these experiments, the authors used liquid alkali activators for geopolymer mixes and varied the modulus (SiO$_2$/Na$_2$O) to adjust the setting time. Nath et al. [9] observed that the setting time and workability of the binder reduced significantly when the slag content was increased in the geopolymer binder, which was in line with other studies [7, 8, 17]. Although, mechanical, durability and microstructural differences of blended FA and slag geopolymer have been extensively studied over the past decades [18-23], only limited attention has been given to properties of fresh geopolymer mixes [24].

Use of solid alkali activators in geopolymer systems is less hazardous than using liquid activators and leads to “cement like” mix, where only water is needed to activate the hydration of the binder. The alkali activators used in solid form instead of a liquid form changes the kinetics of the reaction, as its dissolution occurs during the mixing process. Hence, in many studies a solid activator (in a powder form) is first dissolved and then added to the raw materials [25]. Ravikumar et al. [26] reported a reduction of setting time when using solid activator instead of liquid ones. The authors suggest to do further investigation for finding the reason for this disparity.

Setting and rheology of geopolymer binders are of significant practical importance, particularly for geopolymers activated by solid activators which are intended for field application. In this chapter, the author study the room temperature setting characteristics and workability of blended FA and slag geopolymers, synthesised using two types of solid alkali activators (anhydrous sodium metasilicate (AH) and pentahydrate sodium metasilicate (PH)). Fly ash and slag were mixed at different ratios and activated with the two solid alkali activators mentioned above. Vicat needle method and calorimetric measurements were employed to determine the setting parameters and heat flow of geopolymer mixes. Workability was measured using a flow table to examine the rate of slump loss over time.
4.2 Materials and Methods

4.2.1 Materials

The geopolymer precursor materials used in this investigation were a class F fly ash (FA) – which was a 50/50 mixture of Gladstone and Callide fly ashes obtained from Cement Australia Pty Ltd., and granulated ground blast furnace slag from Independent Cement and Lime Pty Ltd.

Table 4-1 and Table 4-2 show the bulk chemical composition and crystalline phases of these source materials, respectively. Crystalline phase compositions of precursor materials were obtained by XRD analysis carried out using a Bruker D8 Advance X-ray diffractometer. Scans were collected between 5-70° (2θ) with a step size of 0.02° at a scan rate of 5s per step. An internal standard (10%wt corundum, Al₂O₃) was added to allow quantitative analysis using Rietveld refinement. Phase identification and Quantitative Rietveld analysis were carried out using Materials Data, Inc., Jade 9.3 and Bruker Diffracplus Topas softwares respectively.

Table 4-1: Bulk chemical composition of materials

<table>
<thead>
<tr>
<th>Oxides</th>
<th>Slag</th>
<th>FA</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>32.00</td>
<td>51.50</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.51</td>
<td>1.50</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>13.00</td>
<td>27.80</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.40</td>
<td>11.80</td>
</tr>
<tr>
<td>Mn₃O₄</td>
<td>0.30</td>
<td>0.15</td>
</tr>
<tr>
<td>MgO</td>
<td>4.90</td>
<td>1.30</td>
</tr>
<tr>
<td>CaO</td>
<td>41.50</td>
<td>2.20</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.20</td>
<td>0.40</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.33</td>
<td>0.60</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.02</td>
<td>0.73</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.10</td>
<td>0.20</td>
</tr>
<tr>
<td>S²⁻</td>
<td>0.60</td>
<td>-</td>
</tr>
<tr>
<td>LOI</td>
<td>4.20</td>
<td>1.80</td>
</tr>
</tbody>
</table>

Table 4-2: Crystalline phases in fly ash and slag

<table>
<thead>
<tr>
<th>Phase Name</th>
<th>Quartz</th>
<th>Mullite</th>
<th>Calcite</th>
<th>Magnetite</th>
<th>Hematite</th>
<th>Gypsum</th>
<th>Amorphous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slag</td>
<td>-</td>
<td>-</td>
<td>6.2</td>
<td>-</td>
<td>-</td>
<td>7.4</td>
<td>86.3</td>
</tr>
<tr>
<td>GFA</td>
<td>3.7</td>
<td>4.3</td>
<td>-</td>
<td>3.0</td>
<td>3.1</td>
<td>-</td>
<td>85.7</td>
</tr>
</tbody>
</table>
The main component of FA is SiO₂ with (51%) whereas in slag, the main component is CaO (41.5%). FA also contains twice as much Al₂O₃ as slag. FA and slag have the same amorphous content which represents the most reactive part of the precursors. Figure 4-1 shows the particle size distribution of the precursors, obtained using a Cilas laser diffraction particle analyser. Ten grams of was dispersed in water in order to obtain the particle size. Figure 4-1 shows that both fly ash and slag contain a large proportion of smaller size particles (<10 μm) which are desirable for the reactivity of the materials. It also shows that FA has a higher content of smaller particles than slag i.e. 10% < 1 μm for FA and 2.5% < 1 μm for slag, 55%<10 μm FA and 38%<10 μm.

The compositions of the two alkali activators used sodium metasilicate anhydrous (AH): 50.5% Na₂O, 46% SiO₂, 3.5% H₂O and Sodium metasilicate pentahydrate (PH): 28.7% Na₂O, 28.5% SiO₂, and 42.8% H₂O. For all formulations the alkali content was maintained at 4.00%.

The procedure followed in preparing the geopolymer samples is as follows: Firstly, FA and slag were mixed thoroughly (in the proportions given in Table 4-3) for about 1 minute using a small Hobart mortar mixer. Next, water and alkali activator (in powder form) were added to the mix and mixed for another 6 minutes to obtain consistent geopolymer pastes. The mixing was carried out in a room at 23°C and the temperature of each geopolymer pastes was recorded just after the mixing process was completed. All the precursor materials were kept at 23°C before mixing. In order to achieve a similar workability, mixes with high slag content required larger amounts of water.

![Particle size distribution of (a) Slag (b) Fly ash](image)
However, for each pair of geopolymer mixes which contained the same proportion of fly ash and slag and varied only is the type of alkali activator (AH or PH), the water content of the PH was taken into account for that the two mixes had identical amounts of Na$_2$O, H$_2$O and SiO$_2$.

Saturated surface dry sand with a density of 2630 kg/m$^3$ and water absorption of 0.4% was used for geopolymer mortar mixes listed in Table 4-4. The sand to solids precursor (fly ash and slag mass) mass ratio was maintained at 2:1. The water content was varied such that the initial workability was approximately 55-75% (more water was added to mixes with lower fly ash content [27].

Table 4-3: Mix design formulation of geopolymers

<table>
<thead>
<tr>
<th>Mix Name</th>
<th>FA (wt.%)</th>
<th>Slag (wt.%)</th>
<th>Activator type</th>
<th>Na$_2$O content (%)</th>
<th>Water/solid ratio</th>
<th>Temperature of room (°C)</th>
<th>Temperature of binder (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100FA</td>
<td>100</td>
<td>0</td>
<td>PH</td>
<td>0.282</td>
<td></td>
<td>19.5</td>
<td></td>
</tr>
<tr>
<td>90/10(FA/S PH)</td>
<td>90</td>
<td>10</td>
<td>PH</td>
<td>0.282</td>
<td></td>
<td>19.0</td>
<td></td>
</tr>
<tr>
<td>60/40(FA/S PH)</td>
<td>70</td>
<td>30</td>
<td>PH</td>
<td>0.313</td>
<td></td>
<td>18.5</td>
<td></td>
</tr>
<tr>
<td>70/30(FA/S PH)</td>
<td>60</td>
<td>40</td>
<td>PH</td>
<td>0.319</td>
<td></td>
<td>19.5</td>
<td></td>
</tr>
<tr>
<td>50/50(FA/S PH)</td>
<td>50</td>
<td>50</td>
<td>PH</td>
<td>0.324</td>
<td></td>
<td>19.0</td>
<td></td>
</tr>
<tr>
<td>40/60(FA/S PH)</td>
<td>40</td>
<td>60</td>
<td>PH</td>
<td>0.325</td>
<td></td>
<td>18.5</td>
<td></td>
</tr>
<tr>
<td>100S PH</td>
<td>0</td>
<td>100</td>
<td>PH</td>
<td>0.412</td>
<td></td>
<td>19.5</td>
<td></td>
</tr>
<tr>
<td>100FA AH</td>
<td>100</td>
<td>0</td>
<td>AH</td>
<td>0.282</td>
<td></td>
<td>23</td>
<td>19.5</td>
</tr>
<tr>
<td>90/10(FA/S AH)</td>
<td>90</td>
<td>10</td>
<td>AH</td>
<td>0.282</td>
<td></td>
<td>28.0</td>
<td>29.0</td>
</tr>
<tr>
<td>60/40(FA/S AH)</td>
<td>70</td>
<td>30</td>
<td>AH</td>
<td>0.313</td>
<td></td>
<td>28.0</td>
<td>28.0</td>
</tr>
<tr>
<td>70/30(FA/S AH)</td>
<td>60</td>
<td>40</td>
<td>AH</td>
<td>0.319</td>
<td></td>
<td>29.0</td>
<td>30.5</td>
</tr>
<tr>
<td>50/50(FA/S AH)</td>
<td>50</td>
<td>50</td>
<td>AH</td>
<td>0.324</td>
<td></td>
<td>29.0</td>
<td>29.0</td>
</tr>
<tr>
<td>40/60(FA/S AH)</td>
<td>40</td>
<td>60</td>
<td>AH</td>
<td>0.325</td>
<td></td>
<td>28.5</td>
<td></td>
</tr>
<tr>
<td>100S AH</td>
<td>0</td>
<td>100</td>
<td>AH</td>
<td>0.412</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4-4: Geopolymer mortar mix designs (sand: precursor material ratio =2:1, alkali content 4%)

<table>
<thead>
<tr>
<th>Mix name</th>
<th>FA Wt. (%)</th>
<th>Slag Wt. (%)</th>
<th>Activator type</th>
<th>Total Water/Binder mass ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>100FA</td>
<td>100</td>
<td>0</td>
<td>PH</td>
<td>0.30</td>
</tr>
<tr>
<td>90/10(FA/S PH)</td>
<td>90</td>
<td>10</td>
<td>PH</td>
<td>0.31</td>
</tr>
<tr>
<td>70/30(FA/S PH)</td>
<td>70</td>
<td>30</td>
<td>PH</td>
<td>0.33</td>
</tr>
<tr>
<td>60/40(FA/S PH)</td>
<td>60</td>
<td>40</td>
<td>PH</td>
<td>0.34</td>
</tr>
</tbody>
</table>
The effect of activator state (solid or dissolved) on setting was examined using a mix with 50/50 FA to slag ratio, at 4% Na₂O, W/S ratio= 0.324 activated with each activator in the three different given in Table 4-5.

Table 4-5: Activator states used in 50/50% (FA/slag) geopolymer

<table>
<thead>
<tr>
<th>Mix designation</th>
<th>Activator</th>
<th>Sodium metasilicate state</th>
<th>Temperature of the activator (solid/solution)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50/50(FA/S_PH)</td>
<td>PH</td>
<td>Solid</td>
<td>23°C</td>
</tr>
<tr>
<td>40/60(FA/S_PH)</td>
<td>PH</td>
<td>Solution used just after dissolution</td>
<td>17°C</td>
</tr>
<tr>
<td>100S_PH</td>
<td></td>
<td>Solution kept for one day at 23°C before adding</td>
<td>23°C</td>
</tr>
<tr>
<td>100FA_AH</td>
<td>AH</td>
<td>Solid</td>
<td>23°C</td>
</tr>
<tr>
<td>90/10(FA/S_AH)</td>
<td>AH</td>
<td>Solution used just after dissolution</td>
<td>30°C</td>
</tr>
<tr>
<td>60/40(FA/S_AH)</td>
<td>AH</td>
<td>Solution kept for one day at 23°C before adding</td>
<td>23°C</td>
</tr>
<tr>
<td>70/30(FA/S_AH)</td>
<td></td>
<td>Solid</td>
<td>23°C</td>
</tr>
<tr>
<td>50/50(FA/S_AH)</td>
<td></td>
<td>Solution used just after dissolution</td>
<td>30°C</td>
</tr>
<tr>
<td>40/60(FA/S_AH)</td>
<td></td>
<td>Solution kept for one day at 23°C before adding</td>
<td>23°C</td>
</tr>
<tr>
<td>100S_AH</td>
<td></td>
<td>Solid</td>
<td>23°C</td>
</tr>
</tbody>
</table>

4.2.2 Testing procedure

The setting parameters of the geopolymer pastes were measured using a Vicat instrument following the ASTM C191 standard [28]. The setting time was measured from the time that the alkali activator was added into the fly ash, slag and water slurry. The setting test was carried out in a room at 23°C as prescribed in ASTM C191.

Isothermal calorimetry experiments were conducted using a TAM Air isothermal calorimeter, at a base temperature of 23 ± 0.02°C. Fresh paste was mixed externally (mix designs are given in Table 4-3), weighed into an ampoule, and immediately placed in the calorimeter, and the heat flow was recorded with time. All values of heat release rate were normalised by total weight of paste. The elapsed time between the loading of
the ampoule and the metasilicate addition was about 10 minutes. pH variation of the geopolymers were measured periodically up to 2 hours using Aqua-pH instrument. Geopolymer paste specimens were prepared using 1:1 solid to water ratio.

The workability of mortar samples was measured using a small flow table (diameter 100 mm) according to ASTM C230/C230M [29]. Mortar mixes were then cast into 50 mm cube moulds and kept at 23°C. The compressive strengths of mortar cubes were measured in 1, 7 and 28 days as prescribed by ASTM C109 [30].

4.3 Results and discussion

4.3.1 Fresh binder properties

The initial and final setting times of geopolymers (prepared according to the mix design given Table 4-3) activated with PH and AH are show in Figure 4-2. The figure shows that for both activators the setting time decreased when the slag content is increased. In addition, it also shows that geopolymer mixes activated with AH activator always had significantly shorter setting times compared to the PH counterparts (The initial setting of AH activated geopolymer was approximately half that of the PH based binders. The final setting time of AH was also significantly less than PH). This is in spite of the fact that they have equal chemical compositions (i.e. source material and alkali content).

100% FA based geopolymer activated with both AH and PH took more than 800 minutes to set and is not shown in Figure 4-2. Slow setting behaviour in 100% FA based geopolymers has been previously observed with liquid activators in [8, 17, 31] (authors used elevated temperature curing or/and high alkalinity to decrease the setting time).
The workability loss measured over time in geopolymer mixes activated with AH and PH is shown in Figure 4-3. The results show that the workability loss is high for the mixes containing AH (within the first 10-20 minutes) compared to that containing PH. Figure 4-3 also shows a faster workability loss in mixes which contain high slag contents.

A possible reason for the difference in setting characteristics and workability loss of the geopolymers mixes incorporating the two activators (AH and PH) can be the activator dissolution mechanism. The temperature of the fresh geopolymer binders just after mixing (under the heading Temperature of binder) may indicate different mechanisms of dissolution of the two activators. These results show that the temperature of the geopolymers containing AH increased by about 5-7°C compared to initial temperature of 23°C whereas the temperature of mixes with PH activator decreased by 4-5°C. Further detail on the theoretical dissolution mechanism of each activator is presented below.
Figure 4-3: Workability loss of geopolymer mortar binders (a) 90/10 (b) 70/30 (c) 60/40 (d) 50/50 (e) 40/60 (f) 100S

4.3.2 Dissolution of sodium metasilicate solids

In using activators in a solid form the activator must undergo a dissolution period within the overall geopolymerisation process. Sodium metasilicate pentahydrate (PH) solid is formed by hydration of anhydrous sodium metasilicate (AH) with five water molecules. The disparity in enthalpy change during the dissolution of the two activators can be explained as follows: The dissolution enthalpy of either PH or AH is the sum of energy
needed to break the lattice structure (solute-solute), energy to break the solvent lattice structure (H₂O) (solvent-solvent), and the energy of the solvent-solute formation (solvation). The first two steps of the above process are endothermic while the third step is exothermic. As anhydrous and hydrated forms of the sodium metasilicate have the same lattice, the energy required to break the lattice is the same for both activators (ΔH₁, in Figure 4-4)[32]. Furthermore, the solvent-solvent enthalpy is also equal in the dissolution processes of AH and PH, as the solvent (H₂O) is the same in both cases. Hence, the energy difference between the two dissolution processors should be in the solvation step. Figure 4-4 is a schematic presentation of the possible dissolution pathways of the two activators in water. Compared with the PH, which is already hydrated, the AH activator would attract water molecules and would generate some heat of hydration, and this is reflected in the calorimetric analysis as an exothermic peak. This exothermic reaction (formation of additional solvent-solute bonds) can overcome the endothermic reaction (breaking of the salt lattice) and release heat during the dissolution. This explains the increase in temperature during the dissolution of AH compared to the decrease in temperature in PH dissolution.
Figure 4-4: Dissolution of sodium metasilicate anhydrous and sodium metasilicate pentahydrate

Isothermal calorimetric study of the geopolymer paste samples was carried out to identify the heat generation phases of the two binder groups. The heat flow during the first hour of reaction is usually associated with the dissolution of the solid alkali activator, FA and slag [33]. Dissolution of solid activator releases alkali and silicon ions. When enough alkali ions are in the system, FA and slag particles start to dissolve and release Si, Al and Ca ions, which is an exothermic reaction. The observed heat generation during the first hour, shown in

Figure 4-5, is in line with the above theoretical analysis and show that the geopolymer which contains PH have initial negative heat flow (consumption of heat) while the AH solid activated system has a positive heat (generation of heat) flow. The calorimetric results also show that heat flow during the first hour is not affected by the composition of the precursors (FA to slag ratio).
Figure 4-5: Normalized heat flow of (a) 100/0 (b) 70/30 (c) 60/40 (d) 50/50 (f) 40/60 (g) 0/100 FA/S blended geopolymers during 0-1 hours.
Figure 4-6(a) and (b) show the variation of pH in fresh 50/50 FA/Slag and 100% slag based geopolymers during first two hours of setting respectively. Initially, the dissolution of solid alkali activator particles increase the pH of fresh geopolymers gradually until it reaches the maximum value. The dissolution process is completed within the first half an hour which has also been confirmed by the calorimetric results presented in (Figure 4-5 (e) and (g)).

Fresh 50/50 FA/S geopolymer binders with both activator types show a similar pH profile while 100% slag based binder containing AH-SD show a lower pH than that of the binder containing PH-SD. However, the setting times for both 50/50 and 100% geopolymers with AH-SD were higher than that of PH-SD. Therefore it can be concluded that the setting time in geopolymer does not correlate with the pH value of the fresh binder.

![Figure 4-6: pH variation in geopolymers](image)

To elaborate the hypothesis that heat release during the dissolution process is the main factor affecting the variation in properties of fresh geopolymer binders activated by AH and PH, the following experiment was conducted. Mixes with 50/50 FA to slag ratio were activated with each activator in the three different states mentioned earlier (Table 4-5). The initial and final setting times for each combination are given in Figure 4-7. The figure shows that for both types of activator, dissolving the activator in water and adding it immediately to the precursor material, resulted in a significant reduction in the setting time compared to that of adding the solid activator directly. This is due to the immediate availability of soluble silica and alkali ions [27]. When the solution was
rested until it reached to the room temperature of 23°C before being mixed with the precursor material, the setting time for AH and PH-activated systems were found to be the same. This was longer than the setting time for the AH-activated geopolymer whereas it was shorter than that of the PH-activated geopolymer. Figure 4-8 shows the results of the calorimetric analysis for the mentioned above geopolymer systems. When the PH activator is dissolved and immediately added to the mix, the negative peak disappears as the dissolution of the activator largely occurs before the precursor is activated. Moreover, the acceleration of FA and slag dissolution (due to immediate availability of hydroxyl and soluble silica) creates immediate heat flow that cancels out the remaining negative heat flow of the activator dissolution. When the PH activator is dissolved in water and rested prior to mixing (PH-SN-REST) only the peak corresponding to the FA and slag dissolution is observed. When AH activator is dissolved in water and rested (AH-SN-REST), the energy generated due to the dissolution of activator is dissipated prior to the mixing; hence, the sharp initial positive heat flow is reduced to a smaller peak which is due to the dissolution of FA and slag [33, 34]. This setting time results and calorimetric analysis show that the key factor contributing to the variations between AH and PH-activated geopolymer is the heat flow due to the dissolution process of the activators.

Figure 4-7: Setting time with different alkali activator condition
Figure 4-8: Normalized heat flow due to different activator form (a) PH based binders (b) AH based binders (0-1 hour)

Figure 4-9 depicts the heat flow in PH and AH-activated samples in the interval from 1 to 30 hours after mixing. These results are consistent with previously reported results for silicate-activated FA/slag systems [17, 31, 34]. They show that when the slag content is increased, the alkali activation occurs earlier (the induction period is reduced to around 10 hours). In PH activated system with 70% or high FA content (Figure 4-9 (a), (b) and (c)) the induction period is longer than 30 hours. This behaviour is in line with previous studies [31] that show slow reactivity of the high FA system without elevated curing temperature. The additional calcium introduced to the system by slag increases the reactivity of the system. The 60/40 FA/slag based geopolymer with PH solid has an induction period of 20 hours and low acceleration (first peak in Figure 4-9d) which corresponds to a slow precipitation of reaction products. The same system activated with AH presents a much shorter induction period (<10 hours). The delay induced by PH activator is only observable with low level of slag; with the slag contents higher than 50%, induction periods of the two systems (Figure 4-9(e-g)), activated with PH or AH, are similar. Due to the shorter induction period, it would be expected that geopolymers containing high fly ash would develop higher early stage compressive strength in the presence of AH than the geopolymers activated by PH.
4.3.3 Strength development

The different setting behaviours discussed above indicate that the early age strength properties of geopolymers activated by AH and PH could be different. Figure 4-10 shows the compressive strength value of geopolymer mortar after 1, 7 and 28 day of curing (at room temperature). The one day compressive strength of geopolymers made with both PH and AH increase when the slag content is increased, which agrees with the calorimetric results (1 to 30 hours). Furthermore, in the geopolymer mortar with a high FA content (>60%), AH activated mixes (associated with shorter induction period in the calorimetric analysis) showed higher one day strength than their PH-activated counterparts. High heat flow during the AH dissolution stage improve the fly ash reactivity, thereby, higher one day compressive strength.

The strength results after 7 and 28 days of curing show that PH activated geopolymers develop equivalent or higher compressive strength than geopolymers activated with AH activator. This is associated with slower but more uniform reaction kinetics. The heat generated by dissolution of AH activator leads to a rapid geopolymerisation on the surfaces of both the activator grains and the precursor grains, which covers them and inhibits further reaction. Bakharev [35] reported that geopolymers kept at lower temperature (23°C) before being heat cured show higher compressive strengths than the geopolymers subjected to immediate heat curing. The author observed that geopolymers subjected to lower initial heat showed consistent Si/Al ratios in different spots of the gel structure indicating uniform reaction kinetics. Moreover, Fernández-Jiménez [36] also
observed reduction of the degree of cross-linking (reduction in $Q^2$ and $Q^3$ silica species) in the geopolymers under elevated temperature curing. Although this rapid geopolymerisation results in reasonable early age strength gain, the amount of precursors available for further reaction is reduced, resulting in lower long term strength. The slower process involved in the PH-activated system, allows a better, continual dissolution of the precursor, hence, high strength at a later age. The quicker reactivity of the PH-activated, 100% slag based precursor (rather than slag and fly ash blends), does not present a high strength at 7 and 28 day which correlate previous hypothesis.
4.3.4 Reaction kinetics

The reaction kinetics and reaction product formation were studied for 50/50 (FA/S) blends activated by AH and PH in the different forms listed in Table 4-5. The corresponding calorimetric results are shown in Figure 4-11 and the compressive strength values after 1, 7 and 28 day of curing (at room temperature) are shown in Figure 4-12.

Figure 4-11 shows that for geopolymers activated with both AH and PH, the reaction is faster when the activators are first dissolved in water and stabilized at 23°C (i.e. PH-SN-REST and AH-SN-REST). AH-SN-REST and PH-SN-REST also showed similar kinetics (Figure 4-11) and compressive strengths (Figure 4-12). The reaction product formation periods for both PH-SD and PH-SN-IMED was delayed and was longer (by 2 hours) compared to PH-SN-REST. This corresponds to the low initial strength (1 day) and similar long term strength in the PH based binders (Despite initial at 28 days, all geopolymers containing PH activator showed the similar compressive strengths).

The 28 days strength development was lower for the geopolymer that contained the AH activator when it was mixed with water and used immediately with precursors (i.e. SD and IMED).
It is interesting that regardless of the form of activator, PH resulted in the same strength in the long term (28 days). It is possible that over much longer periods (e.g., one year or longer), the two activators (AH and PH) would result in similar final strength values. Nevertheless, early strength gain is an important practical issue and PH activator performs better in this respect. Geopolymer setting parameters and strength gain varies with the type of solid activator used. PH solid activator absorbs heat during the dissolution which cools the geopolymer binder and decelerates the initial geopolymerisation. This property allows PH activator to be used in hot environments (or hot weather) which tends to accelerate the reaction mechanisms. The retarding effect of PH solid can also be used in adjusting the setting in large scale geopolymer concrete production. This characteristic of AH activator can be used to increase the geopolymerisation in cold environment. AH solid based geopolymer is more appropriate in applications where the quick de-moulding (less than a day) is necessary and provides a solution for rapid concrete repairs. Figure 4-12(d) shows the relationship between the compressive strength and normalised heat. When geopolymer produces high heat, the resulting strength is also high.
This chapter investigated the room temperature setting characteristics and rate of workability loss of blended FA and slag geopolymers, synthesised using pentahydrate sodium metasilicate (PH) and anhydrous sodium metasilicate (AH) solid activators. The following conclusions are made from the study.

1. PH based geopolymer binders with identical fly ash and slag composition show slower setting compared to AH solid activators.
2. Geopolymers synthesised using PH has an initial endothermic reaction (heat absorption), whereas the geopolymer made using AH has an initial exothermic reaction (release of heat). The results indicate that the dissolution heat flow is the main factor contributing to the variations in the properties of fresh geopolymers made with AH and PH activators.
3. Other than the obvious practical advantages of using activators in solid form, type of solid activator enables adjustment of properties of the fresh binder.
4. The reaction kinetic upon alkali activation is retarded in hydrated solid activator (PH) based geopolymers (due to heat absorption) leading to a slow reaction mechanism, allowing a longer dissolution and better diffusion of ions from slag and fly ash particles. The slower reaction kinetics leads to high strength development at later age.
5. The heat dissipated during AH dissolution has accelerated the geopolymerisation of binders which contained high fly ash content (>60%), leading to high one day compressive strength.

4.5. References for chapter 4


Development of a geopolymer concrete with granular activator which is suitable for ambient temperature curing

5.1 Introduction

The use of granular (powder) alkali activator instead of the commonly used liquid activators and, the ability to achieve setting at room temperature (as opposed to elevated temperature curing) are significant factors towards making geopolymer convenient in practice. Appropriate blending of slag and fly ash enables the geopolymer concrete to be produced under ambient temperature curing. In addition, blended fly ash and slag geopolymer concrete has also shown superior mechanical properties and durability compared to pure fly ash or slag based geopolymers [1-4]. Even though, the fresh properties and early age strength development of fresh 100% fly ash based geopolymer concrete synthesised using liquid alkali activators have been extensively studied [5-9], the properties of blended fly ash and slag geopolymer concrete with granular alkali activator with ambient curing are yet to be fully investigated.

The induction period during geopolymerisation of the granular form alkali activator is higher than that of the solution form. This is because the granular activators have to dissolve in water before participating in reactions. Furthermore, the variation of the alkalinity within the concrete mix might also be high when using granular activators. Zeobond Group in Melbourne, Australia has also produced the E-Crete™ cement binder which is contained blends of fly ash, slag and alkaline activators [10]. Even though geopolymer with powder alkali activators has been used Zeobond Group for various purposes (small to medium sized construction), the formulations used in the binder (such as alkaline activator type and dosage used, mixing parameters and workability aids such as super-plasticisers) has not been disclosed due to proprietary issues [11].

Guerrieri and Sanjayan [12] used powder hydrous metasilicate in synthesising fly ash and slag based geopolymer and reported that the strength obtained were lower than that of liquid alkali activator based geopolymer systems. However, their study was more focused on fire performance of concrete than strength development. Collins and Sanjayan [13] produced 100% slag based geopolymer concrete using hydrous sodium metasilicate and anhydrous sodium metasilicate. They reported that 100% slag based...
geopolymer can achieve early workability and early age strength equal to OPC. These previous work has shown that there are many unexplored aspects of powder alkali activator based geopolymer concrete.

Blending of fly ash and slag enables to produce geopolymer concrete at ambient curing temperatures [14]. Ismail et al. [14] reported the compressive strength development of ambient cured blended fly ash and slag geopolymer concrete up to 90 days. The authors varied the slag percentage in the range 50-100% and reported an average 28 and 90 days compressive strengths of 60 and 65 MPa respectively. They observed an increase in the compressive strength of geopolymer concrete, with the increase of the slag content of the binder. However, their work was focused on durability of geopolymer concrete. Deb et al. [15] also showed that increasing the slag content in the binder, results in higher compressive strength. Since they used less than 30% slag in the geopolymer binder, they had to use a highly alkaline environment (14 M NaOH solution and sodium silicate solution) to achieve the setting at ambient curing temperature. Ismail et al. [14] also used a similar technique when producing geopolymers with lower slag content (<50% slag). It is known that, increasing alkali content in geopolymer concrete can lead to economic disadvantages and durability problems (i.e. alkali aggregate reaction and efflorescence) [16, 17]. Even though reported studies give an insight on the geopolymer concrete at ambient curing temperatures, the behaviour of fresh blended fly ash and slag geopolymer concrete containing granular alkali activator has not been fully understood.

This study investigates the workability and early age strength development in blended fly ash and slag geopolymer synthesised using ambient temperature curing and granular alkali activators. Firstly, the effect of granular alkali activator content on the rheology and early age strength development of blended fly ash and slag geopolymer. Next, the effect of fly ash to slag ratio on the strength development and rheology of geopolymer concrete in the presence of granular activator at ambient temperature curing is investigated. The relative humidity of the environment is identified as an important parameter in the production of OPC concrete. Therefore, the influence of relative humidity of the environment on geopolymer systems will also be discussed.
5.2 Materials and Methods

5.2.1 Precursor material

A class F fly ash and granulated ground blast furnace slag, with the chemical composition shown in Table 5-1 were used as the alumina-silicate precursor materials. The bulk chemical composition was obtained by X-ray florescence (XRF) analysis. The particle size distributions of fly ash and slag were obtained by using Cilas laser diffraction particle analyser are shown in Figure 5-1. 1-10 g of source material was dispersed in water in order to obtain the particle size. The main component of class F fly is SiO₂ (over 51%) whereas slag contains high amount of CaO (41.5%). It is important to note that fly ash contains twice as much Al₂O₃ as slag. The particle size analysis shows that both fly ash and slag have smaller particle sizes an attributes which is desirable for the geopolymer reaction. It also shows that class F fly ash has a higher content of fine particles compared to slag (Fly ash has 10% of very fine particles (<1 μm), while slag has about 2.5% of very fine particles (<1 μm)).

Table 5-1: Bulk chemical composition of alumina-silicate material

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>Fe₂O₃</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>Mn₃O₄</th>
<th>SO₃</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash</td>
<td>51.9</td>
<td>25.9</td>
<td>4.35</td>
<td>1.54</td>
<td>0.7</td>
<td>12.7</td>
<td>0.71</td>
<td>1.3</td>
<td>0.15</td>
<td>0.24</td>
<td>0.55</td>
</tr>
<tr>
<td>Slag</td>
<td>32.4</td>
<td>12.2</td>
<td>44.0</td>
<td>5.13</td>
<td>0.22</td>
<td>0.45</td>
<td>0.38</td>
<td>0.51</td>
<td>0.35</td>
<td>4.22</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Figure 5-1: Particle size distribution of (a) Slag (b) Fly ash
5.2.2 Activator

Granular sodium metasilicate penta-hydrate (28.7% Na₂O, 28.5% SiO₂ and 42.8% H₂O) solid activator was used to activate the precursors. Usage of solid alkali activators in geopolymer systems is less hazardous than commonly used liquid activators and more convenient for field applications. The amount of activator used was calculated to provide an alkali content of 4% Na₂O by mass of precursor materials.

5.2.3 Aggregate

A nonreactive basalt coarse aggregate of 14 mm nominal particle size and river sand were used in the geopolymer concrete mix. The particle density of coarse aggregates and the sand in saturated surface dry condition (SSD) was 2830 and 2620 kg/m³, respectively, and moisture absorption was 2.2 and 0.3% respectively. Figure 5-2 shows the cumulative particle size distribution of the aggregate.

![Figure 5-2: Particle size distribution of aggregates used in this study.](image)

5.2.4 Preparation of geopolymer concrete using solid alkali activator

All geopolymer concrete mixes in this paper were designed to realise the following parameters:

- Binder content: 400 kg/m³
- Fine aggregate content: 680 kg/m³
- Coarse aggregate content (10 mm): 450 kg/m³
- Coarse aggregate content (14 mm): 630 kg/m³

1. The above aggregate contents are then fine adjusted to obtain the desired mix volume (1 m³). This adjustment is called calculation of yield in the concrete.
After adjusting the aggregate quantities, following procedures are followed to find the aggregate free water.

2. The total moisture content in the aggregate was calculated by oven drying each sample (150°C for 6 hours).

3. The moisture content of the aggregate was obtained according to the AS1289 [18].

4. The free water from aggregate was calculated as:

   \[
   \text{Total free water (kg/m}^3\text{)} = (\text{total moisture content (\%)} - \text{moisture absorption (\%)}) \times \text{aggregate content (kg/m}^3\text{)}.
   \]

5. Total sand to be added to concrete mix (kg/m³) = (Total free water (kg/m³) + aggregate content (kg/m³)) × volume for the batch.

6. Water to be add to system (kg/m³) = Total water required - Sum of free water from all aggregate types. Total water required depends on the precursor used and the water to solid ration was maintained in the range 0.35-0.42. The crystalline water in the alkali activator was taken into the account when calculating water to solid ratio.

7. Sodium metasilicate pentahydrate granular activator was added into the geopolymer mix to obtain required alkali content (Na₂O% by mass of the precursors). Calculation is shown below;

   \[
   \text{Na}_2\text{O\%} = \frac{\text{Mass of granular activator} \times 0.287}{\text{Mass of fly ash and slag}}
   \]

Mixes in Table 5-2-Table 5-5 are used for selecting the appropriate parameters to obtain the target slump and early age strength development.

Table 5-2: Mix designs of geopolymer concrete used for determining the effect of alkali content on the slump and early age strength development.

<table>
<thead>
<tr>
<th>Mix</th>
<th>Fly ash (kg/m³)</th>
<th>Slag (kg/m³)</th>
<th>Alkali content (%)</th>
<th>14 mm aggregate (kg/m³)</th>
<th>10 mm aggregate (kg/m³)</th>
<th>Sand (kg/m³)</th>
<th>Water to solid ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>GP5050-6</td>
<td>200</td>
<td>200</td>
<td>3.7</td>
<td>628</td>
<td>449</td>
<td>670</td>
<td>0.40</td>
</tr>
<tr>
<td>GP5050-7</td>
<td>200</td>
<td>200</td>
<td>4.0</td>
<td>628</td>
<td>449</td>
<td>670</td>
<td>0.40</td>
</tr>
<tr>
<td>GP5050-8</td>
<td>200</td>
<td>200</td>
<td>4.3</td>
<td>628</td>
<td>449</td>
<td>670</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Table 5-3: Mix designs of geopolymer concrete with higher fly ash content (>70% Fly ash)

<table>
<thead>
<tr>
<th>Mix</th>
<th>Fly ash (kg/m³)</th>
<th>Slag (kg/m³)</th>
<th>14 mm aggregate (kg/m³)</th>
<th>10 mm aggregate (kg/m³)</th>
<th>Sand (kg/m³)</th>
<th>Water to solid ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5-4: Mix designs of geopolymer concrete with different fly ash and slag ratios (alkali content = 4%)

<table>
<thead>
<tr>
<th>Mix number</th>
<th>Fly ash (kg/m³)</th>
<th>Slag (kg/m³)</th>
<th>14 mm aggregate (kg/m³)</th>
<th>10 mm aggregate (kg/m³)</th>
<th>Sand (kg/m³)</th>
<th>Water to solid ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>GP7030</td>
<td>280</td>
<td>120</td>
<td>630</td>
<td>450</td>
<td>680</td>
<td>0.37</td>
</tr>
<tr>
<td>GP6040</td>
<td>240</td>
<td>160</td>
<td>633</td>
<td>452</td>
<td>680</td>
<td>0.38</td>
</tr>
<tr>
<td>GP5050</td>
<td>200</td>
<td>200</td>
<td>628</td>
<td>449</td>
<td>670</td>
<td>0.39</td>
</tr>
<tr>
<td>GP4060</td>
<td>160</td>
<td>240</td>
<td>642</td>
<td>459</td>
<td>685</td>
<td>0.39</td>
</tr>
<tr>
<td>GP100</td>
<td>0</td>
<td>400</td>
<td>655</td>
<td>468</td>
<td>690</td>
<td>0.41</td>
</tr>
</tbody>
</table>

Table 5-5: Mix designs of geopolymer concrete used for determining the effect of free water in aggregate to slump and early age strength development (alkali content = 4%)

<table>
<thead>
<tr>
<th>Mix</th>
<th>Fly ash (kg/m³)</th>
<th>Slag (kg/m³)</th>
<th>14 mm aggregate (kg/m³)</th>
<th>10 mm aggregate (kg/m³)</th>
<th>Sand (kg/m³)</th>
<th>Water to solid ratio</th>
<th>Free water in aggregate/total water</th>
</tr>
</thead>
<tbody>
<tr>
<td>GP5050-1</td>
<td>200</td>
<td>200</td>
<td>628</td>
<td>449</td>
<td>670</td>
<td>0.40</td>
<td>0.02</td>
</tr>
<tr>
<td>GP5050-2</td>
<td>200</td>
<td>200</td>
<td>628</td>
<td>449</td>
<td>670</td>
<td>0.40</td>
<td>0.13</td>
</tr>
<tr>
<td>GP5050-3</td>
<td>200</td>
<td>200</td>
<td>628</td>
<td>449</td>
<td>670</td>
<td>0.42</td>
<td>0.20</td>
</tr>
<tr>
<td>GP5050-4</td>
<td>200</td>
<td>200</td>
<td>628</td>
<td>449</td>
<td>670</td>
<td>0.41</td>
<td>0.50</td>
</tr>
</tbody>
</table>

The concrete mixing procedures used in the study is as follows: Firstly, aggregates and precursor materials (quantity obtained from the respective mix design) were mixed thoroughly for 1 minute. Next, water was added to the mix and mixing was continued for another 2 minutes. After that, alkali activator (solid form) was added into wet mix and mixed for additional 7 minutes to obtain consistent geopolymer concrete. Mixing was conducted using concrete pan mixer (70 Litre capacity). The workability of geopolymer concrete mix was measured using the standard slump test as prescribed in AS1012.3.1 [19]. The target slump of geopolymer concrete was 80-100 mm. All the concrete specimens were cast into the moulds as required for each test and compacted using steel rod and vibrator. After casting, the specimens were transferred into a standard fog room (23°C, 100% RH) where they were cured for 24 hours. Next concrete specimens were de-moulded and stored inside a fog room until the test date (During the
storing period in the fog room, the samples were covered with plastic sheets to avoid the water run through the sample).

To identify the suitable relative humidity level, two geopolymer mortar specimens were cast using mixes listed in Table 5-6 and stored at 23°C in three different relative humidity conditions as follows. Specimens used in Test 1–Test 3 were stored in a fog room (100% RH) at 23°C for seven days while specimens used in Test 4 – Test 6 were used stored in 23°C, 50% RH room (Table 5-7). The specimens were then exposed to different relative humidity and temperature as shown in the table. After 14 days, compressive strength of mortar specimens was measured according to ASTM C109 [20].

Table 5-6: Geopolymer mortar mix designs used for assessing the suitable relative humidity conditions

<table>
<thead>
<tr>
<th>Mix</th>
<th>Fly ash (g)</th>
<th>Slag (g)</th>
<th>Alkali content (%)</th>
<th>Sand to binder</th>
<th>Water to solid ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>M5050</td>
<td>500</td>
<td>500</td>
<td>4.0</td>
<td>2:1</td>
<td>0.40</td>
</tr>
<tr>
<td>M100</td>
<td>0</td>
<td>1000</td>
<td>4.0</td>
<td>2:1</td>
<td>0.42</td>
</tr>
</tbody>
</table>

Table 5-7: Curing procedure of mortar cubes

<table>
<thead>
<tr>
<th>Test Number</th>
<th>First week after casting</th>
<th>Second week after casting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td>23°C, 100% RH</td>
<td>23°C, 100% RH</td>
</tr>
<tr>
<td>Test 2</td>
<td>23°C, 100% RH</td>
<td>23°C, Sealed box inside fog room</td>
</tr>
<tr>
<td>Test 3</td>
<td>23°C, 100% RH</td>
<td>23°C, 50% RH</td>
</tr>
<tr>
<td>Test 4</td>
<td>23°C, 50% RH</td>
<td>23°C, 100% RH</td>
</tr>
<tr>
<td>Test 5</td>
<td>23°C, 50% RH</td>
<td>23°C, Sealed box inside fog room</td>
</tr>
<tr>
<td>Test 6</td>
<td>23°C, 50% RH</td>
<td>23°C, 50% RH</td>
</tr>
</tbody>
</table>

5.3 Results and discussion

5.3.1 Selecting granular alkali activator content

Alkali activator content is an important parameter in geopolymer binders that control the rheology and strength development of concrete. The alkali activator in solution form has immediate availability of alkali ions in the mix to react with precursor materials whereas in the granular alkali activator has comparative high initiation time. Ismail et al. [14] showed that when the alkali activator is in the liquid form, the ambient cured
blended fly ash and slag geopolymer concrete containing 4-6% alkali, achieve compressive strength in a range of 40-50 MPa.

Figure 5-3 shows the variation of the slump and early age compressive strength development of geopolymer concrete containing different alkali content. The results (Figure 5-3(b)) show that the compressive strength increases proportionally with the alkali content (when the alkali content is reduced by 0.3% the compressive strength decreases by 5 MPa while when the alkali content is increased by 0.3% the compressive strength increases by 5 MPa). Reduced alkali in geopolymer concrete (3.7% alkali) resulted low one day compressive strength (<10 MPa) creating difficulties in demoulding within 24 hours. On the other hand, increasing the alkali content in the geopolymer mix reduces the workability of geopolymer concrete (Figure 5-3(a)). Despite the fact that high alkali in the geopolymer result in high compressive strength, geopolymer concrete containing 4.3% Na₂O showed very low slump (<50 mm) and created problems during the casting process. Increasing alkalinity in the mix result in faster dissolution of precursor materials in turn monomer species can be formed at a higher rate making the polymerisation more rapid [21].

Additionally, the geopolymer binders containing high alkali content can form efflorescence (sodium bicarbonate white crystal powders) which is harmful for the stability of geopolymer network [16]. The binders containing high alkali content also reacts with aggregates to form alkali-aggregate expansive reaction gel which degrades concrete (please see chapter 8 for more details). Geopolymer concrete prepared using 4% alkali content in the granular form achieved 45 MPa compressive strength in 28 days which is similar to the strength obtained for the geopolymer concrete synthesised using alkali in soluble form [3, 14]. Considering the strength development, slump and durability of geopolymer concrete, the 4% alkali in granular form is used to activate fly ash and slag throughout the study.
Figure 5-3: Effect of alkali on the (a) Slump (b) early age compressive strength of geopolymer concrete (alkali content= Na₂O mass/ binder content (fly ash and slag). Mix designs are given in Table 5-2

5.3.2 Selecting binder composition for ambient cured geopolymer concrete

Due to environmental and economic advantages, usage of high fly ash content in geopolymer is highly desirable. However, it is well known that the geopolymers with higher than 70% fly ash content has adverse setting characteristics [14] and require higher alkali content to set at ambient curing temperature or requires elevated temperature curing [5, 14, 15].

Figure 5-4 shows the early age strength development of geopolymer concrete containing slag percentages in the range 30 – 100%. The figure shows that the one day compressive strength of the concretes increases with the slag content of the binder. Calorimetric analysis of geopolymer pastes with varying slag content (please see chapter 6.3.1 for more details) show that when the slag content is increased, the alkali activation occurs earlier or the induction period is lower (100% slag has induction period lower than 10 hours). High slag based geopolymer produces C-A-S-H and C-S-H phases in a faster rate whereas high fly ash based geopolymer has combination of C-A-S-H and N-A-S-H phases which require longer time to form at ambient curing temperatures [4, 14]. Addition to this, geopolymer containing higher fly ash content had high porous structure compared to high slag based geopolymer resulting in lower initial compressive strength [14].

GP5050 geopolymer concrete shows the maximum 7 days and 28 days compressive strength among all the geopolymer concretes tested. The calorimetric analysis also
showed that the geopolymer with more than 50% slag produces higher heat during the reaction which can results in surface geopolymerisation. This process can cover the precursor materials and retard the continual geopolymer reaction which leads to slower strength development (after one day) [5]. Higher heat during the geopolymerisation may also lead to thermal cracking which can result in binders with reduced compressive strength.

Figure 5-4: Strength development of geopolymer concrete with binder composition

Geopolymers with higher than 70% fly ash content was not used in the above analysis as it is known that such binders have adverse setting characteristics and require higher alkali content to set at ambient curing temperature or requires elevated temperature curing. To confirm this geopolymer samples were casted using 90/10 (FA/S) (GP9010-1). It was observed that the samples disintegrate in a fog room due to the slower hardening process in concrete.

It was also observed that achieving adequate workability was difficult in samples with 70% fly ash content. To further analyse this behaviour of geopolymer concrete containing 70% fly ash was produced with 0.37 (GP7030-2) and 0.40 (GP7030-3) water to solid ratios (mix designs listed in Table 5-3). GP7030-2 mix showed very high initial slump (>200 mm). However, the slump of the above concrete mix reduced rapidly (reduced to 40 mm within 5 minutes) making the casting process difficult. The fast reduction of slump is related to the higher alkali concentration around the precursor materials due to low water content. GP7030-3 mix also showed very high initial slump (>200 mm). However, the rate of slump loss of this mix was very low and it did not achieve initial setting within the first hour (60 mm slump was observed even after 5 hours). The early age compressive strength of 70/30% FA/Slag geopolymer concrete is
shown in Figure 5-6. The results show that the one day compressive strength of both tested geopolymer concrete mixes were relatively low (<5 MPa). Therefore, the de-moulding of concrete specimens was difficult and outer layers of concrete were washed away during the moist curing. De-moulding after at least one day is very important in practice which is a main requirement in precast concrete. The 70/30 FA/Slag based geopolymer concrete with lower water content (i.e. water to solid ratio = 0.37) had lower compressive strength compared to geopolymer with 0.40 water to solid ratio. The sudden slump loss of geopolymer concrete with low water content creates honey combs in geopolymer concrete, reducing the compressive strength (Figure 5-5).

![Figure 5-5](image)

Figure 5-5 (a) Honey comb due to sudden slump loss of (b) reduction of uniformity of geopolymer

![Figure 5-6](image)

Figure 5-6: Compressive strength development of geopolymer concrete containing 70% fly ash at different water to solid ratio (mix designs listed in Table 5-3)

Due to the lower one day strength and inability to control workability, geopolymers containing more than 30% slag content (40%, 50%, 60% and 100% slag) were used in the remainder of this thesis in evaluating the long term properties of concrete.
Water to solid ratio is another important factor that controls the fresh and harden properties of OPC concrete. Geopolymer concrete made according to the mix designs given in Table 5-5 were used to analyse the effect of water to solid ratio on properties of geopolymer concrete. According to the slump values shown in Figure 5-7(a), free water in aggregate has higher influence on the workability of geopolymer concrete than the total water to solid ratio of concrete. It was observed that two geopolymer concrete mixes with the identical water to solid ratio (i.e. 0.40), presented different slump values due to the difference in free water content of aggregate. When the free water content of the aggregate is higher, lower amount of water is added into the mix externally to get the required water to solid ratio. The above result shows that in geopolymer concrete systems, the free water in aggregates may not be effective as much as adding water externally in terms of workability of the binder. Therefore, in geopolymer concrete production, it is important to avoid using aggregate with higher free water content.

Even though free water of aggregate affects the workability of concrete, it does not significantly influence the compressive strength of the geopolymer (Figure 5-7 (b)) for small scale specimens. The average compressive strength of GP5050-4, which contained the highest free water of aggregates, was slightly higher than the others. Even though the compressive strengths has not been significantly affected by the variation in workability for small scale specimens, it is well known that low workability would lead to anomalies in compaction in large OPC concrete structures which could significantly affect the strength of such elements [15].
5.3.3 Effect of relative humidity on the strength development of geopolymers

Concrete exposed in dry environment can have lower reaction product formation, higher shrinkage and lower bond with aggregate than concrete in well-saturated environments [22]. These parameters influence the mechanical properties of harden concrete as well as the durability of concrete. To determine the effect of the relative humidity on the compressive strength of geopolymers, geopolymer mortar specimens (mix designs given in Table 5-5) were exposed to different relative humidity levels according to the criterion shown in Table 5-7. Figure 5-8 shows the variation of the compressive strength of geopolymer mortar exposed to different relative humidity conditions.

The result show that M5050 samples kept at fog room for a week and transferred to the sealed box (Test 2) exhibit similar compressive strength to samples cured in the fog room for entire curing period (Test 1). When M5050 specimens were transferred to lower humid environment after wet curing (Test 3), there is a slight reduction in the strength compared to specimens in Test 1. However, M100 specimens did not show compressive strength variation in Test 1- Test 3.

On the other hand, M5050 specimens stored in 50% RH environment for one week and then transferred to a fog room for the second week curing (Test 4) showed similar compressive strength to the samples in Test 1. When M5050 specimens were transferred to a sealed box from low humid room, there is slight improvement in the compressive
strength compared to Test 1. Moreover, M5050 specimens were cured in a low humid environment for more than one week resulted strength reduction (Test 6). Again, M100 specimens show an identical compressive strength in Test 4- Test 6 tests and the compressive strength of these specimens are similar to that of in the Test 1-Test 6.

The results show that the blended fly ash and slag geopolymer binder needs moist environment to obtain high early age strength. This is because adequate moisture increases the ion movement capacity and poly-condensation process in the geopolymer synthesis [23]. Moreover, lower humidity can accelerate the carbonation of geopolymer mortar leading to a reduction in the alkalinity of the [24]. Reduced alkalinity retards the dissolution of precursor material and geopolymerisation process. Collins and Sanjayan [25] reported that alkali activated binders are very sensitive to curing regimes and change the pore size distribution of the binders. The authors found that the air cured geopolymer samples had higher porosity than that of sealed geopolymer samples.

100% slag based geopolymer binders undergoes larger shrinkage strain than blended fly ash and slag geopolymer in low humid environment (detailed analysis is provided in chapter 6). Influence of the humidity on the compressive strength development in the early age of 100% slag is not significant [26]. Both blended fly ash and slag and 100% slag based geopolymer binders achieve high strength in moist environment therefore, the geopolymer concrete will be stored in a saturated environment throughout the study.

![Effect of relative humidity on the compressive strength of geopolymer binder](image.png)

Figure 5-8: Effect of relative humidity on the compressive strength of geopolymer binder
5.4 Concluding remarks

1. Blended fly ash and slag geopolymer, synthesised with low alkali (4%) and ambient curing, require at least 40% slag content to achieve one day compressive strength adequate for de-moulding of the specimens. Geopolymer concrete with lower than 40% slag also showed difficulty in controlling the workability.

2. Blended fly ash and slag geopolymer concrete is highly sensitive to the alkali content. When alkali content of the binder is increased by 0.3% the compressive strength of the geopolymer concrete is increased by 5 MPa.

3. Relative humidity in the storing environment has greater influence on the compressive strength of blended fly ash and slag geopolymer than 100% slag based geopolymer. Variation of compressive strength in 100% slag geopolymer is only 5 MPa under relative humidity conditions used in this study while blended geopolymer has this value 20 MPa.

4. Similar to OPC or blended concrete, workability of blended fly ash and slag geopolymer is affected by the free water content of the aggregate.

5.5 References for chapter 5


6. Long term mechanical, shrinkage and creep properties of ambient temperature cured geopolymer concrete

6.1. Introduction

There has only been a limited discussion on engineering properties of ambient cured fly ash and slag based geopolymer concrete in literature. Ismail et al. [1] reported the compressive strength development of ambient cured blended class F fly ash and slag geopolymer concrete up to 90 days. The authors varied the slag percentage in the range 50-100% and reported an average 28 and 90 days compressive strengths of 60 and 65 MPa respectively. However, the authors focused more on durability of blended fly ash and slag geopolymer concrete hence other mechanical properties were not discussed (i.e. shrinkage, modulus of elasticity, flexural strength). Deb et al. [2] produced geopolymer concrete under ambient temperature curing using 80/20 FA/Slag blend and reported average compressive strength of 50 and 55 MPa in 28 and 180 days. In the same study, the authors presented that geopolymer concrete achieved a tensile strength of 5 and 6 MPa in 28 and 90 days respectively. Thomas et al. [3] reported modulus of elasticity and poisson’s ratio of ambient cured 100% slag based geopolymer concrete as 34 GPa and 1.29 respectively at 28 days. This chapter reports mechanical properties of geopolymer concrete up to 600 days.

Studies focused on short term and long term properties are missing in the literature [4-8]. Lloyd et al. [9] reported that 100% fly ash or blended fly ash and slag geopolymer did not show any strength reduction upon aging. In the study by Lloyd et al. [9], the specimens were kept at 95°C for accelerated the age effect in geopolymer, which does not fully explain the variations of the strength upon aging in ambient cured geopolymer concrete.

The volume change of concrete with time is an important property that can lead to concrete cracking and needs to be fully investigated before using a new binder in structural and non-structural applications. Shrinkage and creep are time-dependent properties of concrete which cause volume change of concrete and cracking. Shrinkage is the contraction of hardened concrete due to the loss of capillary water or chemical reorganisation of the structure. Shrinkage increases the internal tensile stresses of concrete which leads to concrete cracking and shrinkage warping [10]. Understanding of volume change due to shrinkage in concrete is highly important in designing concrete

133
structures with adequate degree of serviceability. Drying shrinkage of geopolymer concrete can be affected by the precursor materials used in synthesising the geopolymer concrete. It was previously reported that 100% fly ash based geopolymer concrete has lower drying shrinkage compared to OPC concrete [6] while 100% alkali activated slag based geopolymer concrete has higher drying shrinkage compared to OPC concrete [11]. Deb et al. [2] reported a shrinkage strain of blended fly ash and slag geopolymer concrete in the range $450 - 800 \times 10^{-6}$ at 180 days. However, their geopolymer binders contained only lower slag content (<30%).

Creep of the concrete can be defined as the deformation of a structure under a sustained load along the loading axis. Creep is one of the main factor that should be considered during the design of concrete structures to minimize the long term deformation of structures [12]. Wallah et al. [13] and Sagoe-crentsil et al. [14] reported that the creep of 100% fly ash based geopolymer concrete is lower than that of OPC concrete while Un et al. [15] reported that geopolymer concrete synthesised using higher slag content can have higher creep than OPC concrete. The above studies indicate that shrinkage and creep of geopolymer concrete can vary significantly according to the binder composition. Therefore, it is important to obtain comprehensive understanding of creep and shrinkage in ambient cured geopolymer concrete containing both slag and fly ash, which has been not discussed in literature.

The most important proprieties that influence the serviceability of concrete are: compressive strength, tensile strength, modulus of elasticity, shrinkage and creep [12]. In this study, the compressive strength of geopolymer concrete was assessed over 600 days. The tensile strength and modulus of elasticity of geopolymer concrete were also analysed in long term tests. The measured flexural strength and modulus of elasticity of geopolymer concrete was compared with AS3600 and ACI318 standards in order to establish the applicability of existing standards to fly ash and slag based geopolymer concrete. The study also evaluates the deformation characteristics of geopolymer concrete over time using creep and shrinkage measurements of concrete.
6.2. Materials and Methods

6.2.1. Precursor material

Class F fly ash (FA) and granulated ground blast furnace slag (Slag), were used as the alumina-silicate precursor materials. The chemical composition and particle size analysis of the two precursor materials can be found in section 5.2.1.

6.2.2. Activator

Granular sodium metasilicate penta hydrate (28.7% Na$_2$O, 28.5% SiO$_2$ and 42.8% H$_2$O) solid activator was used to activate the precursors. Usage of solid alkali activators in geopolymer systems is less hazardous than commonly used liquid activators and more convenient for field applications. The amount of activator used was calculated to provide an alkali content of 4% Na$_2$O by mass of precursor materials.

6.2.3. Aggregate

A basalt coarse aggregate of 14 mm nominal particle size and river sand were used in the geopolymer concrete mix. The particle density of coarse aggregates and the sand in saturated surface dry condition (SSD) was 2830 and 2620 kg/m$^3$, respectively, and moisture absorption was 2.2 and 0.3% respectively. Figure 6-1 shows the cumulative particle size distribution of the aggregate.

![Figure 6-1: Particle size distribution of aggregates used in this study.](image)

6.2.4. Preparation of geopolymer concrete using solid alkali activator

Concrete mixes listed in Table 6-1 were used to measure the engineering properties of concrete and designated as 60/40 FA/Slag – 0/100FA/Slag while concrete mixes listed
in Table 6-2 were used to analyse the creep behaviour. To study effect of water content on the shrinkage on geopolymers 50/50 FA/Slag geopolymers were produced using 0.40 and 0.42 water to solid ratios. Mix designs used for creep tests were slightly different than the designs used for other tests. These mix designs were selected in order to have higher variation in slag content in geopolymers. 100% fly ash concrete mix was not used in this analysis as pure fly ash based geopolymer requires elevated temperature curing (section 5.3.1).

Table 6-2: Mix designs of geopolymer concrete used for creep test

<table>
<thead>
<tr>
<th>Mix number</th>
<th>Fly ash (kg/m³)</th>
<th>Slag (kg/m³)</th>
<th>14 mm aggregate (kg/m³)</th>
<th>10 mm aggregate (kg/m³)</th>
<th>Sand (kg/m³)</th>
<th>Water to solid ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>50/50 FA/Slag</td>
<td>240</td>
<td>160</td>
<td>633</td>
<td>452</td>
<td>680</td>
<td>0.38</td>
</tr>
<tr>
<td>30/70 FA/Slag</td>
<td>200</td>
<td>200</td>
<td>628</td>
<td>449</td>
<td>670</td>
<td>0.39</td>
</tr>
<tr>
<td>0/100 FA/Slag</td>
<td>0</td>
<td>400</td>
<td>655</td>
<td>468</td>
<td>690</td>
<td>0.41</td>
</tr>
</tbody>
</table>

The concrete mixing procedures used in the study are as follows: firstly, aggregates and precursor materials (quantity obtained from the respective mix design) were mixed thoroughly for 1 minute in a concrete pan mixer. Next, water was added to the mix and mixing was continued for another 2 minutes. After that, alkali activator (granular form) was added into wet mix and mixed for additional 7 minutes to obtain consistent geopolymer concrete. The workability of geopolymer concrete mix was measured using the standard slump test as prescribed in AS1012.3.1 [16]. The target slump of geopolymer concrete was 80-100 mm. All the concrete specimens were cast into the moulds as required for each test and compacted using steel rod and vibrator. After casting, the specimens were transferred into a standard fog room (23°C, 100% RH) where they were cured for 24 hours. Next concrete specimens were de-moulded and
stored inside a fog room until the test date (During the storing period in the fog room, the samples were covered with plastic sheets to avoid water running through the sample).

**Compressive strength**

Geopolymer concrete cylinders (100×200 mm) were stored in standard fog room until the compressive strength test was commenced. Average compressive strength \( f'_{c} \) of the concrete cylinders was obtained according to the AS 1012.9 [16]. Three specimens from each mix were used in testing. The compressive strength of geopolymer concrete was measure up to 600 days.

**Flexural strength**

Geopolymer concrete prisms (75 × 75 × 380 mm) were stored in standard fog room until the flexural strength test was commenced. The average flexural tensile strength \( f_{ct,f} \) of geopolymer concrete was measured according to AS 1012.11 [17]. The flexural strength of geopolymer concrete was measured up to 180 days.

**Modulus of elasticity and poisson’s ratio**

Geopolymer concrete cylinders (100×200 mm) were stored in standard fog room until the modulus of elasticity test was commenced. Stress-strain behaviour of geopolymer concrete was obtained using calibrated Linear Voltage Differential Transducers (LVDTs) attached to the cylindrical specimens in axial and radial directions (see Figure 6-2). Modulus of elasticity of geopolymer concrete was measured at two ages of 28 days and 600 days. The hysteresis loop was obtained by varying the load on each specimen to 40% of the 28 days compressive strength and then unloading for three complete cycles. The loading and unloading was done at a rate of 20 MPa/min.
Shrinkage

Geopolymer concrete prisms (75× 75× 285 mm) were stored in the fog room for 7 days and transferred into drying room (23°C, 50% RH) to accelerate the drying shrinkage. Length change of prisms was measured up to 600 days. The shrinkage test was conducted as prescribed in AS 1012.13 [18].

Creep

Geopolymer concrete cylinders (150× 300 mm) were cast and cured in fog room for 7 days. Samples were then transferred into 23°C, 50%RH room and kept there for 28 days. At 28 days, geopolymer concrete samples were set up in creep jigs and loadings were applied taking 40% of maximum 28 day compressive strength of cylinders. The creep test was carried out according to the AS 1012.16 [19]. Creep strain of each concrete was obtained by subtracting the shrinkage strain in the concrete under similar conditions.

6.3. Results and discussion

6.3.1. Long term compressive strength development of geopolymer concrete

The compressive strength results of geopolymer concrete containing different fly ash to slag ratios (mix designs given in Table 6-1) are shown in Figure 6-4.

The one day compressive strength of all tested geopolymer concrete samples was between 5-10 MPa. One day compressive strength of geopolymer concrete increased with the slag content, where 100% slag based geopolymer concrete has the highest one
day compressive strength (15 MPa). This is consistent with results reported in the literature.

The isothermal calorimetric analysis of the geopolymer paste samples was carried out to analyse the reaction product formation phase of each binder. The heat flow during the first hour of reaction is usually associated with the dissolution of the source materials, the peak produced after that is due to geopolymerisation [20]. Therefore, the heat flow only during 5-43 hours is presented (Figure 6-3). The calorimetric results show that the peak is higher in the binders contained higher FA. The high heat flow indicates the formation of high amount of reaction products, thereby high strength. This is in agreement with the previous studies which show additional calcium introduced to the geopolymer systems by slag increases the reactivity of the system in the early age [21, 22]. These calorimetric results explain the high one day compressive strength in the geopolymer binders with high slag content.

![Figure 6-3: Isothermal calorimetric analysis of the geopolymer paste samples with varying fly ash to slag ratio.](image)

The long term strength result show that the geopolymer concrete (on average) developed 60% of the 600 day compressive strength (60 MPa) within a week while 85% of the compressive strength is achieved at the end of the first month. The rate of strength development of the geopolymer concrete is slower after one month where compressive strength of geopolymer concrete increased by only 10 MPa in time between 28 days to 365 days. The results show that 60/40 FA/Slag, 50/50 FA/Slag and
40/60 FA/Slag satisfy the requirement for 50 MPa grade concrete according to AS 1379 standard [21]. Additionally, the measured compressive strength of geopolymer concrete is similar to the values reported by Ismail et al. [1] for geopolymer with similar binder compositions containing metasilicate alkali activator solution compared to granular alkali activator used in the present study. It is important to mention that Ismail et al. [1] only report strengths up to 90 days. Most importantly, in the time between 365 days to 600 days, geopolymer concrete did not show degradation in the compressive strength and all the geopolymer concrete samples remained at a constant compressive strength level of around 60 MPa.

According to the compressive strength results in Figure 6-4, after 7 days, compressive strength of blended fly-ash and slag geopolymer was slightly higher than the strength of pure slag based concrete. From chapter 4 and Figure 6-3 it is clear that geopolymers containing higher slag produce higher heat than geopolymers containing higher fly ash indicating formation of larger amount of slag. This leads to the formation of geopolymer gel on the surface of precursor materials partially covering the fly ash and slag particles retarding the geopolymerisation [4]. However, with extended curing, 100% slag based geopolymer concrete also achieved similar compressive strength (in 600 days) as those with fly ash. This can be because the partially reacted particles can also participate in the geopolymer network given longer period of time.

Figure 6-4 shows that, at 600 days compressive strength of 60/40 FA/Slag, 50/50 FA/Slag and 40/60 FA/Slag are similar. 40/60 and 50/50 FA/Slag based geopolymers showed the highest strength during first year. 60/40 FA/Slag based geopolymer had the maximum strength at 100 days and thereafter compressive strength is slightly reduced. Ismail et al. [1] found that the main reaction phase in geopolymer with slag percentage in the range of 50-100%, is calcium silicate hydrated gel (C-S-H) and calcium aluminate silicate hydrate (C-A-S-H). Moreover, in these binders, the number of reaction product formations and degree of cross-linking increased with extended curing time. The geopolymer with lower than 50% slag has a combination of C-A-S-H and N-A-S-H reaction products, and the reaction product formation and development of additional cross-linking of the geopolymer is slower compared to geopolymer containing higher slag (>50%).
The results show that fly ash blended and 100% slag based geopolymer did not show significant strength variations after one year. This reveals that geopolymer concrete synthesised using fly ash and slag under ambient curing has stable compressive strength within the test period of two years.

![Graph showing compressive strength development of geopolymer concrete up to 600 days](image)

**Figure 6-4: Compressive strength development of the geopolymer concrete up to 600 days**

### 6.3.2. Flexural strength of geopolymer concrete

The strength of concrete in flexure is an important parameter in both structural and non-structural applications. The flexural tensile strength is required to determine the extent
of cracking due to applied load and deformation [12]. Figure 6-5 (a) shows the flexural strength of geopolymer concrete prisms at two different ages i.e. 28 and 180 days.

The results show that the flexural strength increases slightly with the slag content in 28 day cured geopolymer concrete specimens. However, in the specimens containing high slag content (40/60 FA/Slag and 0/100 FA/Slag), the 180 day flexural strength was lower than the strength achieved at 28 days. This may be due to the higher shrinkage strain observed in high slag based geopolymer concrete (more than 50% slag) than shrinkage strain in concrete containing high fly ash (see shrinkage results in section 6.3.4). The higher shrinkage value in high slag based concrete leads to micro-cracks inside the concrete which may reduce the flexural strength of concrete. The micro-structure analysis presented in section 6.3.6 shows that 100% slag has higher amount of micro-cracks compared to blended fly ash and slag geopolymer binder. During the flexural tensile strength test the capability of extending the micro-cracks is greater compared to compressive strength test as the load is applied as a point load (effective area for the load is lower compared to compressive strength test). The flexural strength with the OPC concrete in AS 3600 standard [23] was compared. The equation in AS 3600 standard [23] is shown in Equation 1.

\[
f_{ct.f} = 0.6\sqrt{f'_c} \tag{1}
\]

In order to access the suitability of using the above mentioned equation in predicting flexural strength of geopolymer based concretes, the predicted and the measured flexural strength values are plotted in Figure 6-5 (b). The results show that the predictions made by the existing standards underestimated the flexural strength of geopolymer concrete. Hence, the existing equations are not suitable to predict the flexural strength of blended fly ash and slag or pure slag based geopolymer concrete. Similar observations were made by Sofi et al. [5] for pure fly ash based geopolymer concrete. In this research, liquid alkali activators (NaOH and Sodium silicate solutions) and elevated temperature curing were used. The above results also show that all the geopolymer mixes tested has higher flexural strengths than indicated by the AS 3600 standard [23].
Stress-strain behaviour of geopolymer concrete

Stress-strain behaviour of a concrete is needed to estimate the stiffness of concrete members and determine the internal actions during the loading. Modulus of elasticity is the parameter that quantifies the stiffness of the concrete that also estimates the instantaneous deformation of concrete and strain induced by imposed stresses during the loading [12]. Stress-strain relationship of geopolymer concrete is not fully understood, in particular the stress-strain relationship for more than one year old geopolymer concrete.

Figure 6-6 shows the axial and radial stress-strain curves of geopolymer concrete containing different binder compositions at 28 days. The axial or radial stress-strain relationships for different compositions are similar. Figure 6-6 (a) and (b) also show the hysteresis loop for 60/40 FA/Slag and 50/50 FA/Slag geopolymer concrete. It can be seen that, stress-strain curves of geopolymer concrete specimens followed the same path in loading and unloading, indicating that the stiffness of fly ash and slag geopolymer concrete is not damaged due to cyclic loading.

Moreover, the ascending branch of the stress-strain curve of geopolymer concrete is similar to that reported for similar grade OPC concrete [3], where the axial strain of concrete at the peak stress level is in the range 2.1 - 2.5×10⁻³ [24]. However, in geopolymer, after stress-curve passed the peak stress, the failure is more sudden and explosive rather than continual softening (the loading has to stop immediately when it is started to explode to prevent damage to LVDTS). It has been reported that the sudden failure observed in fly ash and slag based geopolymer concrete is associated with the micro-cracks formed in geopolymer concrete in the presence of slag compared to OPC.
Brittleness of blended fly ash and slag geopolymer concrete may be associated with the cross linked three dimensional framework. In general cross-linked structures have lower ductility than non-cross linked C-S-H phases (in OPC) [7, 25, 26]. The corresponding stress-strain graph of pure slag based geopolymer concrete showed lower loading capacity than blended fly ash and slag geopolymer concrete which correlates with the compressive strength results discussed in the previous section.

![Stress-strain graphs](image-url)

Figure 6-6: Axial and radial stress-strain behaviour of (a) 60/40 FA/Slag (b) 50/50 FA/Slag (c) 40/60 FA/Slag (d) 0/100 FA/Slag

The stress and strain values in the elastic stage can be used to determine the modulus of elasticity of concrete. As prescribed in AS 1012.17 [27] the following equations (Equations 2 and 3) were used to calculate the modulus of elasticity and Poisson’s ratio of each concrete type:

\[
E \ (\text{Modulus of elasticity}) = \frac{(G_2 - G_1)}{(\varepsilon_2 - 0.00005)} \quad (2)
\]
Where $\varepsilon_4 =$ radial strain at 40% loading point, $\varepsilon_3 =$ radial strain coincides with axial strain 0.00005 and $\varepsilon_2 =$ axial strain at 40% loading point. $G_2$ and $G_1$ are stress of concrete at 40% loading point and stress of concrete when the axial strain is 0.00005 respectively.

Figure 6-7 presents the calculated elastic modulus and poisson’s ratio of geopolymer concrete after 28 and 600 days. At 28 days (Figure 6-7 (a)), ambient cured geopolymer concrete have modulus of elasticity of 30-35 GPa. There is a slight improvement in the modulus of elasticity of concrete with the increase of the slag content. However, 100% slag based geopolymer concrete does not show the highest modulus of elasticity (40/60 FA/Slag has the highest modulus of elasticity).

The modulus of elasticity obtained for these geopolymer concrete systems at 28 days, which contained granular alkali activator, is similar to modulus of elasticity reported by Thomas et al. [3] for ambient cured 100% slag based geopolymer concrete contained 4% alkali in liquid form. Previous studies on elevated temperature cured geopolymer concrete concluded that lower modulus of elasticity (less than 30 GPa) of geopolymer concrete [5, 6]. Duxson et al. [28] suggested that the microstructure, composition and degree of geopolymerisation have a significant effect on the elastic modulus of geopolymer concrete rather than its compressive strength. The disparity between ambient cured and heat cured geopolymer may be attributed to slower reaction mechanism in the ambient cured geopolymer concrete which can produced uniform and denser microstructure leading to high stiffness.

The present study and Thomas et al. [3] show that the modulus of elasticity of ambient cured geopolymer concrete is in the range of the modulus of elasticity of OPC concrete [3]. Most importantly, this study indicates that the addition of granular alkali activator instead of liquid alkali activators produced geopolymer concrete with similar stiffness. This suggests the different curing regimes can result in different modulus of elasticity.

Figure 6-7 (a) shows that stiffness of geopolymer concrete does not degrade with maturity of the concrete, indicating that geopolymer can get similar degree of serviceability after one year. Geopolymer concrete containing adequate content of slag
complete the reaction process within first month, therefore the compressive strength and modulus of elasticity of concrete remained in similar.

Figure 6-7 (b) shows the poisson’s ratios of geopolymer concrete at 28 and 600 days. At 28 days, poisson’s ratios of geopolymer concrete are in the range of 0.15-0.18 which is similar to that of OPC concrete. After 600 days, the poisson’s ratios of geopolymer concrete also show similar values as in 28 days. The poisson’s ratios obtained for geopolymer concrete in our experiments is slightly higher than that obtained by Thomas et al. [3] for ambient cured alkali activated slag concrete.

![Figure 6-7: (a) Elastic modulus (b) poisson’s ratio of geopolymer concrete containing different slag content (mix designs are given in Table 6-1)](image)

The stiffness or elastic behaviour of geopolymer concrete depends on the packing efficiency of the reaction products and the binder chemistry. The main reaction products
Previous research has revealed that the C-S-H gel formed in alkali activated slag at
20°C (humid chamber) can have elastic modulus in the range of 12-48 GPa while N-A-
S-H have constant elastic modulus of around 17-18 GPa which is independent from the
alumina-silicate material and curing regime used [29]. Moreover, the same study, found
that modulus of elasticity of C-S-H remained the same after substitution of aluminium
ions (i.e. C-A-S-H) [29]. The calculated modulus of elasticity of blended fly ash and
slag geopolymer concrete is in the range of 30-34 GPa. This result is in agreement with
the reported values for the gel phases of the blended fly ash and slag geopolymer which
have higher content of C-A-S-H phases than N-A-S-H.

Australian standards also provide methods to predict the elastic modulus of concrete
binders which are validated against the values obtained for OPC concrete. However, the
applicability of the prediction using these equations for blended fly ash and slag
geopolymer concrete has to be established. To predict the modulus of elasticity of
geopolymer concretes equations provided in AS3600 [23] standard and ACI 318-08
[30] were used. The standards used the compressive strength ($f_c$ MPa) and the density
($\rho$ kg/m$^3$) of concrete as inputs (see Equation 4).

\begin{align*}
E_c &= \rho^{1.5} \left(0.024\sqrt{f_c} + 0.12\right) \\
E_c &= 4700 (f_c)^{1/2}
\end{align*}

The predicted and the measured elastic modulus of geopolymer concrete specimens are
shown in Figure 6-8. The figure shows that the measured moduli of elasticity in 28 and
600 days have closer relationship with both AS3600 and ACI 318. The above results
show that the existing standards used predictions of the modulus of elasticity ambient
cured blended fly ash and slag geopolymer concrete in 28 days are in the same range.
6.3.4. Shrinkage of geopolymer concrete

Shrinkage of concrete can occur due to drying of concrete or chemical reorganization of the structure. Shrinkage increases the internal tensile stresses of concrete which leads to concrete cracking and warping [10, 12]. Understanding of volume change due to shrinkage in concrete is highly important in designing concrete structures with adequate degree of serviceability. Shrinkage of OPC concrete is known to depend on the various factors including mix proportions, water to cement ratio, mixing and curing regimes and humidity of the environment.

In order to evaluate the effect of water to solid ratio of the binder on shrinkage, the author made geopolymer concrete specimens with 50% fly ash and 50% slag (GP5050EN) and used two water to solid ratios (0.40 and 0.42). The shrinkage and mass loss values up to 600 days, measured according to the standard [18], are shown in Figure 6-9 (a) and (b) respectively. According to the results shown in Figure 6-9 (a), geopolymer concrete has very high rate of volume shrinkage during the first week. Concrete in drying environment, initially evaporates water from macros pores at a high rate of evaporation [31]. As a result, the concrete specimen undergoes high mass loss as indicated in Figure 6-9 (b) and consequently the volume shrinks rapidly. During the period between 7 and 100 days the volume of geopolymer concrete continues to decrease rapidly, but at a slightly slower rate compared to the first week. The evaporation of the moisture occurs from mesopores within this period [31]. After 100 days the geopolymer specimens showed linear shrinkage at a much slower rate (compared to initial rate) and the shrinkage strain of blended fly ash and slag geopolymer concrete at 600 days was around $900 \times 10^{-6}$. It is worthwhile to note that
while the mass loss of geopolymer concrete follows the general trend as the shrinkage of concrete, the shrinkage did not show a direct correlation with the water content in the binder. Similar shrinkage values were observed for geopolymers with water to solid ration in the range 0.40 to 0.42.

The shrinkage of blended fly ash and slag geopolymer at varying fly ash to slag ratios was analysed. Figure 6-10 (a) and (b) show the shrinkage of geopolymer concrete and mass for the different mix proportions. According to Figure 6-10 (a), all blended fly ash and slag geopolymer concrete specimens had similar shrinkage values up to 500 days (GP6040EN, GP5050EN and GP4060EN). However, pure slag based geopolymer concrete exhibited significantly higher shrinkage (strain $1000 \times 10^{-6}$ in 300 days) than in the blended fly ash and fly ash geopolymer concrete (strain $800 \times 10^{-6}$ in 300 days). Despite the fact that, slag based geopolymer concrete has higher shrinkage, the mass loss of slag based geopolymer concrete follows the same trend as the blended fly ash and slag geopolymer concrete (see Figure 6-10 (b)). This illustrates that the shrinkage of geopolymer concrete cannot be fully explained by the mass loss alone (drying shrinkage), indicating significant chemical shrinkage especially in long term (after 100 days). The formation of calcium silicate hydrate products (C-S-H) with time in the slag based geopolymers increase the porosity of the binder [32]. Collins and Sanjayan [11] found that alkali activated slag has higher drying shrinkage than OPC concrete at the same age. In the same study they found that the trend of the mass loss of the two binders is completely opposite. Nelto et al. [31] also reported that 100% alkali activated slag concrete exhibited higher autogeneous shrinkage (chemical shrinkage) than its drying shrinkage. The authors found that 100% slag based concretes have high content (82%) of mesopores compared to OPC concrete (37%).

The results also show that blended fly ash and slag geopolymer concrete has slightly higher shrinkage strain than that of OPC concrete which was reported by Sagoe-crentsil et al. [14] as $500 \times 10^{-6}$ in 350 days. Moreover, the incorporation of fly ash in geopolymer concrete reduces the shrinkage of geopolymer concrete significantly. Deb et al. [33] reported that geopolymer concrete containing higher fly ash has lower volume shrinkage due to the compactable nature of geopolymer matrix and spherical unreacted fly ash particles that acts as micro aggregate filler. All the geopolymer concrete specimens tested, including pure slag based geopolymer concrete have drying shrinkage
strains below $1000 \times 10^{-6}$ in 56 days which satisfies the requirements of AS1379 standard [21].

![Figure 6-9: (a) Shrinkage of (b) Mass loss of 50/50 FA/Slag based geopolymer concrete](image)

![Figure 6-10: (a) Shrinkage of (b) Mass loss geopolymer concrete with different binder compositions (FA/Slag ratio)](image)

6.3.5. Creep

When a concrete specimen is subjected to a load for an extensive period of time both immediate and time-dependent deformations occur which is called the creep of concrete. The deformation of concrete occurs in the direction of the applied. Creep is one of the main factors that should be considered during the designing process of concrete structures in order to satisfy the serviceability objectives [12, 34].

In this study the creep strain was measured as described in the section 6.2 and data was used to calculate basic creep coefficient and specific creep.
The basic creep coefficient \( (\varphi_{cc}) \) is defined as the ratio between creep strain \( (\varepsilon_{cc}(t, \tau)) \) and the instantaneous elastic strain \( (\varepsilon_{ce}(\tau)) \) when the sustained load first applied. This measures the resistance to deformation of concrete under constant load.

\[
\varphi_{cc,b} = \frac{\varepsilon_{cc}(t, \tau)}{\varepsilon_{ce}(\tau)}
\]

The measured basic creep coefficient of blended fly ash and slag geopolymer concrete Figure 6-11(a) is in the range of 2.0-2.5 whereas the basic creep coefficient of slag based geopolymer is around 3.5 which is significantly higher than blended fly ash and slag geopolymer concrete. Concrete with higher basic creep coefficient has the possibility to undergo large deformations under constant load. According to the AS 3600 [23], the basic creep coefficient of similar grade OPC concrete is in the range 2.4-2.8 which is close to the values observed in blended fly ash and slag geopolymer.

The specific creep obtained by normalising the measured creep strain by the applied stress (MPa) is shown in Figure 6-11 (b)-(d). The results show that specific creep of 50/50 FA/Slag and 30/70 FA/Slag geopolymer concrete follow the same trend and at 200 days the value reached \( 60 \times 10^{-6} \) per MPa which is similar to specific creep reported for OPC based concrete [14]. However, 100% slag-based geopolymer concrete has specific creep \( 100 \times 10^{-6} \) per MPa Figure 6-11 (d) which is significantly higher.

The specific creep of concrete can be derived using the equations provided in AS3600 standards. According to AS3600 [23], specific creep strain at any time \( (t) \) can be calculated using the following equations:

\[
\varepsilon_{cc} = \frac{\varphi_{cc}}{E_c}
\]

\[
\varphi_{cc} = k_2 k_3 k_4 k_5 \varphi_{cc,b}
\]

Where, \( E_c \) is the mean modulus of elasticity of the concrete at 28 days [(50/50 FA/Slag = 32 GPa, 30/70 FA/Slag = 32 GPa and 0/100 FA/Slag = 31 GPa)] ; \( \varphi_{cc} \) is the design creep coefficient at time \( (t) \) (calculated as described in AS 3600 [23]). The measured specific creep values are compared with the predicted values in Figure 6-11 (b) - Figure 6-11 (d), which show that the specific creep strains of 50/50 and 30/70 FA/Slag geopolymer are the same or below the values predicted by AS3600. However, the
increasing trend observed in high slag based geopolymer concrete (30/70 FA/Slag and 0/100 FA/Slag) is a concern. Previous studies showed that the heat cured geopolymer concrete undergoes low creep which is about 50% of the predicted creep for OPC concrete [13, 35]. Un et al.[15] also observed slightly higher creep for ambient cured high slag based (90/10 FA/Slag) geopolymer concrete. The present study and Un et al. [15] exhibit that the ambient cured geopolymer concrete has higher rate of creep than that of heat cured geopolymer concrete.

In addition, the results in section 6.3.4 showed that slag based geopolymer concrete has higher shrinkage strain than 100% fly ash based geopolymer concrete. This higher shrinkage and micro-cracks that probably formed in 100% slag concrete enhance the creep of the concrete under sustained load. Moreover, the spherical shape of fly ash particles increases the compactness by acting as a micro-aggregates reducing the shrinkage and creep of the concrete containing fly ash compared to binder with higher slag content (>70%) [14, 33].
Figure 6-11: (a) Basic creep coefficient (b) Specific creep strain of 50/50 FA/Slag (c) Specific creep strain of 30/70 FA/Slag (d) Specific creep strain of 0/100 FA/Slag of geopolymer concrete

6.3.6. Explanation of shrinkage behaviour using microstructure analysis

Figure 6-12-Figure 6-14 show the SEM/EDX analysis of blended fly ash and slag geopolymer and 100% slag based geopolymer.

Figure 6-12 EDX point ‘A’ shows very similar composition to the composition of slag with absorbed Na (alkali). Figure 6-12 shows that geopolymer concrete containing higher fly ash content (>50%) has higher content of unreacted fly ash particles (spherical particles as indicated by “B” on the image) and the corresponding EDX analysis at point ‘B’ shows that the chemical composition of unreacted fly ash particles is similar to the initial composition of the precursor materials. The peak corresponding to Na in the EDX graph is due to the alkali absorbed from the activator into precursor material. EDX analysis at point ‘C’ shows high silicon, aluminium, calcium and sodium indicating the presence of calcium aluminium silicate hydrate (C-A-S-H) and sodium aluminate silicate hydrate (N-A-S-H type gel).

The SEM and EDX analysis on 50/50 FA/Slag geopolymer shown in Figure 6-13, indicates that compared to 60/40 FA/Slag, 50/50 FA/Slag geopolymer has denser microstructure with less unreacted fly ash and slag particles. Incorporation of slag with fly ash based geopolymer leads to a higher rate of geopolymerisation. Compared to high fly ash based geopolymers, precursor materials containing higher slag content dissolve quickly and form the geopolymer network. Unreacted fly ash and slag particles have similar chemical composition to the ones found in 60/40 FA/S. Figure 6-12 ‘A’, Figure 6-12 ‘B’ and Figure 6-13 ‘A’ Figure 6-13 ‘B’ show that the composition of gel phases formed in 60/40 FA/Slag is similar to the ones formed in 50/50 FA/Slag geopolymer and it’s influenced by the slag composition.

SEM/EDX analysis of 100% slag based geopolymer given in Figure 6-14, show that there were only a very few unreacted or partially reacted slag particles. Point ‘A’ is an unreacted slag particle and ‘B’ is slightly reacted slag grain. Unlike the unreacted fly ash particles slag particles has irregular shapes. As shown in Figure 6-14 ‘C’ the main
reaction product in 100% slag based geopolymer was sodium aluminate silicate with some calcium ((N)/C-A-S-H type gel).

Other than the disparity in the type of gels formed, the binders show different crack formation where the blended fly ash slag geopolymer shows lower content of cracking than the 100% slag based geopolymer. The 100% slag based geopolymer shows more extensive cracking than the blended fly ash and slag geopolymers. It can be also observed that cracks formed in the blended fly ash and slag geopolymer propagate around the particles instead of propagating through them which helps to limit the crack formation in fly ash and slag blended geopolymer concrete. It is important to note here that granular metasilicate activator particles added to mix was not detected in SEM/EDX indicating that they have dissolved completely during the aging of the concrete.

Figure 6-12: SEM images and EDX analysis of 60/40 FA/Slag geopolymer
6.4. Concluding remarks

1. Ambient cured geopolymer concrete showed rapid compressive strength development up to 28 days and thereafter the strength development slowed and
reached its maximum value (60 MPa) in one year. Fly ash blended and 100% slag based geopolymer did not show any strength regression after one year indicating high stability in the compressive strength for the test period of two years.

2. Flexural strength of blended fly ash and slag geopolymer concrete was in the range of 6-8 MPa. These values are higher than the values predicted for OPC using equations in the Australian standards AS 3600.

3. Ambient cured geopolymer concrete has similar elastic modulus as OPC concrete. The elastic modulus of geopolymer concrete did not show a significant change for the test period of two years.

4. The shrinkage values of blended fly ash and slag geopolymer were within the limits recommended by Australian standards and were lower than the values of 100% slag based geopolymer concrete. The shrinkage of ambient cured (at 23°C) fly ash and slag blended geopolymer concrete is comparable with the shrinkage of heat cured geopolymer concrete.

5. The specific creep strain of 50/50 FA/S geopolymer concrete is well within the predicted values provided by AS3600. The increasing trend is with age for fly ash and slag blended geopolymer concrete

6.5. References for chapter 6


[30] American Concrete Institute, ACI 318-08: Building code requirements for structural concrete and commentary, 2008.,


7. Abrasion resistance of ambient temperature cured fly ash and slag based geopolymer concrete

7.1. Introduction

Surface erosion or abrasion due to repeated mechanical action for concrete roads or in industrial floors which are subjected to repeat vehicle or machinery traffic that takes place over a long period of time frame is a major cause of concrete degradation. Abrasion removes the surface layer of concrete, and exposes the inner part of the structure to the environment which may accelerate durability problems like corrosion and sulphate attacks. Structures that are susceptible to abrasion need regular high costs maintenance or may even require replacement [1].

Abrasion of OPC based concrete pavers are known to be influenced by factors like compressive strength of concrete, binder content and type, aggregate characteristics, age of concrete, surface finishing and bond between aggregate and cement paste [1-4]. The work by Naik et al. [5] and Siddique [6] showed that the abrasion resistance of concrete highly correlates with the compressive strength of concrete. Furthermore, Biexing et al. [7] showed that the abrasion resistance of concrete is controlled by the binder compressive strength and the crushing value of aggregates (hardness of the aggregates). The effect of binder content (in OPC concrete) on abrasion resistance was studied by Gencel et al. [8] and they showed that increasing the binder content (300-450kg/m$^3$) would lead to an increase in the abrasion resistance. Gencel et al. [8] also showed that aggregates containing rough and porous behaviour create high bond with cement paste, leading to increased abrasion resistance of concrete. The effect of the surface finishing on the abrasion resistance of the concrete was studied by Sadegzadeh et al. [4]. The authors tested the abrasion of concrete specimens with surfaces finished using several methods (i.e. manual floating and trowelling operations, single floating and power trowelling, repeated power finishing and multiple power trowelling operations) and found that different finishing methods produces different porosity level in the concrete surface which influences to the abrasion resistance.

Even though, the abrasion resistance of the OPC concrete is extensively covered, literature on abrasion resistance of geopolymer concrete is limited [9]. Ramujee et al. [9] analysed the abrasion resistance of 100% fly ash based geopolymer concrete and found that geopolymer concrete has better abrasion resistance compared to OPC
concrete. Mohebei et al. [10] reported that the abrasion resistance of elevated temperature cured 100% slag based geopolymer concrete well within the limit as prescribed by ASTM C 1138 [11]. The above mentioned studies are conducted using elevated temperature cured geopolymer concrete which is less convenient in practice. Zeobond Pty Ltd. [12] placed geopolymer concrete in a heavy duty workshop and evaluate the performance of the abrasion resistance of the floor. This case study reported that the abrasion resistance of geopolymer concrete floors are similar to that of OPC concrete floors.

There are several studies on the abrasion resistance of concrete containing supplementary cementitious materials (SCMs), including fly ash or slag. The hardening (in SCMs) is due to hydration and pozzolanic activity compared to alkali activated polymerisation in geopolymer systems. Atış [13] studied the abrasion of high volume fly ash based concrete and concluded that concrete containing fly ash showed lower abrasion resistance than OPC concrete. Naik et al. [14] studied the abrasion resistance of class C fly ash blended cement based concrete and concluded that abrasion resistance of 100% OPC based concrete is high relative to the blended OPC based concrete. In another study, Naik et al. [5] reported that inclusion of fly ash up to 40% in concrete has no adverse influence on the abrasion resistance. The authors also reported that abrasion resistance was primarily controlled by the compressive strength of concrete. Yen et al. [3] reported that inclusion of less than 15% of class F fly in to OPC does not have any adverse effects in terms of abrasion resistance. However, increasing the class F fly percentages beyond 15% lead to decreased resistance to abrasion in resulting concrete. Alaa et al. [15] reported that when OPC is blended with granulated blast furnace slag, the resulting concrete has lower resistance to abrasion compared to pure OPC concrete.

This study evaluates the abrasion resistance of geopolymer concrete with varying fly ash to slag ratios and cured at ambient temperature. Abrasion resistance of each concrete specimen was determined using the depth of wear after abrasion testing according to EN13892-4 standard. Both surfaces of the concrete specimens (i.e. top and bottom surfaces) were analysed to study the variation in abrasion resistance with surface quality and setting characteristics. The tests were carried out at two ages of 28 days and 200 days to determine the effect of age of geopolymer concrete on the abrasion resistance.
7.2. Materials and Methods

7.2.1. Materials

Class F fly ash (Gladstone and Callide fly ash mixture from Cement Australia Pty Ltd.) and granulated ground blast furnace slag (Independent Cements Australia Pty Ltd), were used as the alumina-silicate precursor materials. The chemical composition and particle size analysis of the two precursor materials can be found in section 5.2.1.

A basalt coarse aggregate of 14 mm nominal particle size and river sand were used as the aggregates. Granular sodium metasilicate penta hydrate (28.7% Na2O, 28.5% SiO2 and 42.8% H2O) in solid form was used as the activator.

7.2.2. Preparations of the concrete specimens for the abrasion tests and test procedure

To analyse the abrasion behaviour of blended fly ash and slag geopolymer, concrete slabs of size 500 x 500 x 75 mm were casted according to the mix designs given in Table 7-1 and the test procedures are described in the chapter 5. Concrete specimens were compacted using a vibrating table. The top surface of the fresh concrete slab was finished using steel towel. Next, the specimens were covered with plastic sheets and stored in a 23°C standard moist room. After 3 days, specimens were de-moulded and again stored in the temperature controlled room until testing.

Table 7-1: Mix design proportions

<table>
<thead>
<tr>
<th>Binder type</th>
<th>Binder content (kg/m³)</th>
<th>Aggregate (kg/m³)</th>
<th>W/S</th>
<th>Slump (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sand</td>
<td>14 mm</td>
<td>10 mm</td>
</tr>
<tr>
<td>50/50 FA/Slag</td>
<td>400</td>
<td>680</td>
<td>630</td>
<td>450</td>
</tr>
<tr>
<td>30/70 FA/Slag</td>
<td>400</td>
<td>680</td>
<td>630</td>
<td>450</td>
</tr>
<tr>
<td>0/100 FA/Slag</td>
<td>400</td>
<td>680</td>
<td>630</td>
<td>450</td>
</tr>
<tr>
<td>100 OPC</td>
<td>400</td>
<td>680</td>
<td>630</td>
<td>450</td>
</tr>
</tbody>
</table>

The abrasion of each specimen was measured using the dressing wheel method to accelerate the wear of concrete according to the standard EN13892-4 [16]. The measurements (depths of the wear) were taken using electronic depth gauge with an accuracy of 0.001 mm. Readings were taken every 15 minutes for 60 minutes (or 6.5 mm depth wear 2350 circles, wheel speed was 157 rpm.) at eight locations on the circular path for each specimen. To test the effect of surface condition on abrasion the
author subjected both the top (rough) and bottom surface (smooth) of each specimen to the abrasion test. The concrete specimen, test apparatus and several steps of the measurement process is shown in Figure 7-1.

![Figure 7-1: Abrasion testing procedures](a) Initial measurement (b) Abrasion test (c) After the test (d) Measurements of abraded depth

### 7.3. Results and discussion

Abrasion resistance of concrete specimens was determined using depth of wear at two ages of concrete i.e. 28 and 200 days. Figure 7-2 to Figure 7-4 show the abraded depth of 28 days old geopolymer concrete specimen with time (subfigure (a) and (b) show the depth of wear in the bottom and top surface respectively). The mean abrasion depth of bottom surface gradually increased with abrasion time and attained a median depth of around 2-3 mm at 60 minutes. 28 days old specimens (Figure 7-5(a)) showed similar abrasion resistance in the bottom surface.

The results (depth of wear on both top and bottom surfaces) indicate that the variation in fly-ash to slag content in the geopolymer binder did not significantly affect the abrasion resistance of the concrete. As discussed earlier abrasion resistance of concrete is controlled by factors like: compressive strength of concrete, binder content and type,
aggregate characteristics, curing, surface finishing and bond between aggregate and cement paste. Given that the aggregate characteristics, curing and surface finish are equal, the compressive strength is a main factor controlling the wear resistance of concrete. As shown in section 6.3.2., geopolymer concrete with different fly-ash to slag ratios has similar compressive strength at 28 days which explains the similar abrasion behaviour.

For all specimens the abrasion on the bottom surface was less than that of the top surface. The bottom part of the concrete slab is better compacted with aggregate hence the resistance to abrasion would increase. Another reason for the high abrasion in the top surface may be the bleeding and segregation [1] during compaction, which results in a week layer of concrete on the top called ‘laitance’. However, it should be noted that previous research has reported that alkali-activated cement systems (100% fly ash based geopolymer) have low bleeding due to its cohesive/sticky behaviour. Therefore, the effect of bleeding on the abrasion rate of the geopolymer concrete is expected to be lower than in OPC concrete [17].

The results also shows that the top surface of OPC sample abraded at a much lower rate (3 mm after 60 minutes) than the geopolymer samples (median depth 4-5 mm) even though the compressive strengths of geopolymer concretes at 28 days were similar to that of OPC. In addition to the disparity found in the mean abraded depth of two binders, much higher scatter was observed between each test point on the same specimen of geopolymer than OPC. The abrasion test cycles of some of the geopolymer concrete were limited to two or three due to the abraded depth was in out of the range in the electronic depth gauge. The cause of higher rate of abrasion in the ambient cured geopolymer concrete is not very clear at this stage.

Figure 7-6 to Figure 7-9 show the abraded depth of 200 days old geopolymer concrete and OPC concrete specimens. After 60 minutes of abrasion test, the bottom surface of geopolymer concrete was abraded 4 mm which was slightly higher than the 28 day abrasion depth in geopolymer concrete. However, the abrasion resistance of OPC based concrete increased upon aging of the concrete. After 60 minutes of abrasion test, the bottom surface of OPC concrete was abraded only 1 mm which is slightly lower than abraded depth in 28 days, as expected.
The abrasion depth of the top surface of geopolymer was greater than 6.5 mm within 45 minutes of abrasion test which is considerably higher than the depth obtained for the top surface in 28 days. Similar to 28 day results, the top surface of both geopolymer and OPC concrete has lower abrasion resistance than the bottom. Geopolymer concrete also showed scattered results for surface wear compared to OPC concrete.

Previous research study [3] has shown that, the concrete containing supplementary cementitious materials (blended cement) has lower abrasion resistance than 100% OPC concrete, and that OPC concrete containing more than 15% fly ash showed higher abrasion rate at the same strength level as pure OPC concrete. Similarly, slag blended OPC concrete also showed higher rate of abrasion compared to OPC concrete [3, 13, 14]. However, the above research did not identify the reason for the variation of abrasion resistance.

The porosity in the concrete is also an important factor that influences the abrasion resistance of concrete. Table 7-2 shows the volume of permeable voids (VPV %) in several layers of OPC and geopolymer concrete. The results show higher amount of VPV % on the top surface of geopolymer concrete compared to the OPC concrete. Variability in value of VPV % can cause the abrasion to happen unevenly on different regions of a surface. According to Table 7-2 results, the top and bottom have different VPV% values which is expected, so top and bottom abrasion resistance expected to be different. But, the abraded depth is different in the different locations in the specimen which can be influenced by the proportion of aggregate and paste in the test area.

Table 7-2: Apparent volume of permeable voids (AVPV %)

<table>
<thead>
<tr>
<th>Mix Formulation</th>
<th>Cutting section of the cylinder</th>
<th>Apparent Volume of Permeable Voids AVPV (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50/50 FA/Slag</td>
<td>Top</td>
<td>17.55</td>
</tr>
<tr>
<td></td>
<td>Middle</td>
<td>16.84</td>
</tr>
<tr>
<td></td>
<td>Bottom</td>
<td>16.84</td>
</tr>
<tr>
<td>OPC</td>
<td>Top</td>
<td>15.40</td>
</tr>
<tr>
<td></td>
<td>Middle</td>
<td>14.90</td>
</tr>
<tr>
<td></td>
<td>Bottom</td>
<td>13.50</td>
</tr>
</tbody>
</table>
Figure 7-2: Abrasion depth of 50/50 FA/Slag (a) Bottom (b) Top Surface in 28 days (the redline indicate the median of the abraded depth, the box indicates the third and second quartile of data while the upper and lower quartiles are show as the horizontal line)

Figure 7-3: Abrasion depth of 30/70 FA/Slag (a) Bottom (b) Top Surface in 28 days

Figure 7-4: Abrasion depth of 0/100 FA/Slag (a) Bottom (b) Top Surface in 28 days
The difference in settlement mechanisms may have also contributed towards the disparity in the abrasion resistance of the two binders (OPC and geopolymer). Kosmatka [18] reported that surfaces of concrete (their work was based on OPC) can set faster compared to the middle or bottom part of concrete and some of the paste-aggregate can settle quickly compared to others. Even though, this mechanism can stop bleeding of concrete, additional air voids can be created. The uneven settling of concrete can also lead to water deposit under the aggregates (or on the sides) creating lower bond between aggregates and paste [18]. According to Kosmatka [18], concrete with uneven settling mechanism can have weak surface layer compared to other parts of concrete. During the settlement of geopolymer concrete bleeding may carry unreacted fine fly ash particles, partially dissolved materials and alkali ions towards the surface which can create a sudden surface hardening. Further studies are needed to identify the relationship between settlement of the geopolymer concrete and abrasion resistance.

The results of this study shows that according to the standard EN13892-4 [16] test method, ambient cured geopolymer concrete has slightly lower abrasion resistance than OPC concrete. However, Mohebei et al. [10] reported that the abrasion resistance of elevated temperature cured 100% slag based geopolymer concrete is well within the limit as prescribed by ASTM C 1138 [11]. These results are in agreement with the results obtained for elevated temperature cured 100% fly ash based concrete presented by Ramujee et al. [9]. Heat curing of geopolymer concrete may provide additional resistance in regards to abrasion which has to be investigated further. Addition to this, the case study by Zeobond Pty Ltd [12] reported that ambient cured geopolymer concrete pavements have excellent wear resistance. The company placed the geopolymer concrete in a heavy duty work shop floor which is used to store heavy vehicles. Comparing the results reported in the literature and results obtained for this
study, it can be concluded that EN13892-4 [16] method can lead to aggressive abrasion conditions which does not occur in concrete pavements or floors in their service life. However, different test standards should be investigated further to correlate with actual abrasion conditions in the concrete pavements.

Figure 7-6: Abrasion depth of 50/50 FA/Slag (a) Bottom (b) Top Surface at 200 days

Figure 7-7: Abrasion depth of 30/70 FA/Slag AB (a) Bottom (b) Top Surface at 200 days

Figure 7-8: Abrasion depth of 0/100 FA/Slag (a) Bottom (b) Top Surface at 200 days
Figure 7-9: Abrasion depth of 100 OPC (a) Bottom (b) Top Surface at 200 days

Figure 7-10: Comparison of geopolymer and OPC concrete after each test cycle
7.4. Concluding remarks

1. Abrasion resistance of ambient cured geopolymer concrete is lower than that of OPC concrete.
2. The volume of permeable voids in top surface of geopolymer concrete is slightly higher than in OPC concrete, in turn the abraded depth of top-surface layer is higher.
3. The age of ambient cured geopolymer concrete does not have significant influence while abrasion resistance of OPC concrete is increase upon aging of the concrete.
4. Comparing results obtained in this study and previous work, the test procedure used here appears to provide very aggressive abrasion conditions which are not available in actual pavements or floors. Therefore, the results can give an overestimation on the abrasion experienced in the field.

7.5. References for chapter 7


8. Susceptibility of geopolymer concrete to alkali aggregate reactivity (AAR)

8.1. Introduction

Alkali aggregate reaction (AAR) is one of the main durability problems found in ordinary Portland cement (OPC) concrete. AAR is caused by the reaction between alkali hydroxide present in the hydrated cement and reactive phases that may be present in the aggregates. This reaction creates highly hydrated AAR gel in the concrete, which is an expansive product and can induce significant expansion and cracking of the affected elements [1]. Major structures have suffered due to alkali-aggregate reaction reducing their service life or requiring large repair costs [2-4]. One approach to reduce AAR is the use of non-reactive aggregate in the concrete. However, this method is not always possible due to practical difficulties in acquiring non-reactive aggregates locally.

In previous studies, it has already been recognized by other studies that AAR expansion can be reduced by using supplementary cementitious materials like low calcium fly ashes [3, 5]. This is due to factors such as reduction in alkalinity of pore solution and lower availability of calcium in the binder [6]. Geopolymer has a silica based polymer structure which has shown superior durability compared to OPC. It has less CaO and higher Na₂O compared to OPC. Previous studies showed that the pH value of pore solution is above 11.5; which is adequate to attack reactive silica phases in aggregate [7]. However, AAR formation in geopolymer concrete is different from that of OPC concrete due to the crossed linked SiO₄ and AlO₄ in geopolymer compared to C-S-H in OPC. Therefore, it is important to understand the susceptibility geopolymer binder to AAR expansion. Geopolymer binder which is formed after a series of chemical reactions between silicon, aluminium and alkali hydroxides does not have hydrated phases or free calcium, which is an important factor in AAR-induced expansion development. Instead geopolymer contains three dimensional silicon polymer networks which can resist most of the above durability issues of OPC concrete.

Davidovits [8] stated that geopolymer based mortar bars which contained high alkali content (Na₂O= 9.2%) have shown less expansion compared to OPC mortar bars.
Kupwade-Patil and Allouche [9] reported that, mortar bars of alkali activated fly ash did not create any expansive gel due to absence of calcium. Although, they did not provide initial curing condition used in their study, it is well known that 100% class F fly ash based geopolymer needs to be cured at elevated temperature (over 23°C) [10]. García-Lodeiro et al.[6] also compared alkali aggregate reaction of alkali activated 100% class F fly ash binder with Portland cement binder using accelerated mortar bar method (1M NaOH, 80°C). They reported that fly ash based geopolymer mortars showed less expansion compared to OPC mortars due to AAR. However, they cured samples initially at elevated temperature (85°C). Expansion measurements after elevated curing are not ideal as expansion can occur before the zero measurement due to acceleration of AAR reaction at elevated temperature.

Although some aspects of AAR formation in class F fly ash based geopolymer has been studied so far, AAR in geopolymer mortars or concrete formulated with calcium rich material (i.e slag) and other alumino-silicate material has not been fully investigated. Bakhrev et al. [11] and Puertas et al. [12], reported that concrete made with 100% alkali activated slag can show larger expansions than OPC concrete. Addition of a calcium-rich source into geopolymer systems is necessary as it enhances the setting behavior and mechanical properties of geopolymers [13]. Ground granulated blast furnace slag is mostly used as the calcium source in geopolymer systems due to its high reactivity in alkaline environment. The reaction product of slag contains calcium silicate hydrate (C-S-H) as well as geopolymer network. Despite the fact that slag improves the engineering properties of geopolymer binder excess calcium in geopolymer system can create phases like portlandite Ca(OH)₂ which may facilitate AAR. Blended fly ash and slag geopolymer binders contain less calcium, but their AAR susceptibility has not been thoroughly studied in the past.

This chapter evaluates the susceptibility of blended fly ash and slag geopolymer concrete cured at ambient temperature to alkali aggregate expansive reaction. Geopolymer mortar and concrete specimens were cast with different fly ash to slag ratios and aggregates which exhibit different level of reactivity. The alkali level of the binder was also changed in this study. Accelerated AAR expansion tests were conducted on geopolymer mortars which were initially cured at room temperature (23°C) prior to the accelerated testing in 1M
NaOH at 80°C according to RMS 363 [14]. The alkali aggregate reactivity of geopolymer concrete specimens was also evaluated using according to RMS 364 [15] test method. Microstructural information obtained through SEM/EDX, XRD and NMR techniques was used to study the nature of AAR and AAR products in geopolymer concrete.

8.2. Materials and methods

8.2.1. Materials

Geopolymer solids

A class F fly ash and granulated ground blast furnace slag, with the chemical composition shown in Table 8-1 were used as the alumina-silicate precursor materials. The bulk chemical composition was obtained by X-ray florescence (XRF) analysis. The main component of class F fly is SiO$_2$ (over 51%) whereas slag contains high amount of CaO (41.5%). It is important to note that fly ash contains twice as much Al$_2$O$_3$ as slag.

Alkali activator

Granular sodium metasilicate penta-hydrate (28.7% Na$_2$O, 28.5% SiO$_2$ and 42.8% H$_2$O) was used as solid activator to activate the precursors. Usage of solid alkali activators in geopolymer systems is less hazardous than commonly used liquid activators and more convenient for field applications. The amount of activator used was calculated to provide an alkali content of 4% Na$_2$O and 6% Na$_2$O by mass of precursor materials.

<table>
<thead>
<tr>
<th>Oxides</th>
<th>GP Cement</th>
<th>Slag‡</th>
<th>Fly ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>19.30</td>
<td>32.00</td>
<td>51.50</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.30</td>
<td>0.51</td>
<td>1.50</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>5.50</td>
<td>13.00</td>
<td>27.60</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>2.90</td>
<td>0.40</td>
<td>11.80</td>
</tr>
<tr>
<td>Mn$_3$O$_4$</td>
<td>0.20</td>
<td>0.30</td>
<td>0.15</td>
</tr>
<tr>
<td>MgO</td>
<td>1.40</td>
<td>4.90</td>
<td>1.30</td>
</tr>
<tr>
<td>CaO</td>
<td>62.00</td>
<td>41.50</td>
<td>2.20</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.06</td>
<td>0.20</td>
<td>0.40</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.40</td>
<td>0.33</td>
<td>0.60</td>
</tr>
</tbody>
</table>
### Aggregates

Three types of aggregates including one non-reactive and two reactive were used in this study to identify the AAR behaviour.

- Non-reactive basalt (NR)
- Moderately reactive aggregate (R1) of gneissic origin
- Reactive aggregate (R2) of hydrodacite origin

Aggregates were crushed and sieved according to ASTM C-1260 [16] to obtain the desired size range.

Non-reactive, saturated surface dry sand with a density of 2630 kg/m$^3$ and water absorption of 0.4% was used for geopolymer concrete mixes. The reactivity of the sand was measured prior to using it in the experiments. The results of the reactivity measurements are given in Figure 8-1. Both RMS T 363 and RC 376.03 standard [17] classify fine aggregates that show expansions less than 0.15% as non-reactive aggregates.

<table>
<thead>
<tr>
<th></th>
<th>0.11</th>
<th>0.02</th>
<th>0.73</th>
</tr>
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<tbody>
<tr>
<td>$P_2O_5$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$SO_3$</td>
<td>2.46</td>
<td>2.10</td>
<td>0.20</td>
</tr>
<tr>
<td>S$^-$</td>
<td>0</td>
<td>0.60</td>
<td>0</td>
</tr>
<tr>
<td>LOI</td>
<td>5.3</td>
<td>4.90</td>
<td>1.80</td>
</tr>
<tr>
<td>Total</td>
<td>99.93</td>
<td>100.7</td>
<td>99.78</td>
</tr>
</tbody>
</table>

‡ LOI in slag includes 3.7% sulfur in the form of $SO_3$

I indicate the presence of limestone in the cement
Figure 8-1: Length change of OPC mortar bar containing sand

8.2.2. Testing procedures

_Geopolymer binder preparation for mortar bar expansion test (AMBT)_

The mix designs used in the mortar bar test are shown in Table 8-2. Total binder and crushed aggregate masses used in all the mixes were 440 g binder and 990 g aggregate, respectively. In geopolymer binders, the total solid content (combination of aluminosilicate source material and alkali activator) was considered as the binder. The mixing of the precursor materials were done according to the procedures given in RMS T363 [14]. The mix was then cast into (25× 25 × 285 mm) mould and the mortar samples were cured in fog room at 23°C for 24 hours. The samples were then de-moulded and cured further for 2 days in moist curing condition before exposure to accelerated curing environment (1M NaOH, 80°C). Shayan et al. [18] demonstrated that RMS-T363 test method, is more appropriate compared to ASTM C-1260 [16] procedures particularly for slowly reactive aggregates. Hence, all the mortar bar tests were conducted according to RMS T363 procedures.
Table 8-2: Binder formulations with different aggregates

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Aggregate type</th>
<th>Fly ash wt. (%)</th>
<th>Slag wt. (%)</th>
<th>OPC wt. (%)</th>
<th>Na₂O wt. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M70/30FA/S-4-NR</td>
<td>NR</td>
<td>70</td>
<td>30</td>
<td>0</td>
<td>4</td>
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<td>M50/50FA/S-4-NR</td>
<td>NR</td>
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<td>50</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>M30/70FA/S-4-NR</td>
<td>NR</td>
<td>30</td>
<td>70</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>M0/100FA/S-4-NR</td>
<td>NR</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>M70/30FA/S-6-NR</td>
<td>NR</td>
<td>70</td>
<td>30</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>M50/50FA/S-6-NR</td>
<td>NR</td>
<td>50</td>
<td>50</td>
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<td>6</td>
</tr>
<tr>
<td>M30/70FA/S-6-NR</td>
<td>NR</td>
<td>30</td>
<td>70</td>
<td>0</td>
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</tr>
<tr>
<td>M0/100FA/S-6-NR</td>
<td>NR</td>
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<td>100</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>M70/30FA/S-4-R1</td>
<td>R1</td>
<td>70</td>
<td>30</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>M50/50FA/S-4-R1</td>
<td>R1</td>
<td>50</td>
<td>50</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>M30/70FA/S-4-R1</td>
<td>R1</td>
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<td>70</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>M0/100FA/S-4-R1</td>
<td>R1</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>M70/30FA/S-6-R1</td>
<td>R1</td>
<td>70</td>
<td>30</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>M50/50FA/S-6-R1</td>
<td>R1</td>
<td>50</td>
<td>50</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>M30/70FA/S-6-R1</td>
<td>R1</td>
<td>30</td>
<td>70</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>M0/100FA/S-6-R1</td>
<td>R1</td>
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<td>100</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>M70/30FA/S-4-R2</td>
<td>R2</td>
<td>70</td>
<td>30</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>M50/50FA/S-4-R2</td>
<td>R2</td>
<td>50</td>
<td>50</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>M30/70FA/S-4-R2</td>
<td>R2</td>
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<td>70</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>M0/100FA/S-4-R2</td>
<td>R2</td>
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<td>6</td>
</tr>
<tr>
<td>M50/50FA/S-6-R2</td>
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<td>6</td>
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<tr>
<td>M30/70FA/S-6-R2</td>
<td>R2</td>
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<td>70</td>
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<td>6</td>
</tr>
<tr>
<td>M0/100FA/S-6-R2</td>
<td>R2</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>OPC-NR</td>
<td>NR</td>
<td>0</td>
<td>0</td>
<td>100</td>
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<tr>
<td>OPC-R1</td>
<td>R1</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>OPC-R2</td>
<td>R2</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
</tbody>
</table>

* FA and S refer to fly ash and slag, respectively. The numerals refer to percentage of each component in the binder. Number 4 and 6 refer to percentages of Na₂O content in the binder.

**Geopolymer concrete preparation for concrete prism tests (CPT)**

Geopolymer concrete prisms (75×75×285mm) were cast according to RMS T364 [15] using concrete mix designs listed in Table 8-3 and Table 8-4. The specimens were demoulded 24 hours after casting and kept in 23°C moist room for another 6 days, after which the initial length reading was taken and then they placed in suitable boxes and transferred to
40°C temperature room. During this storage period, samples were kept in the well-sealed box supported on pieces of PVC pipe rings with water at the base of the box to keep the conditions moist inside the box. Damp cloths were also used to line the box provide additional moisture to keep the humidity in the range of 98-100%.

Table 8-3: Concrete mixes used in CPT test

<table>
<thead>
<tr>
<th>Concrete mix</th>
<th>Binder content (kg/m³)</th>
<th>Coarse aggregates (kg/m³)</th>
<th>Fine aggregates (kg/m³)</th>
<th>Water to geopolymer solid ratio</th>
<th>Slump value (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C70/30FA/S-4</td>
<td>400</td>
<td>1080</td>
<td>780</td>
<td>0.38</td>
<td>80</td>
</tr>
<tr>
<td>C50/50FA/S-4</td>
<td>400</td>
<td>1080</td>
<td>780</td>
<td>0.39</td>
<td>150</td>
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<td>C30/70FA/S-4</td>
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<td>780</td>
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<tr>
<td>C0/100FA/S-4</td>
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<td>1080</td>
<td>780</td>
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<td>C30/70FA/S-6</td>
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<td>1080</td>
<td>780</td>
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<td>C0/100FA/S-6</td>
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<td>1080</td>
<td>780</td>
<td>0.41</td>
<td>80</td>
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<tr>
<td>OPC</td>
<td>400</td>
<td>1080</td>
<td>780</td>
<td>0.42</td>
<td>75</td>
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</table>

Table 8-4: Binder composition of concrete specimens

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Aggregate type</th>
<th>Fly ash wt. (%)</th>
<th>Slag wt. (%)</th>
<th>OPC wt. (%)</th>
<th>Na₂O wt. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C70/30FA/S-4-NR</td>
<td>NR</td>
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<td>C70/30FA/S-6-NR</td>
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<td></td>
<td></td>
</tr>
<tr>
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<td>NR</td>
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<td>70</td>
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<td></td>
</tr>
<tr>
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<tr>
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<td>70</td>
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<tr>
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<td></td>
</tr>
<tr>
<td>C0/100FA/S-6-R2</td>
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<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>COPC_NR</td>
<td>NR</td>
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<td>0</td>
<td>100</td>
<td>1.38</td>
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<tr>
<td>COPC_R2</td>
<td>R2</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>1.38</td>
</tr>
</tbody>
</table>
NMR technique for structure analysis of binders

$^{29}$Si magic angle spinning (MAS) NMR spectra were collected at 119.141 MHz on an Agilent (Varian) VNMRS-600 (14.1 T) instrument with a pulse width of 7 μs, relaxation delay of 120 s and between 1k to 6k scans were accumulated. The chemical shifts were referenced to tetramethylsilane (TMS). $^{27}$Al MAS NMR and $^{23}$Na MAS NMR spectra were acquired at 156.261 MHz and 157.261 MHz, respectively, with a pulse width of 4 μs, a relaxation delay of 2 s and 2k scans. The chemical shifts were referenced to $\text{AlCl}_3$ and NaCl, respectively. All spectra were acquired with a MAS speed of 10 kHz at 23°C and 8k zero-filling and 100 Hz line-broadening were applied.

Scanning Electron microscopy (SEM) and Energy dispersive X-ray (EDX) analysis

Specimens subjected to mortar bar test and concrete prism test were sectioned for examination the microstructure and presence AAR products. Fracture surfaces of 50/50 FA/Slag, 0/100 FA/Slag and OPC binder based mortars were selected for this analysis. The microstructure analysis was carried out using scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis, at an accelerating voltage of 15 kV (FEI Quanta SEM instrument was used).

X-Ray diffraction patterns

The XRD analysis was carried out using a Bruker D8 Advance X-ray diffractometer. Scans were collected between 5-70° (2θ) with a step size of 0.02° and a scan rate of 5s per step. An internal standard (10%wt corundum, $\text{Al}_2\text{O}_3$) was added to allow quantitative analysis using Rietveld refinement. Phase identification was completed using Materials Data, Inc., Jade 9.3 software and Quantitative Rietveld analysis using Bruker Diffracplus Topas software.

8.3. Results and Discussion

8.3.1. AAR expansion of geopolymer mortar bars

Length change of the mortar bars with time, measured according to the procedure given in RMS T363 [14] are shown in Figure 8-2, Figure 8-3 and Figure 8-4. Three identical mortar bars were made for each test and the average expansion values are plotted in the figures.
RMS standard classifies aggregates/binder showing expansion values ≥ 0.1% in 10 days as reactive and aggregates/binder showing expansion values ≥ 0.1% in 21 days as slowly reactive.

Figure 8-2 (a) and (b) show the expansions of the mortar bars with NR aggregate. Expansion of geopolymer mortars with NR basalt was well below the threshold given in standard [14]. As expected, the reference OPC mortar bars also did not show any deleterious expansion in the presence of NR basalt aggregate. The expansion level remains low even when the alkali content in the geopolymer binder was increased to 6% Na₂O. Basalt is mineraly a silica-deficient, mafic rock, absent free of silica minerals, thus it is not susceptible to AAR.

Figure 8-2 : Average expansion of mortar bars containing NR aggregate at a) 4% Na₂O b) 6% Na₂O

The expansion potential reactivity of the binders in combination with the reactive aggregates was also examined. The two reactive aggregate types R1 and R2 are known to cause significant expansion when used in OPC concrete specimens containing elevated levels of alkali. Figure 8-3 (a) and (b) show the expansion behavior of geopolymer based mortar bars with R1. The results show that 100% slag based geopolymer binder (M0100FAS-4, M0100FAS-6) and OPC binder caused large expansion when combined with R1 aggregate. The OPC mortar bars exceed the 0.1% expansion level in 10 days indicating the aggregates to be reactive. Mortar bars with 100% slag based geopolymer containing 4% alkalinity showed a slower expansion rate compared to OPC but it also exceeded the 0.1% expansion limit in 21 days. Increase of the alkali content of the binder to 6%, increased the expansion of M0100FAS-6, where it exceeded the 0.1% threshold in 10
days. No significant expansion was observed in geopolymer mortar bars made with blended fly ash and slag containing 4% or 6% alkali.

Figure 8-3: Average expansion of mortar bars containing R1 aggregate at (a) 4% Na$_2$O (b) 6% Na$_2$O

Figure 8-4 illustrates the expansion behavior of mortar bars containing R2 aggregate. Again mortar bars made with OPC binder showed significant expansion (0.2% and 0.4% in 10 days and 21 days respectively). The specimens made with alkali activated 100% slag binder and R2 aggregate also showed significant expansion (0.1% and 0.2%, in 10 days and 21 days respectively). At high alkali content (6%), the initial expansion (up to 21 days) of mortar bars with alkali activated slag slightly exceeded the expansion of mortar bars containing OPC binder. However, after 21 days, the expansion values of OPC mortar bars were slightly higher than M0100FAS-6.

Figure 8-4: Average expansion of mortar bars containing R2 aggregate at (a) 4% Na$_2$O (b) 6% Na$_2$O
The results (Figure 8-3 and Figure 8-4) show that OPC mortars produce higher expansion than blended fly ash and slag geopolymer mortars in the presence of reactive aggregates. OPC binders contain higher level of calcium than blended fly ash and slag geopolymers. In the presence of calcium, hydroxyl, reactive silica phases (from aggregates) and alkali ions, OPC concrete forms sodium calcium silicate hydrate (N-C-S-H) type AAR expansive gel. This AAR gel absorbs the surrounding water from the concrete pores leading to volume change in concrete or swelling [19]. The Alkali aggregate reaction products formed in concrete containing low calcium has low viscosity. Therefore those products can disperse into the binder through pores [19]. However, AAR gel formed in calcium rich environment has high viscosity, preventing it from being dissipated in the pores. The high viscosity AAR gel products accumulate forming large expansive AAR gel eventually leading to concrete expansion [20]. OPC binders has Ca(OH)$_2$ solid which is soluble extent of 1.8g/l. In addition, Ca(OH)$_2$ solid in concrete buffers the pH to about 12.5 in OPC [21].

On the other hand, the pore solution of geopolymers contains high level of alkali hydroxyl which reduces the solubility of the calcium as a result of the common ion effect. Moreover, as sodium silicate is used to activate fly ash and slag, Ca(OH)$_2$ availability in the pore solution is further reduced [22]. Therefore Geopolymers containing slag does not produce high amount of Ca(OH)$_2$ products limiting the formation of expansive AAR gel.

The alkali binding capacity of OPC and geopolymer binders is also different due to the disparity in the composition of the two binders. Geopolymer binders consisting of slag produce calcium-silicate-hydrate (C-S-H) and C-A-S-H as the main reaction products. These products have lower Ca/Si ratio than the ratio for the calcium rich hydrates produced in OPC binders. When the Ca/Si ratio in the hydrates (C-S-H or C-A-S-H) is low, the negative surface charge of the binder is reduced allowing stronger attraction of alkali ions (i.e. Na$^+$, K$^+$) into the structure with stronger bonds [23]. Therefore the availability of alkali ions to react with aggregate and make AAR expansive gel is reduced.
The expansion results also show that increasing the slag content of the geopolymer binder can increase the susceptibility to AAR. However, previous chapters have shown that slag addition to geopolymer synthesis increases the setting characteristics as well as the mechanical properties of the binders. Hence, it is important to identify the optimum level of slag that should be added to geopolymer systems, to achieve better mechanical performance in concrete as well as minimizing the risk of alkali aggregate reaction.

Figure 8-5(a) shows the AAR expansion of geopolymer mortar containing varying levels of slag. The results show a gradual increase of mortar bar expansion with the slag percentage up to about 70% slag. Increasing the slag content of the binder beyond 70%, results in a rapid increase in the expansion values, where expansion of geopolymer mortar bars containing 80% slag reach AMBT threshold of 0.1% in 10 days. Slag rich geopolymer mortar samples have higher amount of calcium bearing phases which are more susceptible to expansive alkali aggregate reaction. When geopolymer binder has higher calcium phases the free alkali in the pore solution is also higher than the geopolymers containing sodium alumina silicate phases.

Figure 8-5(b) shows the variation of expansion at 4% and 6% alkalinity. The results show that the expansion of mortar bars with slag content beyond 70% (M0100FA/S) is accelerated when alkali content of the geopolymer is increased from 4% to 6%. However, the expansion of geopolymer mortar bars with 30-70% slag is not affected by the elevated levels of alkali in the binders. This indicates that the alkali ions alone cannot cause expansive AAR gel in concrete. AAR gel formation also requires adequate level of calcium in the binder.
Figure 8-5: Expansion of geopolymer mortar bars containing (a) different slag content and R2 aggregate at 6% Na$_2$O in 10 and 21 days (b) different slag content and R2 aggregate at 4 and 6% Na$_2$O in 21 day

The influence of the precursor material composition on the AAR gel formation will be analyzed next. Figure 8-6(a) shows the variation in expansion of geopolymer mortar bars, containing reactive aggregates, with \((Ca + Na)/Al\) molar ratio in the binder. The results show that the expansion values linearly increases with the \((Ca + Na)/Al\) molar. It is known that increasing the calcium content of the binder, results in decreasing the alkali binding capacity of hydrated phases [23]. In addition, alkali ions maintain the pH of pore solution at high level. These factors directly support the formation of AAR expansive gel in concrete [24, 25].

Figure 8-6(b) shows that the expansion of geopolymer mortar bars with the \(Si/Al\) molar ratio of the fly ash and slag blends. Again the expansion increases with the \(Si/Al\) ratio. This is because, alkali activation of precursor materials containing high aluminum content, produces N-A-S-H and (Ca/Na)-A-S-H phases [26] with higher degree of cross linking. In addition, these phases have higher alkali binding as a result more negative surface charge which reduce the alkali concentration of the pore solution [27]. Compared to 100% slag binder blended fly ash and slag geopolymers have higher content of aluminium (lower \(Si/Al\) ratio) and high alkali binding which leads to reduction of AAR expansive gel formation.
8.3.2. AAR expansion of geopolymer concrete prisms

This section analyses the AAR expansion result of the concrete prisms specimens fabricated according to the mix designs and procedure given in section 8.2.2. Length change of the concrete prisms with time, measured according to the procedure given in RMS T364 [15] are shown in Figure 8-7 and Figure 8-8.

Figure 8-7 (a) and (b) show the expansions of the concrete prism samples with non-reactive basalt (NR) aggregate up to 600 days at 4% and 6% alkali levels respectively. Consistent with the observations made on mortar bars, geopolymer concrete prisms containing NR aggregate showed no significant expansion.

Figure 8-8(a) and (b) show the expansion of concrete prisms in the presence of reactive aggregate R2 at 4% and 6% alkali levels respectively. At 4% alkali level all geopolymer concrete specimens including 100% slag based geopolymer concrete showed no significant expansion. When alkali content of the geopolymer binder is increased to 6%, the expansion of the geopolymer concrete containing 100% slag content also increased while blended fly ash and slag geopolymer concrete prisms did not show any significant expansion (Figure 8-8(b)). The expansion of 100% slag based geopolymer up to 100 days was similar to that of OPC concrete. However after 100 days, the expansion of OPC concrete accelerated compared to the 100% slag. This is because the microstructure of slag based geopolymer continuously evolves during the first few months whereas the microstructure of OPC remains the same. Geopolymer containing slag, high degree of cross linked C-S-H and C-
A-S-H phases is generated with maturity. The cross-linked C-S-H and C-A-S-H phases limit the exchange of calcium and sodium ions that supports the alkali aggregate reaction. On the other hand, OPC concrete has non-cross linked C-S-H phases which can exchange calcium and alkali ions required to continue the AAR expansion. Availability of alkali in the initial OPC binder provide additional hydroxyl environment to continue alkali aggregate reaction at a high rate. Figure 8-9 (a) and (b) show the appearance of two example concrete prisms containing the two binders at 600 days. They show map cracking of the OPC concrete prism while no map cracking was visible on the 100% slag based geopolymer concrete prism. The map cracking pattern occurs due to the internal pressure created by strong AAR induced expansion.

The expansion results obtained from the mortar bar test, concrete prism test for various compositions are compared in Figure 8-10. The expansion results for blended fly ash and slag geopolymer concrete prism correlate well with the accelerated mortar bar test results. However, the expansion behaviour of 100% slag based geopolymer concrete does not follow the observations made in mortar bar test. The 100% slag mortar bars at 4% alkalinity showed very high reactivity. This may be due to the high aggressive environment present in the mortar bar test compared to the concrete prism test. During the accelerated mortar bar test, the specimens were soaked in 1M NaOH solution at 80°C which provides continual hydroxyl ions to the pore solution.

Considering both mortar bar and concrete prisms test results it can be concluded that the incorporation of fly ash into geopolymer concrete inhibits the alkaline aggregate expansion in concrete. However, 100% slag based geopolymer concrete is susceptible to alkali aggregate reaction in the presence of reactive aggregates and high alkali content above 4%.
Figure 8-7: Length change of concrete prisms containing non-reactive aggregates at (a) 4% (b) 6% alkali level

Figure 8-8: Length change of concrete prisms containing R2 aggregate at (a) 4% (b) 6% alkali level

Figure 8-9: Appearance of concrete after 600 days (a) C0/100FA/S-6-R2 (b) OPC-R2
8.3.3. MAS-NMR spectra variation of different binders

To identify the variations in geopolymers structure with changes slag to fly ash ratio $^{27}$Al, $^{29}$Si and Na solid-state Nuclear Magnetic Resonance (NMR) spectroscopy was used. The 100% OPC and OPC blended binders (i.e. Fly ash blended and slag blended) were also subjected to NMR spectroscopy for comparisons.

Figure 8-11 shows the $^{29}$Si spectra of the geopolymer and OPC based binders. In the analysis, ‘Q’ is used to represent different silica species, $Q^4$ denotes SiO$_4$ tetrahedral which connects to four other atoms of the same type via shared oxygen atoms and $Q^3$ denotes three oxygen bonded tetrahedral and so on.

70/30 FA/S and 50/50 FA/S geopolymers show resonance in the range -110 to -120 ppm indicating complete cross-linking of SiO$_4$ and AlO$_4$ units ($Q^4$). The Q4 based structure in geopolymer, has rigid well organized framework preventing exchanging of ions from the surrounding. 70/30FA/S and 50/50FA/S geopolymers also show resonance corresponding to $Q^3$ (-110 to -100 ppm), $Q^2$ (-100 to -92 ppm) and $Q^1$ (-94 to -84) and $Q^0$ (-85 to -75 ppm) species which have incomplete 3-D polymerization with loose of silica structure. While 100S also show resonance around –85 to -79 ppm corresponding to a mixture of $Q^1$, $Q^2$ and $Q^3$ type species, it does not show significant resonance corresponding to $Q^4$. This indicates
that 100% slag binder does not contain high degree of cross-linking similar to blended fly ash and slag geopolymers. The Q$^1$ and Q$^2$ species in 100S represent a chain type structure (mainly C-S-H) generated during cement hydration. This chain like structure is less polymerized compared to blended fly ash and slag geopolymers which has a 3D structure [28]. The chain type structure can be altered and rearranged in alkali environment leading to AAR expansion. Figure 8-11 also shows that when the fly ash content is increased in the geopolymer, the peaks in the resonance signal corresponding to Q$^1$, Q$^2$ and Q$^3$ shifts towards the negative direction (shielding effect). Provis et al. [29] stated that $^{29}$Si NMR spectra shifts towards the negative direction due to the higher connectivity with oxygen (or lower non bridging oxygen) in the structure.

Similar to 100% slag based geopolymers, 100% OPC binder containing alkali does not show resonance corresponding to Q$^4$ type structure. However there are three resonances at -73.7 ppm (34%), -80.8 ppm (47%) and -86.2 ppm (19%), indicating Q$^1$ to Q$^3$ silicon structure. The results also show that the addition of fly ash into OPC binder produces minor peak corresponding to Q$^4$ type structures. Previous research has shown that Q$^4$ type structures in blended cement can reduce the effects of alkali aggregate reactivity [8].

The above results show that blended fly ash and slag geopolymers have high degree of cross linking which leads to rigid well organized framework preventing exchanging of ions from the surrounding. Therefore, the alkali aggregate reactivity has lower potential to affect the structure of geopolymer.
Figure 8-11: $^{29}$Si MAS NMR spectra from powders acquired at 10 kHz spinning speed and 23°C (except bottom spectrum run at 4 kHz spinning speed). Asterisks identify spinning side bands.

Figure 8-12 shows the $^{27}$Al MAS NMR spectra for geopolymer and OPC binders. The $^{27}$Al shifts in aluminosilicates allow to distinguish between tetrahedral (AlO$_4$ or ‘T’), pentahedral (AlO$_5$) and octahedral (AlO$_6$ or ‘O’) coordination to oxygen. The corresponding resonance of AlO$_4$ tetrahedra coordinated with 3 SiO$_4$ tetrahedra (Al$^T$ Q$^3$Si) is in the range 70-80 ppm, whereas the corresponding resonance of Al exclusively coordinated with four SiO$_4$ tetrahedra (Al$^T$ Q$^4$Si) is between 50-70 ppm.

Fly ash blended geopolymers show resonance between 50-70 ppm indicating aluminium tetrahedral coordination. This is attributed to the the cross linking briding C-A-S-H gel. This result again indicate the high level of cross linking in blended fly ash and slag geopolymer bindes which are stable structures.
100% Slag based geopolymer contain in octahedral coordination 4% Na₂O showed a major contribution (93%) at 16.3 ppm which corresponding to Al and a small contribution (7%) at 10.8 ppm from Al in octahedral coordination. However, 100% fly ash based geopolymer with 4% Na₂O produced a single broad resonance at ~ 62 ppm, indicating Al in an tetrahedral environment.

The $^{27}$Al MAS-NMR spectrum of pure OPC containing 1.2% of Na₂O shows a main resonance at 15.2 ppm (75%) and a smaller component at 11.8 ppm (25%), both indicating Al located in octahedral coordination sites, but within a different chemical environment. Addition of 25% fly ash slightly increased the contribution centred at 15.2 ppm to 85% and decreased it to 51% with addition of 65% of slag.

![Figure 8-12: $^{27}$Al MAS NMR spectra from powders acquired at 10 kHz spinning speed and 23°C.](image)

Figure 8-13 shows the $^{23}$Na MAS NMR spectra for geopolymer binders and OPC binders. The $^{23}$Na MAS NMR spectrum of pure OPC containing 1.2% of Na₂O shows a single
resonance at -6.2 ppm. Addition of 25% fly ash or 65% of slag slightly induced an upfield shift to -6.5 ppm. Fly ash with 4% Na$_2$O shifted the resonance downfield to -5.9 ppm while a downfield shift to -7.6 ppm was observed with 100% slag geopolymers. The mixture containing 70% fly ash produced a large upfield shift to -4 ppm, while the resonance chemical shift was observed at -6.6 ppm if reduced to 50%. These differences in chemical shift may indicate the preferential interaction of Na$^+$ with bridging oxygen (BO) and non-bridging (NBO) oxygen and/or BO in Al-O-Al and Si-O-Al environments. When the polymerization is more complete (in fly ash and slag based geopolymers) the non-bridging oxygen content is lower. These non-bridging oxygen has potential to convert into hydroxyl ions [30].

Figure 8-13: $^{23}$Na MAS NMR spectra from powders acquired at 10 kHz spinning speed and 23°C.
8.3.4. X-Ray diffraction of alkali activated binders

The XRD patterns of the blended fly ash and slag geopolymer binders at two ages i.e. 28 and 270 days are shown in Figure 8-14. The results show that geopolymer binders containing higher than 50% slag have C-S-H phases indicated by the peak at 29°20. C-S-H has a disordered structure similar to riversideite and do not have 3-dimensional cross linking.

When the Fly ash percentage is increased beyond 50% the resulting binders show a peak corresponding to N-(C)-A-S-H type garronite phases and N-A-S-H type zeolite crystalline phases. The high fly ash binders also showed a hump between 25-30°20 corresponds to the amorphous geopolymer gel. The XRD patterns at 28 days also show the presence of crystalline phases corresponding to unreacted particles from the original fly ash (mullite, quartz, and hematite). However, at 270 days, the height of these peaks decreased indicating continual geopolymerisation reaction.

Above XRD results shows that geopolymers containing higher slag content produce higher content of calcium bearing phases including disordered calcium silicate hydrate phases. These phases do not have 3-dimensional cross linking like N-A-S-H phases which are produced in high fly ash binders. The disorderly structure in high slag binders can be easily attacked by chemically. These observations confirm the high susceptibility to AAR expansive reaction shown by geopolymer concrete containing higher slag.
Figure 8-14: XRD patterns of geopolymer binders (a) 70/30 FA/S (b) 50/50 FA/S (c) 30/70 FA/S (d) 0/100 FA/S

8.3.5. Microstructural analysis of alkali aggregate reaction products in geopolymer mortars

As discussed earlier, the ingredients of the binder significantly impact the AAR expansion. The combination of OPC or 100S with reactive aggregate caused excessive mortar bar expansion, whereas the use of at least 30% fly ash in binder prevented the expansion during the test period. SEM/EDX analysis was used to compare microstructural features of mortars incorporating the different aggregates in combination with 5050FA/S, 100S and OPC binders. Note that, the specimens used for this study were coated with evaporated gold (Au)
and the Au peaks noted in the EDX spectra are related to the coating not the specimen itself.

Figure 8-15, Figure 8-16 and Figure 8-17 show the different forms of products found in mortars with different binders in the presence of reactive aggregates R1 and R2 and non-reactive aggregates NR. Figure 8-15 (a) shows a reaction product formed in M5050FA/S-6-NR mortar (marked ‘X’ on the SEM image). According to EDX composition, this product is a sodium alumino silicate, which appears crystalline and probably a zeolite-like composition. This is a geopolymerisation product which is unrelated to the aggregate phase. Figure 8-15 (b) shows M0/100FA/S-6-NR also contain zeolite-like product but with lower aluminium and higher calcium content compared to that noted in Figure 8-15 (a). Zeolite type product formation in geopolymer mortar is common, particularly at elevated temperatures (mortar bar test was conducted at 80°C for 60 days). However, based on the mortar bar expansion results, these products did not change the volume the mortar bars. Figure 8-15 (c) shows a reaction product found in OPC-NR mortars with composition similar to that of calcium silicate hydrate.

Figure 8-16 shows the microstructures of geopolymer and OPC mortar bars containing reactive aggregate (R1). OPC and 100S binders reacted with aggregate R1 and formed massive AAR gel, filling a pore (Figure 8-16 (a)) and platy crystalline rosettes products as shown in Figure 8-16 (b). These products has high amount of silicon, sodium and calcium which is the composition of typical AAR products. These products were abundant in these mortar bars indicating severe alkali aggregate reaction which caused the large expansion measured for the corresponding mortar bars. Figure 8-16(c) shows that M50/50FA/S-6-R1 in the presence of aggregate R1, formed zeolite-like product with lower aluminium content than the zeolite products which are geopolymerisation products. Typical AAR products were not noted in the latter mortar bars.

Figure 8-17 shows the composition of binder and AAR products in mortar bars containing reactive aggregate R2. Area ‘A’ as marked on each image represents a region of non-reacted binder. The EDX spectrum of both OPC and 100% slag binders shows higher calcium and lower silicon typical of calcium silicate hydrate. Even though, both spectra (OPC and 100% slag) show a composition of calcium silicate hydrate, Ca/Si ratio in OPC binder is higher than that of slag binder which is expected. Mg identified in the in the EDX spectrum.
spectrum of 100% slag geopolymer originates from the unreacted slag or hydrotalcite type phases. Area ‘B’ marked on each image represents AAR products. The main reaction products formed in OPC and 100% slag geopolymer mortars were identified as typical AAR product like rosette-type crystals as seen in Figure 8-17. Most of the AAR related products found in the mortars in the presence of reactive aggregates are similar in nature. Observed AAR products were rich in silicon and sodium but poor in aluminium which is typical of composite of AAR products.

(a) M5050FA/S-6-NR

(b) M0100FAS-6-NR
(c) MOPC-NR
Figure 8-15: Reaction products found in mortars with different binders in the presence of NR basalts. Each EDX spectrum represents the composition of the area marked on the corresponding image.
Figure 8-16: Reaction products found in mortars with different binders in the presence of reactive aggregate R1. Each EDX spectrum represents the composition of the area marked on the corresponding image.
Figure 8-17: Reaction products found in mortars with different binders in the presence of reactive aggregate R2

Figure 8-18 shows that mortar specimens made with blended fly ash and slag geopolymer exhibit clear microstructural differences compared to those made with 100S. Whereas in the latter AAR products, such as the rosettes shown in Figure 8-18 (a), were present in the latter. Na-aluminosilicate materials (Figure 8-18 (b) were present in the blended fly ash and slag geopolymers. The aluminium content in these products was relatively large, whereas typical AAR products (as seen in Figure 8-18(a) contain very small aluminium contents. The products formed in blended fly ash and slag geopolymers could belong to zeolite type phases generated in addition to geopolymer gel. García-Lodeiro et al. [6] also observed similar products in their fly ash based geopolymers.
EDX spectrum ‘C’ in (Figure 8-18) shows that AAR gel was present in this mortar (M5050FAS-6-R2), and that the geopolymer phases were formed in association with the AAR gel. Overall, the SEM/EDX study confirmed that different hydrated phases develop in 100% slag geopolymer and blended fly ash and slag geopolymer. AAR products were also confirmed in mortar bars containing OPC and 100% slag based geopolymer binder, but not in blended fly ash and slag geopolymers.

Figure 8-18: Products formed in mortars (a) M0100FAS-6-R2 (b) M5050FAS-6-R2
8.4. Concluding remarks

The following conclusions can be drawn from this work:

1. Blended fly ash and slag geopolymer binders show lower susceptibility to expansive alkali aggregate reaction than OPC based binders in the presence of reactive aggregates.

2. Increasing the slag content of the blended fly ash and slag geopolymer binder increase the susceptibility to alkali aggregate expansive reaction in the presence of reactive aggregates. Geopolymer binders with less than 70% slag did not show significant expansion in the presence of reactive aggregates.

3. In general concrete prism test results correlates well with the accelerated mortar bar test results for blended fly ash and slag geopolymer mortars and OPC concrete specimens. The only exception was 100% slag binder in the presence of reactive aggregates which showed lower expansion in concrete prism test than in mortar bar test.

4. SEM/EDX analysis showed that OPC and alkali activated 100% slag based mortars produced typical AAR product such as rosettes, in the presence of reactive aggregates. On the other hand, blended fly ash and slag geopolymer generated zeolitic type products which contain significantly higher aluminum content compared the products of 100% slag based geopolymer or OPC.

8.5. References for chapter 8


9. Chloride ingress and steel corrosion in geopolymer concrete based on long term tests

9.1. Introduction

As mentioned in the previous chapter, to date, geopolymer concrete has had relatively minor application in field concrete due to the limited knowledge base on its durability. Its long-term durability properties as well as its protection against reinforced corrosion are yet to be fully investigated [1]. Some studies of marine-exposed concrete specimens have shown that the performance of geopolymer concrete specimens is comparable to that of Ordinary Portland cement (OPC) concrete with respects to reinforced corrosion [2].

Corrosion is one of the main durability problems that leads to premature degradation of concrete structures. Statistics have shown that 80% of concrete structure degradations happen due to corrosion [3]. Corrosion causes longitudinal cracking of concrete cover, reduction of rebar cross section and loss of steel-concrete bond. These factors can significantly reduce the service life of a structure. The cost involved with repairing and demolishing of damaged structures due to corrosion is very high [3]. Therefore, the performance of concrete made with new binder and its corrosion resistance should be well understood. Ideally, the susceptibility to corrosion of geopolymer concrete should be lower or at least the same as that of OPC concrete.

The main cause of corrosion in concrete structures, particularly in concrete structures in marine environment is the chloride ingress [4, 5]. Chloride ions from external sources can penetrate into concrete up to the steel level and destroy the protective passive layer leading to formation of rust in the steel [5]. Chloride ions can enter to concrete structure either as a result of contaminated ingredients (source material, aggregates, water) or through prolonged exposure to chloride rich environments. While chloride transportation and chloride induced corrosion of OPC structures has been well studied, there is only limited number of studies on chloride diffusion and chloride induced corrosion.

Ganesan et al. [6] studied the chloride diffusion of 100% fly ash based geopolymer and reported that chloride diffusion of geopolymer and OPC concrete are similar. In their
study authors employed AgNO$_3$ spraying to identify the depth of chloride penetration, as suggested by ASTM C1556 [7]. In contrast, the study by Olivia et al. [8] reported that the rate of chloride penetration in 100% fly ash based geopolymer concrete is higher than that of OPC concrete. Chindapasirt et al. [1] reinforced class C fly ash based geopolymer concrete and transferred them to tidal zone of a marine site to analyse the chloride diffusion and corrosion rate. They found that the alkali content used for synthesising geopolymer concrete controls the diffusion rate and chloride binding capacity. Their results showed that the corrosion rate depends on the compressive strength of the geopolymer. Shayan et al. [9] characterised the properties of a 100% slag-based geopolymer concrete after having been in service for five years in the retaining walls of a bridge structure on the Yarra river in Melbourne, Australia. The rapid chloride permeability test ASTM 1202 [10] showed very low chloride permeability. Based on NT Build 443 [11] chloride diffusion coefficient was an order of magnitude lower than that of blended slag cement concrete used in the retaining walls of the same bridge. More recently, Ma et al. [12] followed NT build 443 test method [11] to evaluate the chloride diffusion coefficient of 100% slag-based geopolymer and found that chloride diffusion rate of slag based geopolymer concrete is lower than OPC concrete. However, in the same study, Ma et al. [12] found that the corrosion rate of rebar inside prism specimens is similar to that of the embedded rebar inside OPC concrete.

The above studies were mainly focused on corrosion due to chloride ingress. There are also a few studies on chloride induced corrosion in contaminated concrete. Monticelli et al. [13] added 2% chloride by mass of binder to 100% class F fly ash based geopolymer during the mixing process. The authors reported that the availability of silicate ions in the pore solution of contaminated geopolymer concrete can provide additional protection for the passivity of rebar. Miranda et al. [14] observed that addition of 2% chloride by mass of binder to fly ash based geopolymer mix increase the corrosion rate by 100 times compared to uncontaminated geopolymer concrete. They also found that the steel embedded in contaminated geopolymer did not have the protective passive layer and show similar corrosion behaviour to OPC. The result of Bastidas et al. [15] is in agreement with the previous observations.
Blending of class F fly ash and slag enables geopolymers to set at ambient temperature curing which is more convenient in practice than elevated temperature curing. Blending of slag and fly ash also modifies the reaction phases and the microstructure of geopolymer compared to 100% fly ash or 100% slag based geopolymer leading to different level of chloride binding capacity [16]. Therefore, it is important to study the effect of fly ash or slag content of the binder on its susceptibility of chloride induced corrosion. Ismail et al. [17] measured the chloride diffusion of blended fly ash and slag concrete using AgNO₃ colorimetric method and found that chloride diffusion of blended fly ash and slag concrete is lower than that of OPC concrete. It is known that the results obtained from the colour change boundary of the AgNO₃ colorimetric have shown large variations [18, 19]. The rate of chloride diffusion into a concrete structure is quantified using the diffusion coefficient. When concrete matures the pore structure refines and with additional reaction products leads to a reduction in diffusion coefficient [20]. Ignoring the variations in diffusion coefficient with aging can result in overestimation of the chloride penetration rate leading to over-designed structures (aimed at preventing chloride induced corrosion) [21].

Although few studies have been undertaken on the chloride-induced corrosion and chloride diffusion rate in geopolymer, the effects of aging on the rate of chloride diffusion has not been investigated. In the present study more accurate potentiometric titration method [12, 22] was used to determine the effect of the binder composition on the chloride diffusion of geopolymer concrete. Further to Ismail et al. [17], the authors of this study also analyse both chloride ingress and the state of corrosion of re-bar in blended fly ash and slag geopolymer concrete immersed in NaCl solution up to 500 days. This study also examines the change in chloride diffusion rate with time in blended fly ash and slag geopolymer using rapid chloride permeability test at three different ages. The results are also used to predict the time taken to initiate chloride induced corrosion in embedded rebar in the presence of different binders. These results were then compared with the actual corrosion states of re-bars embedded in those binders. Finally, the study evaluates the corrosion state of the embedded rebar in blended fly ash and slag geopolymer concrete contaminated with 2% (by mass of binder) The purpose is to accelerate the corrosion so that the investigation can be completed in realistic time period.
9.2. Materials and methods

9.2.1. Materials

Precursor materials

A class F fly ash (FA) which was a 50/50 mixture of Gladstone and Callide fly ashes (FA) and granulated ground blast furnace slag (Slag), with the chemical compositions shown in Table 9-1 were used as the alumino-silicate precursor materials. The bulk chemical compositions were determined by X-ray florescence (XRF) analysis. The main component of class F fly ash is SiO$_2$ (over 51%) whereas slag contains high amount of CaO (41.5%). It is important to note that fly ash contains twice as much Al$_2$O$_3$ as slag does. The particle size distributions of fly ash and slag, obtained using a Cilas laser diffraction particle analyser are shown in Figure 9-1. The particle size analysis shows that both fly ash and slag have small particle sizes which are desirable for the geopolymer reaction. It also shows that class F fly ash has 10% of very fine particles (< 1μm), while slag has about 2.5% of finer than 1μm.

Table 9-1: Bulk chemical composition of materials (wt. %)

<table>
<thead>
<tr>
<th>Oxides</th>
<th>GP Cement</th>
<th>Slag</th>
<th>FA</th>
</tr>
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<tbody>
<tr>
<td>SiO$_2$</td>
<td>19.30</td>
<td>32.00</td>
<td>51.50</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.30</td>
<td>0.51</td>
<td>1.50</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>5.50</td>
<td>13.00</td>
<td>27.60</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>2.90</td>
<td>0.40</td>
<td>11.80</td>
</tr>
<tr>
<td>Mn$_3$O$_4$</td>
<td>0.20</td>
<td>0.30</td>
<td>0.15</td>
</tr>
<tr>
<td>MgO</td>
<td>1.40</td>
<td>4.90</td>
<td>1.30</td>
</tr>
<tr>
<td>CaO</td>
<td>62.00</td>
<td>41.50</td>
<td>2.20</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.06</td>
<td>0.20</td>
<td>0.40</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.40</td>
<td>0.33</td>
<td>0.60</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.11</td>
<td>0.02</td>
<td>0.73</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>2.46</td>
<td>2.10</td>
<td>0.2</td>
</tr>
<tr>
<td>S$^-$</td>
<td>0.00</td>
<td>0.60</td>
<td>0.00</td>
</tr>
<tr>
<td>LOI</td>
<td>5.3</td>
<td>4.9</td>
<td>1.8</td>
</tr>
</tbody>
</table>
Figure 9-1: Particle size distribution of (a) Slag (b) Fly ash. 1-10 g of source material was dispersed in water in order to obtain the particle size.

Alkali activator

Granular sodium metasilicate penta-hydrate (28.7% Na₂O, 28.5% SiO₂ and 42.8% H₂O) was used as solid activator to activate the precursors. Usage of solid alkali activators in geopolymer systems is less hazardous than commonly used liquid activators and more convenient for field applications. The amount of activator used was calculated to provide an alkali content of 4% Na₂O by mass of precursor materials.

Aggregates

A coarse basalt aggregate of 14 mm nominal particle size and river sand were used in the geopolymer concrete mix. The particle density of coarse aggregates and the sand in saturated surface dry condition (SSD) was 2830 and 2620 kg/m³, respectively, and moisture absorption was 2.2 and 0.3% respectively.

9.2.2. Preparation of geopolymer concrete

The mix designs for the geopolymer concretes employed in this work are shown in Table 9-2. The concrete mixing procedures consistent of: First, sand, coarse aggregate and precursor materials were mixed thoroughly for 1 minute. Next, water was added to the mix and mixing was continued for another 2 minutes. Subsequently, alkali activator (solid form) was added into wet mix and mixed for around 7 minutes to obtain workable geopolymer concrete. The workability of geopolymer concrete mix was measured using the standard slump test according to AS1012.3.1 [23]. The target slump was 80-100 mm.
Two identical concrete prisms (95 × 95 × 300 mm) were cast from each, mix embedding a 20 mm diameter carbon steel rebar. A sample prism is shown in Figure 9-2. The concrete mixes were also used to cast cylindrical specimens (100×200 mm) for NT build 443 testings. The cast specimens were transferred into a standard fog room (23°C, 100% RH). After 24 hours, concrete specimens were de-moulded and stored inside fog room until 28 days. During the storing period in the fog room, the samples were covered with plastic sheets to avoid the water dropping on the sample.

To identify the corrosion behaviour in contaminated concrete, 50/50 FA/Slag geopolymer concrete specimens were cast with added 2% NaCl by mass of binder and partially immersed in water. The temperature during the immersion test was maintained at 23°C. An OPC concrete prism was also cast with added 2% NaCl by mass of binder as a control. The corrosion state of the rebar embedded in concrete was determined using Gecor8 instrument (Cu/CuSO₄ reference electrode).

Table 9-2: Mix design for concrete (Alkali content = 4% for geopolymers)

<table>
<thead>
<tr>
<th>Mix</th>
<th>FA (kg/m³)</th>
<th>Slag (kg/m³)</th>
<th>OPC (kg/m³)</th>
<th>Aggregate (kg/m³)</th>
<th>Water/Solid ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>60/40 FA/Slag</td>
<td>240</td>
<td>180</td>
<td>0</td>
<td>680 630 450</td>
<td>0.390</td>
</tr>
<tr>
<td>50/50 FA/Slag</td>
<td>200</td>
<td>200</td>
<td>0</td>
<td>680 630 450</td>
<td>0.425</td>
</tr>
<tr>
<td>40/60 FA/Slag</td>
<td>180</td>
<td>240</td>
<td>0</td>
<td>680 630 450</td>
<td>0.449</td>
</tr>
<tr>
<td>OPC</td>
<td>0</td>
<td>0</td>
<td>400</td>
<td>680 630 450</td>
<td>0.464</td>
</tr>
</tbody>
</table>

Figure 9-2: Specimens used for chloride induced corrosion testing (Dashed line shows the level of NaCl solution during the immersion process)
9.2.3. Testing procedure

Chloride diffusion tests

After 28 days of moist curing at 23°C each concrete cylinder was segmented to three parts with heights 51 (cast-end, cut-end), 51 (cut-end, cut-end) and 98 mm (cut-end, cast-end) respectively. The curved surfaces of the cylindrical segments were then coated with quick setting epoxy which prevented chloride transportation into the concrete from the sides.

Chloride diffusion coefficients of geopolymer and OPC concretes were measured using NT Build 443 [11] method. The 98 mm cylindrical section was immersed in 2.826 M sodium chloride solution vertically such that approximately 1/4 of the height was submerged inside the solution. Cylindrical specimens were mounted on PVC rings in order to maintain uniform chloride exposure through the bottom surface. The chloride solution was stirred frequently in order to have a uniform solution. After 5 weeks of immersion, the concrete specimens were drilled in 1 mm depth increments using a profile grinder to obtain fine concrete powder from each 1 mm layer (75 mm diameter circular area is drilled). The obtained concrete powder was dried at 105°C for 24 hours (powder was covered properly avoiding direct heat exposure). Approximately, 5 g mass of the dried concrete powder was mixed with distilled water (1:5 solid to water ratio) and HNO₃. The resulting solution was boiled and filtered to extract the chloride ions from concrete powder. Potentiometric titration was conducted on the filtered solution using standard 1N AgNO₃ solution to obtain the chloride content (acid soluble chloride) of each layer.

The rapid chloride permeability of concretes was measured using ASTM 1202 standard [10]. In this test each ends of a 51 mm concrete cylinder is exposed to 0.6 mole/L NaCl and 0.3 mole/L NaOH respectively. Then 60V electrical field is applied between the two ends for 6 hours. The electrical field is used to accelerate the chloride penetration. Chloride permeability of geopolymer concrete was measured at three ages, namely 28 days, 180 days and 500 days.
Measurements of corrosion state of embedded rebar

After 28 days of ambient curing at 23°C, the concrete prisms were partially immersed in 2.826 and 0.6 M NaCl solutions up to 500 days. Temperature of the storing room was 23°C. After 500 days, immersed concrete prisms were split to observe the corrosion state of embedded rebar. Chloride penetration depth and chloride content at the rebar were calculated using potentiometric titration [11].

9.3. Results and Discussion

9.3.1. Chloride diffusion rate of concrete in unsaturated condition

Corrosion due to chloride ingress is initiated when sufficient amount of chloride ions penetrate to the depth of reinforcement steel [5]. The resistance against chloride transportation into concrete is quantified using the chloride diffusion coefficient [24]. To determine the rate of chloride diffusion into concrete NT build 443 test as described in section 9.2 was conducted. The apparent diffusion coefficient of a concrete (D_a mm²/year) can be calculated using the Fick’s second Law of Diffusion. According to this law the relationship between the calculated chloride content of concrete (C_{t,x}), and the depth from the exposed surface (x) is as follows:

\[ C_{(t,x)} - C_0 = (C_S - C_0) \text{erfc} \left( \frac{x}{\sqrt{2D_a t}} \right) \tag{1} \]

Where C_S is the chloride concentration at the surface (x=0), C_0 is the chloride concentration in concrete before immersion and t is time in years and t_s age of concrete when exposure started. The chloride profile of concrete specimens obtained using the above procedure was then used to calculate the chloride coefficient of each concrete type.

Figure 9-3 shows the chloride profiles obtained for the geopolymer and OPC concretes while Table 9-3 shows the calculated chloride diffusion coefficients. The chloride profile and the chloride diffusion coefficient results show that the chloride diffusion rate decreases significantly when the slag content of the geopolymer binder is increased.
Geopolymer concrete containing significant level of slag has the following main reaction products: calcium silicate hydrate (C-S-H), calcium aluminate silicate hydrate (C-A-S-H), sodium aluminate silicate hydrate (N-A-S-H) and hydrotalcite phases [17, 25, 26]. When the slag content of the geopolymer blends increases, the resulting binder consists more C-S-H, C-A-S-H than N-A-S-H and higher amount of hydrotalcite phases [17, 27]. It is known that C-A-S-H products have higher a binding capacity for chloride ions (and accompanied Na ions) compared to N-A-S-H which can limit the ingress of those ions [17]. Hydrotalcite (Mg₆Al₂(OH)₁₆CO₃·4H₂O) has a layered double hydroxide structure. This layered crystal structure consists of an outer layer with hydroxide and an inner layer with anions and water molecules [27-29]. Therefore, hydrotalcite has large specific area which increase its capability to exchange ions with the concrete pore solutions and absorb anions to its structure [29]. Previous studies have shown that the addition of hydrotalcite into a chloride contaminated system externally result in the reduction of chloride content in the concrete without changing the structure of hydrotalcite [27, 30].

The SEM/EDX shows the indication of hydrotalcite type phases with significant magnesium level in fly ash and slag based geopolymer which is also confirmed in literature [27]. Geopolymer containing lower slag content mainly produces N-A-S-H type phases which have high pore volume [17, 25]. Provis et al.[16] and Lloyd et al. [31] showed that substitution of fly ash for slag increases the porosity of the geopolymer significantly. They stated that geopolymer containing high slag content have high bound water (induced by calcium) which leads to more pore-filling capacity than geopolymer containing high fly ash [16]. This is in agreement with the studies by Yang et al. [32] and Li et al. [33]. The higher porosity of high fly ash based geopolymer can absorbs more external chloride ions and deposit in the binder pore solution than geopolymers containing high slag. Previously it has been reported that geopolymers containing higher fly ash content (>50%) has halite (NaCl) in their pore solution than that of high slag based geopolymers [17]. The above mentioned factors explain the reduction in diffusion coefficient in geopolymers with the increase of slag content.
The chloride diffusion coefficients results in Table 9-3 also show that the resistance to chloride transportation is higher in blended fly ash and slag geopolymer concrete compared to OPC based concrete. Geopolymer concrete containing significant level of calcium produces cross-linked tobermorite-like C-A-S-H which are high density structures compared to non-cross linked tobermorite-like C-S-H phases formed in OPC concrete [34]. These cross linked structures reduce the chloride diffusion rate of blended fly ash and slag geopolymer compared to that of OPC concrete. OPC binder also contains calcium aluminates and calcium aluminoferrite phases that can absorb chloride ions forming $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ (Friedel’s salt). However, the study by Florea et al. [35] stated that Friedel’s salt formation in OPC binder is significant only in chloride contaminated concrete during the initial hydration process. The Friedel’s salt formation after cement hydration is very slow hence this process would not be effective in absorbing chloride coming from the external sources in the long term [36, 37]. This explains the higher chloride diffusion in OPC concrete.

![Figure 9-3: Chloride profiles of concrete cylinders after 5 weeks of immersion test](image)

<table>
<thead>
<tr>
<th>Geopolymer formulation</th>
<th>Surface Cl⁻ % ($C_a$) (%wt. by concrete mass)</th>
<th>Apparent chloride diffusion coefficient ($D_a$) $10^{-12}$ m²/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>60/40 FA/Slag</td>
<td>0.80</td>
<td>5.17</td>
</tr>
<tr>
<td>50/50 FA/Slag</td>
<td>0.89</td>
<td>2.38</td>
</tr>
<tr>
<td>40/60 FA/Slag</td>
<td>0.81</td>
<td>1.01</td>
</tr>
<tr>
<td>OPC</td>
<td>0.80</td>
<td>6.70</td>
</tr>
</tbody>
</table>

Table 9-3: Chloride diffusion coefficient and surface chloride content of concrete
Table 9-4 shows the chloride content (Cl% by mass of concrete) at the different depth of geopolymer and OPC concrete after 500 days immersion in 2.83 M NaCl solution. The results show that the chloride content of OPC concrete is higher than geopolymer concrete at all depths. At the rebar (40 mm depth), OPC concrete has 0.077% chloride (by mass of concrete) which is above the threshold chloride value that initiates corrosion [38]. On the other hand, geopolymer concrete shows 10 times lower chloride content at the rebar after 500 days which is not sufficient to initiate chloride induced corrosion.

The resistance to chloride ingress rate into concrete is reduced upon aging of the geopolymer concrete. It is well known that chloride diffusion rate of OPC concrete decreases with the age of concrete as a result of chloride binding and refinement in the pore structure [39]. It was reported that a 1 day old OPC binder has pore size range 8 nm to 700 nm while more than 365 days old OPC binder has pores in the range of 16 nm to 64 nm [39] which significantly affects the chloride diffusion coefficient of concrete. Ignoring this effect can result in overestimation of the chloride penetration rate [21]. Resistance to chloride ingress into concrete can vary due to modified microstructure and additional reaction products formed during extended curing. Geopolymerisation is a continual reaction process that can have different microstructure and new reaction phases in the later stages compared to premature age of concrete. Puertas et al. [26], showed that when blended fly ash and slag geopolymer matures, FTIR (T-O-T T: tetrahedral Si or Al) band shifted towards a higher value indicating higher degree of cross-linking in geopolymer than in early age concrete. This is attributed to the continual development of N-A-S-H and C-A-S-H cross-linking and increase of number of reaction products. Their results are in agreement with several other studies [20, 40].
Provis et al. [16] reported that longer curing of blended fly ash and slag geopolymer increases the pore-network tortuosity and decreases the porosity due to space filling nature of C-(N)-S-H phases. Xu et al. [20] reported that in the presence of slag, geopolymerisation is continual as slag provides hydroxyl buffering to react with the precursors in the later age. Moreover, the authors found that channels in the pore structure are disconnected due to maturity of geopolymer concrete. These studies show that resistance to chloride ingression into concrete is expected to be lower in the later age of geopolymer concrete. In the next section, the age factor of geopolymer concrete will be quantified and analysed the factors affecting it.

Table 9-4: Chloride percentage in the different depth of concrete after 500 days of immersion in 2.83 M NaCl solution

<table>
<thead>
<tr>
<th>Concrete type</th>
<th>Average depth of the concrete (mm)</th>
<th>Measured chloride (%wt. by concrete mass)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50/50 FA/Slag</td>
<td>1</td>
<td>0.880</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.300</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.020</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.007</td>
</tr>
<tr>
<td>OPC</td>
<td>1</td>
<td>0.989</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.364</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.299</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.077</td>
</tr>
</tbody>
</table>

9.3.2. Quantifying the age factor for geopolymer concrete

The influence of the age on the chloride diffusion coefficient is an important parameter for service-life modelling of any concrete structure [41]. The chloride diffusion of concrete $D(t)$ varies with the time as shown in the equation (7) [41]:

$$D(t) = D_{ref}(\frac{t_s}{t})^m$$  \hspace{1cm} (7)

Where, $m(>0)$ is the age factor, $D_{ref}$ is the chloride diffusion rate obtained using NTBuild 443 test (Table 9-3) and $t$ is exposure time in years and $t_s$ age of concrete when exposure started. Rapid permeability test results at several ages of concrete can be used to obtain the value of $m(>0)$ for concrete. The rapid chloride permeability test (RCPT) ASTM C1202 [10] provides information on the instantaneous chloride
diffusion of concrete as it is conducted within a short period of time (6 hours), whereas NTBuild 443 [10] test involves 35 days immersion period. Previous studies have shown that the changes in RCPT results upon aging would reflect the changes in the chloride diffusion change [42, 43]. In order to calculate the \( m \) factor of concrete, rapid chloride permeability of concrete was conducted at three ages of concrete (i.e. 28, 180 and 500 days) and total charges passed through the concrete is calculated according to the procedure described in section 9.2.3 [24, 44]. The charges passed through concrete obtained from ASTM C1202 [10] test method is used to calculate the \( m \) factor as shown in the equation (8) [45, 46].

\[
G(t) = G_0 t^{-m}
\]

Where \( G(t) \) = charge passed through concrete at age \( t \) of concrete, \( G_0 \) = charge passed through concrete at age \( t_0 \).

Figure 9-4 shows the charges passed through concrete at different ages of concrete. The results show that the charges passed through 28 days old geopolymer concrete is in the range of 1000-2000 Columbus which is classified as low permeable concrete [10]. Even though, 28 days old OPC concrete can be also classified as low permeable concrete, the number of charges passed through OPC concrete is slightly higher than the corresponding value for geopolymer concrete. At 180 days, the charges passed through geopolymer concrete are significantly lower than in 28 days. This changes the permeability classification of geopolymer concrete to “very low” permeable concrete range [10]. The charges passed through geopolymer concrete after one year is only slightly lower than that at 180 days. All the geopolymer concretes reached to the same level of permeability level after one year, with charges passed through concrete being 300-330 Columbus. On the other hand, the 180 days old OPC concrete had the same permeability category (low) as the 28 days old OPC concrete. When the OPC concrete was older than one year the change in the permeability level was not significant.

The calculated age factors are presented in Table 9-5. The results show that the age factor of geopolymer concrete is in the range of 0.400-0.600. On the other hand age factor of OPC concrete is only 0.200 which is half of the age factor of geopolymer concrete. The value obtained for 100% OPC concrete is similar to the values reported in
previous studies [46, 47]. This shows aging improves the resistance of geopolymer concrete for chloride diffusion more significantly than for OPC concrete. As mentioned previously, when fly ash and slag geopolymer concrete matures, a higher degree of cross-linked structure is achieved than in early age, more reaction products (like hydrotalcite) are formed from unreacted fly ash and slag particles and pore structure of the binder is refined [16, 17, 27]. The combination of these parameters reduced the chloride diffusion of the concrete upon aging at a higher rate than for OPC concrete. Even though the pore structure is refined upon aging of OPC binder, not as much additional products are formed for binding chloride [36, 37, 39] in turn a lower age factor is obtained.

Previous studies [48, 49] have reported that, when used on geopolymer binders, the outcome of the RCPT test is greatly influenced by the ion mobility of the pore solution rather than the chloride permeability. However, current study found that RCPT results correlates well with the chloride induced corrosion.

![Figure 9-4: The change of charged passed through concrete for concrete specimens of different ages](image)

<table>
<thead>
<tr>
<th>Mix proportions</th>
<th>Age factor of concrete (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60/40 FA/Slag</td>
<td>0.407</td>
</tr>
<tr>
<td>50/50 FA/Slag</td>
<td>0.604</td>
</tr>
<tr>
<td>40/60 FA/Slag</td>
<td>0.509</td>
</tr>
<tr>
<td>OPC</td>
<td>0.192</td>
</tr>
</tbody>
</table>
Service life prediction of concrete

Evaluation of the time to initiate corrosion on the embedded rebar in concrete is essential in modelling the service life of concrete structures. The results in Table 9-4 and the state of rebar (see section 9.3.4) shows that in OPC corrosion has initiated at a chloride level of 0.077% by mass of concrete. This chloride level has also been identified as the threshold level of the chloride to initiate corrosion process in rebar embedded in OPC concrete [38].

Assuming the same threshold level for geopolymer concrete, the time taken to initiate the corrosion can be calculated using the equations (9)-(16) [50]. The following assumptions are used in the calculation of the corrosion initiation time.

1. The threshold chloride level for the initiation of the steel corrosion is 0.077% by weight of concrete.
2. The diffusion rate only changes during the initial 10 years. There after it is assumed to be constant.

\[
D_a = \begin{cases} 
D_{\text{ref}} \left( \frac{t_{\text{ref}}}{t} \right)^m, & t < 0 \\
D_{\text{ref}} \left( \frac{t_{\text{ref}}}{10} \right)^m, & t \geq 0 
\end{cases} 
\]  

(8)

\[
C(t, x) = C_s \cdot \text{erfc} \left( \frac{x}{\sqrt{4D_a \cdot t}} \right) 
\]  

(9)

\[
C(t, x) = C_s \cdot \text{erfc} \left( \frac{x}{\sqrt{4 \int_{t_s}^{t_{\text{exp}}} D(t) \, dt}} \right) 
\]  

(10)

\[
D(t)_{\text{avg}} = \int_{t_s}^{t_{\text{exp}}} D(t) \, dt 
\]  

(11)

\[
D(t)_{\text{avg}} = \int_{t_s}^{t_{\text{exp}}} D_{\text{ref}} \left( \frac{t_{\text{ref}}}{t} \right)^m \, dt 
\]  

(12)

\[
D(t)_{\text{avg}} = D_{\text{ref}}(t_s)^m \int_{t_s}^{t_{\text{exp}}} t^{-m} \, dt 
\]  

(13)

\[
D(t)_{\text{avg}} = D_{\text{ref}}(t_s)^m \cdot \frac{1}{1-m} \cdot (t^{1-m})_{t_s}^{t_{\text{exp}}} 
\]  

(14)
Where $t=$ time in years, $C(t, 25) =$ chloride threshold at 25 mm depth
concrete, $t_{ref} = t_s =$ starting time (28/365 years)

The results presented in Table 9-6 shows the time taken to initiate chloride induced
corrosion when the cover thickness of concrete is 25 and 40 mm and the environment
chloride concentration is 2.826 M. According to the calculations OPC concrete initiate
corrosion in 0.69 years which is consistent with the observations. OPC concrete takes
1.95 years to initiate corrosion when the cover thickness is 40 mm.

On the other hand geopolymer concrete has very high corrosion initiation time,
particularly the geopolymer concrete containing higher slag (>50%). The time taken to
initiate chloride induced corrosion is increased with the slag content in the geopolymer
concrete. This results show that geopolymer concrete structures would have higher
service life in chloride environment compared to OPC concrete structures. It should be
noted that a typical marine environment has a chloride concentration of around 0.6%
which is approximately a quarter of the concentration used for the calculations (2.8%).
Therefore, the initiation time will be much longer. The corrosion state of the rebar is
consistent with the chloride calculations.

Table 9-6: Number of years to reach chloride level of 0.077% in 2.826 M NaCl
solutions. (Chloride (%) = mass of chloride/ concrete mass)

<table>
<thead>
<tr>
<th>Mix proportions</th>
<th>Number of years to reached 0.077% chloride in different concrete depths</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25 mm</td>
</tr>
<tr>
<td>60/40 FA/Slag</td>
<td>1.28</td>
</tr>
<tr>
<td>50/50 FA/Slag</td>
<td>7.87</td>
</tr>
<tr>
<td>40/60 FA/Slag</td>
<td>13.19</td>
</tr>
<tr>
<td>OPC</td>
<td>0.69</td>
</tr>
</tbody>
</table>

Results presented in the previous section showed that chloride diffusion in blended fly
ash and slag geopolymer concrete is lower than in OPC concrete. Therefore, the
initiation time for corrosion is expected to be longer in geopolymer concrete than in OPC. To determine the corrosion state of the rebar, the specimens which had been immersed in the 2.826 M NaCl solution for 500 days were split, and immediately 0.1M AgNO₃ solution was sprayed to measure the chloride penetrated depth, based on the depth of white colour observed due to formation of AgCl. In general, when the chloride content of concrete is in the range 0.02-0.23, the colour change is observed [18, 19]. Figure 9-5 shows the concrete samples after spraying AgNO₃ solution and Table 9-7 shows the measured chloride penetrated depth of concrete obtained from AgNO₃. The depth obtained using AgNO₃ colorimetric method is based on the apparent chloride content of the concrete. Geopolymer concrete immersed in 2.826 M NaCl solution has very low chloride penetrate depth (lower than 5 mm). Moreover, when the geopolymer concrete prisms were immersed in 0.600 M NaCl solution, apparent chloride penetration depth is further reduced to 2 mm. On the other hand, OPC concrete immersed in 2.826 M and 0.600 M NaCl solutions respectively showed 35.0 mm and 25.0 mm chloride penetration depth which is significantly higher than that of geopolymer concrete samples. Since all the geopolymer concrete types had similar corrosion and chloride penetrated depth, only the 50/50 FA/Slag geopolymer concrete was samples are shown in the Figure 9-5.
Figure 9-5: Chloride penetration depth of concrete (a) 50/50 FA/S geopolymer immersed in 2.832 M NaCl solution (b) 50/50 FA/S geopolymer immersed in 0.6 M NaCl solution (c) OPC concrete immersed in 2.826 M NaCl solution (d) OPC concrete immersed in 0.6 M NaCl solution

Table 9-7: Depth of chloride obtained from AgNO₃ colorimetric method

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Depth in 2.826 M NaCl solution (mm)</th>
<th>Depth in 0.6 M NaCl solution (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60/40 FA/S</td>
<td>4.2</td>
<td>1.2</td>
</tr>
<tr>
<td>50/50 FA/S</td>
<td>4.0</td>
<td>2.5</td>
</tr>
<tr>
<td>40/60 FA/S</td>
<td>4.1</td>
<td>1.8</td>
</tr>
<tr>
<td>OPC</td>
<td>35.0</td>
<td>18.0</td>
</tr>
</tbody>
</table>

Figure 9-6 shows the corrosion state of rebar inside 50/50 FA/Slag geopolymer and OPC concrete after immersion in 2.826 M NaCl solution. Rebar inside geopolymer concrete retained its passivity after 500 days (Figure 9-6(b)) while chloride induced corrosion was initiated in rebar embedded in OPC and rust products are evident in Figure 9-6 (d). No rust products formed in either geopolymer concrete or OPC concrete for immersion in 0.6 M NaCl solution for 500 days (Figure 9-7).

Figure 9-6: (a) geopolymer concrete with rebar (b) embedded rebar in geopolymer concrete (c) OPC concrete with rebar (d) embedded rebar in OPC concrete immersed in 2.826 M NaCl
As observed in the previous section, the chloride ions take a long time to reach the embedded rebar in geopolymer concrete. Therefore, to accelerate the chloride induced corrosion the authors prepared specimens with added chloride. The corrosion current of embedded rebar was measured using Cu/CuSO\(_4\) (CSE) reference electrodes and the corrosion current was converted into the corrosion rate using Faraday's Law [51].

Figure 9-8(a) shows the corrosion rate of rebar in geopolymer concrete and OPC concrete respectively. Embedded rebar inside OPC concrete shows corrosion current approximately 1 \( \mu \text{A/cm}^2 \) in 100 days indicating high corrosion activity (high risk of corrosion) while, the rebar inside 50/50 FA/Slag geopolymer concrete show corrosion current in between 0.1 and 0.5 \( \mu \text{A/cm}^2 \) which is a sign for low to moderate corrosion activity [52]. Figure 9-8(b) shows the corresponding corrosion rate of the rebar. The rebar in OPC concrete corrodes approximately 10 \( \mu \text{m} \) per year while the rebar in...
geopolymer concrete corrodes 5 μm per year which is half of the previous value. The results show that rebar in contaminated geopolymer concrete has slower corrosion rate than OPC concrete which is important in the concrete structures.

It is well known that the pore solution of slag rich geopolymer concrete has high content of sulphide species (S²⁻ and S₂O₃²⁻) [12, 53, 54]. These sulphide ions can oxidize into sulphur consuming locally available oxygen [12, 53]. The absence of oxygen in the rebar inhibits the cathode reaction in turn the corrosion is controlled. Previous studies [12, 53] also observed that the corrosion the rebar in geopolymers containing slag reduces the corrosion of the rebar. Therefore, the corrosion rate of the rebar in geopolymer concrete is lower than that of rebar in OPC concrete.

![Figure 9-8: (a) Corrosion current (b) Corrosion rate of rebar in chloride contaminated geopolymer and OPC concrete](image)

**9.3.5. Microstructural analysis of 500 days old concrete**

Microstructural analysis of 500 days old geopolymer and OPC concrete was conducted using SEM/EDX technique.

Figure 9-10 shows the microstructural features of OPC concrete after 500 days. OPC concrete has sharp peaks corresponding to calcium and silicon with higher Ca/Si ratio which correspond to C-S-H type products. These microstrural analysis shows that the geopolymer pore solution is highly alkaline and better protects the steel against the corrosion.

Figure 9-9 shows an example of different microstructural features of 50/50 FA/Slag geopolymer concrete three different locations were analysed by EDX. The gel mainly
consists of significant level calcium, silicon and aluminium rich phases with small amount of sodium which correspond to C(N)-A-S-H gel. Moreover, based on the semi quantitative EDX analysis, these gels have Ca/Si ratios about 0.8-1.0 and Al/Si ratio 0.5-0.6. This chemical composition of the gel in 50/50 FA/Slag geopolymer is in agreement with previous studies [17, 55]. Significant level of magnesium was also identified in the geopolymer binder which is indication of hydrotalcite phases formed in the blended fly ash and slag geopolymer. Number of un-reacted particles observed in 500 days old geopolymer concrete samples is very low. Fe found in the binder and is attributed to unreacted magnetite or hematite crystalline phases in the fly ash.

Figure 9-9: Microstructure of 50/50 FA/Slag geopolymer concrete after 500 days
9.4. Concluding remarks

1. Apparent chloride diffusion coefficient of blended fly ash and slag geopolymer concrete is lower than that of OPC concrete. The diffusion coefficient decreased with the slag content in the binder (This is for 40-60% slag content in this experiment).

2. Blended fly ash and slag geopolymer concrete has higher age factor than in OPC concrete indicating improved the resistance to chloride ingress with time. The lower permeability is attributed to the higher binding capacity in the hydrotalcite phases and higher degree of geopolymerisation in blended fly ash and slag which have been reported in the literature.

3. The time taken to initiate the corrosion in the rebar in blended fly ash and slag geopolymer concrete is significantly higher than that of OPC concrete. The time is longer when the slag in the geopolymer is higher.

4. Chloride induced corrosion started in the rebar in OPC concrete exposed to 2.826 M NaCl solution for 500 days while the blended fly ash and slag geopolymer concrete bar did not corrode. The chloride content at the rebar in geopolymer is ten times lower than chloride content in OPC concrete. The results are consistent with the calculated initiation time.
5. Corrosion rate of embedded rebar in contaminated geopolymer concrete is lower than corrosion rate of embedded rebar in contaminated OPC concrete. This is due to reduction in oxygen around the rebar in the presence of slag in the binder (which has been confirmed by the previously reported work).

9.5. References for chapter 9


[5] N. Silva, Chloride Induced Corrosion of Reinforcement Steel in Concrete Threshold Values and Ion Distributions at the Concrete-Steel Interface, Chalmers University Of Technology, Sweden., 2013.


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[46] A. Xu, Shayan, A., Determination of Chloride Diffusion Coefficient of Concrete: Comparison of Bulk Diffusion and Electrical Field Method, 27th Biennial National Conference of the Concrete Institute of Australia in conjunction with the 69th RILEM Week, Melbourne, Australia, 2014.


10. Ductility of reinforced geopolymer concrete beams

10.1. Introduction

A comprehensive understanding of the performance of geopolymer-based structural elements is essential in encouraging widespread usage of this sustainable concrete. The ultimate load carrying capacity, deflection, crack formation and ductility are some of the key factors to be analysed in concrete structure to ensure adequate degrees of safety and serviceability are achieved [1]. Even though, mechanical properties of unconfined small scale geopolymer concrete made at both elevated and room temperature cured have been extensively analysed in the past [2], the behaviour of large scale steel reinforced geopolymer concrete elements is yet to be fully investigated.

There are very few studies in the literature on the characterisation of geopolymer based structural elements. Sumajouw and Rangan [3] studied the behaviour of class F fly ash based geopolymer concrete beams and columns with different tensile reinforcement ratios. They found that the load carrying capacity and failure modes of under-reinforced geopolymer concrete beams were similar to those of the OPC beams. More recently, Yost et al. [2] studied class F fly ash based geopolymer concrete beams with three different reinforcement designs (under-reinforcement, over reinforcement and shear critical). They reported that under flexure failure mode, geopolymer concrete beams were more brittle than their OPC counterparts. Yost et al. [2] also observed that maximum load of the geopolymer beams dropped quickly at failure resulting in sudden and complete collapse of the compression zone in the inner span, a behaviour which was different to that of OPC beams. However, they did not provide an explanation of this sudden failure in geopolymer beams. Cross et al. [4] studied the structural behaviour of class C fly ash based geopolymer concrete beams. They stated that crack propagations, failure modes and ductility were analogous with OPC beams.

The above studies have provided an insight on flexural behaviour of geopolymer concrete structures, particularly for elevated temperature cured geopolymers concrete based on class F fly ash. However, the flexural behaviour of geopolymer concrete elements made from fly ash and slag blends and cured at room temperature, and the ductility of reinforced geopolymer concrete beams are yet to be fully analysed. High ductility of structural elements (i.e. beam, column and load bearing wall), or the ability to undergo extensive inelastic deformation near its ultimate load carrying capacity,
would provide prior warning of failure and help avoid any premature brittle failures [5].

Ductility of reinforced beams depends on the reinforcement configuration and material characteristics, and can be adjusted by varying the tensile reinforcement ratio. However, varying the tensile reinforcement ratio may adversely affect the flexural capacity of the beams [6]. Incorporating adequate stirrups in concrete beams can increase both the ductility and the flexural capacity [6], as the concrete within the stirrups is confined, the beam can undergo higher deflections. The effect of confinement due to stirrups in geopolymer concrete beams does not seem to have been investigated in the past.

In this study, four cast-in-situ beams were prepared with two different stirrup contents using blended fly ash and slag geopolymer concrete at ambient temperature. One OPC concrete beam was used as a control. These beams were subjected to 3-point and 4-point loading tests to obtain load-deflection responses. The results were then used to analyse the behaviour of geopolymer beams in ultimate state as compared with OPC beams. Furthermore, the differences in post-yield deflection between OPC and geopolymer beams are identified and its relationship with the length of the plastic hinge zone was investigated (The Inelastic deformation of a structural element is determined by the capacity of plastic rotation which is proportional to the length of plastic area).

The author also compared the calculated plastic hinge length values (calculated using load deflection measurements and a numerical model) with the values predicted by several existing models to predict plastic hinge length of OPC beams.

10.2. Materials and Methods

10.2.1. Alumino-silicate material

A class F fly ash and granulated ground blast furnace slag, with the chemical composition shown in Table 10-1 were used as the alumino-silicate precursor materials. The bulk chemical composition was obtained by X-ray florescence (XRF) analysis.

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>Fe₂O₃</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>Mn₃O₄</th>
<th>SO₃</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash</td>
<td>51.9</td>
<td>25.9</td>
<td>4.35</td>
<td>1.54</td>
<td>0.7</td>
<td>12.7</td>
<td>0.71</td>
<td>1.3</td>
<td>0.15</td>
<td>0.24</td>
<td>0.55</td>
</tr>
<tr>
<td>Slag</td>
<td>32.4</td>
<td>12.2</td>
<td>44.0</td>
<td>5.13</td>
<td>0.22</td>
<td>0.45</td>
<td>0.38</td>
<td>0.51</td>
<td>0.35</td>
<td>4.22</td>
<td>0.08</td>
</tr>
</tbody>
</table>
10.2.2. Alkali activator

Granular sodium metasilicate penta-hydrate (28.7% Na₂O, 28.5% SiO₂ and 42.8% H₂O) was used as solid activator to activate the precursors. Usage of solid alkali activators in geopolymer systems is less hazardous than commonly used liquid activators and more convenient for field applications. The amount of activator used was calculated to provide an alkali content of 4% Na₂O by mass of precursor materials.

10.2.3. Aggregates

A nonreactive basalt coarse aggregate of 14 mm nominal particle size and river sand were used in the geopolymer concrete mix. The particle density of coarse aggregates and the sand in saturated surface dry condition (SSD) was 2830 and 2620 kg/m³, respectively, and moisture absorption was 2.2 and 0.3% respectively. Figure 10-1 shows the cumulative particle size distribution of the aggregate.

![Figure 10-1: Sieve analysis of aggregates.](image)

10.2.4. Reinforcement details

All beams in this study were 2550 mm long, 200 mm wide and 300 mm deep and the concrete cover depth was 20 mm. Three sizes of steel bars were used for reinforcement cages and the yield strength of the each reinforcement bar provided by steel supplier (ARC Pty Ltd) is given in Table 10-2.

<table>
<thead>
<tr>
<th>Bar diameter (mm)</th>
<th>Nominal area (mm²)</th>
<th>Yield strength (MPa)</th>
<th>Product description</th>
</tr>
</thead>
</table>

Table 10-2: Steel reinforcement properties
Bar diameter (mm) | Nominal area (mm²) | Yield strength (MPa) | Product description
--- | --- | --- | ---
10 | 78.5 | 200 | Hot rolled round rebar
12 | 113 | 547 | Hot rolled deformed rebar
24 | 452 | 548 |

The beams were tested as simply supported over a span of 2400 mm ($L_e$). Two geopolymer beams were designed with a vertical reinforcement ratio ($\rho_{sv}$) of 0.31% and two beams with $\rho_{sv}$ of 0.79%. One beam of each pair was subjected to 3-point and other to 4-point loading. One OPC concrete beam of the same design with $\rho_{sv}=0.79\%$ was also designed and tested under 4-point loading for a comparison. All the beams have identical horizontal reinforcement ratio $\rho_{sh}=1.75\%$. The layout of each reinforcement configuration is given in Figure 10-2. The designations used in Table 10-3 refer to loading mode (3 or 4-point), material type and stirrup spacing in mm. For example, 3Geo-250 represents a geopolymer concrete beam subjected to 3-point load with stirrup spacing of 250 mm.

![Figure 10-2: Layout of the reinforced beams](image)

<table>
<thead>
<tr>
<th>Beam</th>
<th>Loading patterns</th>
<th>$\rho_{sv}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3Geo-1250</td>
<td>3-point</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 10-3: Test matrix ($B=200$ mm, $D=300$ mm, $L_e=2400$ mm, $\rho_{sh}=1.75\%$)
The concrete mix design used in the geopolymer concrete beams is shown in Table 10-4. Two cubic meter geopolymer concrete mixing was carried out in a pre-mix truck provided by Hanson Pty Ltd (Victoria, Australia). The process is as follows: (1) the required quantities of fly ash, slag and aggregates were batched and mixed in the commercial batching plant; (2) The moisture in the aggregates were assessed prior so that the amount of water that needed to be added was calculated; (3) The activator bags were added to the mix on site. A raised platform was needed to add the activator via the back of the truck. (4) The additional water required was added in stages and the concrete was mixed for 10 minutes after each stage of water addition and the slump reading was taken.

The concrete mix was designed to achieve 80 mm slump but the actual slump obtained was only 35 mm. This shows that the geopolymer concrete does not mix as well as lab mixer. Therefore, the mix should be robust to handle the insufficient mix processes. The OPC concrete beam was cast by Westkon pre-cast concrete Pty Ltd using a similar mix design and curing conditions.

Figure 10-3 shows the stages of the geopolymer concrete beam casting process. Immediately after casting, the beams were covered with wet hessian cloths and polythene sheet in order to avoid moisture loss. After 7 days, beams were de-moulded and MasterKure 100WB was applied (AS 3799-1998) to prevent drying shrinkage. The samples were again covered with hessian and polythene until tested (28 days). All the cast geopolymer beams were kept at ambient temperature which range from 15°C to 30°C during the time between casting and testing. Along with concrete beams, geopolymer concrete cylinders (100 × 200 mm) were cast from the same truck mix in order to analyse the mechanical properties of plain geopolymer concrete. Similar to the
beams, these cylinders were cured at ambient temperature. Compressive strength of these cylinders was tested up to 28 days as recommended in AS 1012.9 [7].

The elastic modulus and Poisson ratio of geopolymer concrete cylinders were also measured according to AS 1012.17 [8].

The average flexural tensile strength \((f_{ct,d})\) of geopolymer concrete (at 28 days) was measured according to AS 1012.11 [9] using 100 × 100 × 400 mm concrete prisms cast with the same truck mix (in Table 10-4). Compressive strength and density values of OPC concrete were provided by Westkon Pty Ltd. The flexural strength and modulus of elasticity of OPC were calculated from the values accordance with AS 3600-2009 sections 3.1.1.3 and 3.1.2 [10].

Table 10-4: Mix design of geopolymer concrete

<table>
<thead>
<tr>
<th>Kg/m³</th>
<th>Fly ash</th>
<th>Slag</th>
<th>Solid alkali activator</th>
<th>Coarse aggregate (14 mm)</th>
<th>Sand</th>
<th>Added Water</th>
<th>Water/solid ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>200</td>
<td>200</td>
<td>61.36</td>
<td>1180</td>
<td>695</td>
<td>170</td>
<td>0.45</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>0</td>
<td>0</td>
<td>42.80</td>
<td>5.20</td>
<td>8.20</td>
<td>-</td>
<td>0.45</td>
</tr>
</tbody>
</table>
After 28 days, two LVDTs were attached to each beam using a steel plate (Figure 10-4) and tested by 5 MN capacity testing equipment. Figure 10-4 also shows the loading setup of the reinforced beams. The load rate was maintained at a displacement rate of 2mm/minute in order to complete the test within 10-15 minutes which avoids the effect of creep.
10.3. Results and Discussion

10.3.1. Properties of geopolymer concrete

The results of compressive strength testing of concrete cylinders are given in Figure 10-5. The results show a fast initial strength development in geopolymer concrete where approximately 50% and 75% of the 28 day strength (45.5 MPa) was achieved within the first two and seven days, respectively. The variation in the compressive strength for samples tested at each age was relatively small, indicating a consistent geopolymer concrete mix. The flexural strength and modulus of elasticity of geopolymer concrete and OPC concrete are shown in Table 10-5.
Figure 10-5: Compressive strength development of geopolymer concrete measured according to AS 1012.9

Table 10-5: Mechanical properties of unconfined OPC and geopolymer concrete

<table>
<thead>
<tr>
<th>Concrete type</th>
<th>$f'_{c}$ (28 days)</th>
<th>$E_{c}$(GPa)</th>
<th>Poisson’s ratio</th>
<th>Flexural strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geopolymer</td>
<td>45.5</td>
<td>22.5</td>
<td>0.15</td>
<td>3.70</td>
</tr>
<tr>
<td>OPC</td>
<td>50.0</td>
<td>34.5</td>
<td>0.20</td>
<td>4.24</td>
</tr>
</tbody>
</table>

10.3.2. Load-deflection of the beams

Beams with adequate stirrups would reach their flexure capacity before reaching the shear capacity under loading. In the following text, four geopolymer concrete beams and one OPC beam with stirrups were used to analyse such behaviour.

The load-deflection responses of the four geopolymer concrete beams and the OPC beam are analysed below. Figure 10-6 (a) shows the load-deflection response of beams 4Geo-250 ($\rho_{sv}=0.31\%$) and 4Geo-100 ($\rho_{sv}=0.79\%$) under 4-point loading. Even though both beams show similar ultimate load carrying capacity, the inelastic deflection of the beam with closely spaced stirrups was higher than the one with sparsely spaced stirrups. Similar observations were made in geopolymer beams (3Geo-250 and 3Geo-100) tested under 3-point loading (shown in the Figure 10-6(b)). It is known that, the concrete confinement due to stirrups changes the post-peak deflection which is further analysed in section 10.3.5. In addition to increasing the concrete confinement, stirrups (shear reinforcement) also enhance the shear capacity in reinforced concrete beams as they improve shear transfer mechanisms (i.e. dowel action), restrain crack propagation and

Figure 10-6: Load-deflection responses of beams under (a) 4-point loading (b) 3-point loading

Comparison of the load-deflection responses of geopolymer and OPC concrete beams with $\rho_{sv}=0.79\%$ under 4-point loading (Figure 10-7) showed similar ultimate load carrying capacity while the post-yield deflection of the OPC beam was significantly higher compared to that of the geopolymer beam. The load-deflection response (Figure 10-7) corresponding to the 4OPC-100 showed an extensive post-yield plateau with a minor decrease in maximum load carrying capacity which is a good indicator for high ductility. The ductility of both OPC and geopolymer beams will be analysed next.

Figure 10-7: Load-deflection response of Geopolymer beam and OPC beam ($\rho_{sv}=0.79\%$) under 4-point loading

10.3.3. Ductility of beams

Ductility of structural elements (e.g., beam, column and load bearing wall), or the ability to undergo extensive inelastic deformation (near its ultimate load carrying capacity) is an important parameter for load redistribution and robustness [12]. The inelastic
Deflection ($\Delta_p$) of a beam is defined as the difference between the deflection at ultimate load point ($\Delta_u$) and the deflection at yield point ($\Delta_y$) i.e., $\Delta_p = \Delta_u - \Delta_y$, while the displacement ductility index of a beam is defined as the ratio of $\Delta_u$ and $\Delta_y$ i.e., ductility index $= (\Delta_u) / (\Delta_y)$ [3]. The ultimate deflection and the yield deflection of a beam are obtained from the measured load-deflection curve as follows: The ultimate deflection ($\Delta_u$) is the deflection of the beam when the load (after peaking $P_{\text{max}}$) has dropped to 0.9 $P_{\text{max}}$ (on the descending branch of load-deflection response). The yield deflection ($\Delta_y$) is the deflection of the beam where the secant going through 0.75 $P_{\text{max}}$ (on the ascending branch of the load-deflection curve) intersects $P_{\text{max}}$ [13]. The measured values of inelastic deflection ($\Delta_p$) and ductility index ($\Delta_u / \Delta_y$) are given in Table 10-6. The geopolymer beams with higher stirrup content ($\rho_{sv}=0.79\%$) showed higher ductility compared to the beam with lower stirrup content. It is well known that, the ductility of a reinforced concrete member subjected to flexure is influenced mainly by its tensile reinforcement ratio. The ductility and the flexural capacity of reinforced concrete members can also be influenced by the number of stirrups in the bending zone [6]. Jang et al. [6] reported that the confinement of concrete due to stirrups cause higher ductility in beams. Another study on OPC concrete beams [13] showed that when the stirrup spacing is reduced by 30% the ductility is increased by 20%. Our observations for geopolymer beams agree with these findings. The ductility values in Table 10-6 show that geopolymer beam (4Geo-100) has lower ductility than OPC beam (4OPC-100) at the same reinforcement ration and loading setup. The ductility of the beam mainly depends on the rotation capacity of a beam about its hinges before collapse.

Table 10-6: Ductility index of Geopolymer and OPC beams.

<table>
<thead>
<tr>
<th>Beam</th>
<th>$\Delta_u$ mm</th>
<th>$\Delta_y$ mm</th>
<th>$\Delta_p$ mm</th>
<th>Displacement ductility index ($\Delta_u / \Delta_y$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3Geo-250</td>
<td>24.08</td>
<td>12.03</td>
<td>12.05</td>
<td>2.00</td>
</tr>
<tr>
<td>3Geo-100</td>
<td>34.53</td>
<td>10.18</td>
<td>24.35</td>
<td>3.39</td>
</tr>
<tr>
<td>4Geo-250</td>
<td>22.37</td>
<td>15.31</td>
<td>7.06</td>
<td>1.46</td>
</tr>
<tr>
<td>4Geo-100</td>
<td>27.03</td>
<td>14.39</td>
<td>12.64</td>
<td>1.88</td>
</tr>
<tr>
<td>4OPC-100</td>
<td>76.24</td>
<td>15.30</td>
<td>60.97</td>
<td>4.98</td>
</tr>
</tbody>
</table>

Inelastic deflection of the beam depends on the rotation capacity of the beam which is concentrated to a certain region called plastic hinge length. When a beam reaches its yield point, the regions under high bending moment enter a fully plastic region leading
to plastic hinge formation. When the plastic hinges are formed, the beam starts to rotate under constant moment about hinge. From this point onwards, the beam could not sustain any further increase in stresses or loads and would largely deform resulting in beams’ collapse or permanent deformation. Within this region the beam’s bending moment is greater than \( M_{\text{yield}} \) (bending moment at yield) and less than \( M_{\text{ ultimate}} \) (bending moment at failure point) [14]. The plastic hinge length can be physically observed in the beam at failure point. This is the region in the structural element which suffers major damage including wide cracks, spalling of concrete cover and yielding of reinforcement [15]. Figure 10-8 and Figure 10-9 show observed plastic hinge regions on OPC and geopolymer beams. They show wide cracks in a large region on the OPC beam, whereas the geopolymer beams had very few narrow cracks in a small region, indicating smaller plastic hinge region. The plastic hinge length is quantified in the next section.

![Image of OPC beam with cracks](image1)

**Figure 10-8**: Crack patterns of beams after failure (a) 4Geo-100 (b) 4OPC-100

![Image of geopolymer beam with cracks](image2)

**Figure 10-9**: Enlarged images of crack patterns of beams after failure (a) 4Geo-100 (b) 4OPC-100
It should also be noted that there is no noticeable inflection in the load deflection-responses for tested beams at the first cracking point. This is because the beams used in this analysis had high horizontal reinforcement ratio $\rho_{sh}=1.75\%$ (that is close to the maximum reinforcement content of $\rho_{sh} = 2.00\%$) and high amount of stirrups which help maintain the stiffness of the concrete at the same level even after the first crack [2]. All the beams reached their ultimate flexural strength with yielding of the tensile reinforcement steel followed by concrete crushing in the compression zone of the beam.

10.3.4. Quantifying plastic hinge length

Plastic hinge length ($L_p$) is an important parameter for the ductility of reinforced concrete beams. Thorough attention is needed in detailing reinforcement requirement within the plastic hinge region as a beam is expected to have most of the energy dissipation within this region [15]. The illustration of 3-point and 4-point loading in Figure 10-10 are used in the derivation of plastic hinge length of OPC and geopolymer concrete beams. The relationship between the plastic deformation ($\delta_p$) and the angle of total rotation ($\theta_p$) for 3-point loaded beam and 4-point loaded beam can be written as shown in equations (1) and (2) respectively: [16]

$$\Delta_p = \frac{\theta_p L_e}{4} \quad (1)$$

$$\Delta_p = \frac{\theta_p L_e}{3} \quad (2)$$

![Diagram of 3-point and 4-point loading](image.png)

Figure 10-10: Beam mechanisms for the plastic analysis for (a) 4-point (b) 3-point loading [16]

The plastic hinge rotation ($\theta_p$) in the above equations depends on the curvature of beam at yield ($K_y$) and ultimate point ($K_u$) and the plastic hinge length ($L_p$) [14]. The
relationship between plastic hinge length and rotation about hinge can be expressed as in equations (3)-(5).

\[
\Delta_p = (K_u - K_y) \times L_p \tag{3}
\]

\[
L_p = \frac{4\Delta_p}{(K_u - K_y)L_e} \quad \text{(3-Point)} \tag{4}
\]

\[
L_p = \frac{3\Delta_p}{(K_u - K_y)L_e} \quad \text{(4-Point)} \tag{5}
\]

In order to obtain the two curvature values \((K_y \text{ and } K_u)\), the moment curvature relationship of the beams needs to be identified.

10.3.5. Moment-curvature relationship of a beam with transverse reinforcements

The numerical model used to obtain the moment-curvature relationship for beams with transverse reinforcements (or stirrups) is presented below. The following assumptions were made in this analysis: tensile strength of concrete is negligible, plane section of the beam remains the same after bending and beam does not have bond-slip [17].

First, the stress-strain relationships for unconfined \((\sigma_{uc}(\varepsilon))\) and confined \((\sigma_c(\varepsilon))\) concrete were derived using the models proposed by Attard and Setunge [18]. The confinement pressure was obtained using Mander’s model [17, 19]. Figure 10-11 depicts the calculated confined and unconfined stress-strain curves for both the geopolymer and OPC concrete.

![Stress-Strain curves of confined and unconfined concrete](image)

Figure 10-11: Stress-Strain curves of confined and unconfined concrete (a) Geopolymer (b) OPC
Next, a thin slices perpendicular to the beams length were considered for the calculations. For this slice, the strain profile is taken as linear function of the strain at ultimate compression fibre ($\varepsilon_0$) and neutral axis depth ($d_n$). The area of the slice was then separated into confined (the area within the stirrups and above the neutral axis) and unconfined segments as shown in Figure 10-12. For each segment the strain profile was converted into stresses using the respective stress-strain curves. The resulting force in each segment and its centroid can then be calculated as shown in equations (6-13). The forces in compressive reinforcement ($F_{sc}$) and tensile reinforcement ($F_{st}$) can be obtained by the stress-strain curve of steel (for steel reinforcement, a linearly elastic, perfectly plastic stress-strain curve is adopted [17]).

\[
F_{cc,a} = \frac{d_n b_0}{\varepsilon_0} \int_0^{\varepsilon_{cc}} \sigma_c(\varepsilon) d\varepsilon
\]

\[
F_{cc,b} = \frac{t d_n}{\varepsilon_0} \int_0^{\varepsilon_0} \sigma_{uc}(\varepsilon) d\varepsilon
\]

\[
F_{cc,c} = \frac{b_0 d_n}{\varepsilon_0} \int_{\varepsilon_{cc}}^{\varepsilon_0} \sigma_{uc}(\varepsilon) d\varepsilon
\]

\[
F_{st} = A_{st} \sigma_{st}
\]

\[
F_{sc} = A_{sc} \sigma_{sc}
\]

\[
\bar{\varepsilon}_{cc,a} = \frac{d_n}{\varepsilon_0} \frac{\int_0^{\varepsilon_{cc}} \sigma_c(\varepsilon) \varepsilon d\varepsilon}{\int_{\varepsilon_{cc}}^{\varepsilon_0} \sigma_c(\varepsilon) d\varepsilon}
\]

\[
\bar{\varepsilon}_{cc,b} = \frac{d_n}{\varepsilon_0} \frac{\int_0^{\varepsilon_0} \sigma_{uc}(\varepsilon) \varepsilon d\varepsilon}{\int_{\varepsilon_0}^{\varepsilon_{cc}} \sigma_{uc}(\varepsilon) d\varepsilon}
\]

\[
\bar{\varepsilon}_{cc,c} = \frac{d_n}{\varepsilon_0} \frac{\int_{\varepsilon_{cc}}^{\varepsilon_0} \sigma_{uc}(\varepsilon) \varepsilon d\varepsilon}{\int_{\varepsilon_{cc}}^{\varepsilon_0} \sigma_{uc}(\varepsilon) d\varepsilon}
\]

Here $b$ is the beam width, $t$ is the clear thickness, $d_s = 12$ mm is the diameter of stirrup, $A_{st} = 905$ (N/mm²) is the area of tensile reinforcement and $A_{sc} = 226$ (N/mm²) is the area of compressive reinforcement. Furthermore, $b_0 = (b - 2t)$ and $d_0 = \left(d_n - t - \frac{d_s}{2}\right)$.
Figure 10-12: Stress and strain profiles for a beam section (the shapes of the stress profiles in the figure do not represent the calculated stress profiles).

Using the above equations, the neutral axis depth for a specified $\varepsilon_0$ can be calculated by means of force equilibrium. This neutral axis depth can then be used to calculate the moment and the curvature values. The complete procedure of the moment curvature calculations is given in Algorithm 1.

**Algorithm 1: Numerical model for calculating Moment-Curvature**

**Inputs:** Beam Parameters, Mechanical properties of binder, mechanical properties of steel reinforcement.

**Output:** Moment curvature values ($M, K$).

1: Calculate confinement pressure using Mander's model.

2: Generate stress-strain curve, $\sigma_{uc}(\varepsilon)$, for unconfined concrete using model in [18].

3: Generate stress-strain curve, $\sigma_c(\varepsilon)$, for confined concrete using model in [18].

4: Assign $\varepsilon_0$ = Vector(0 to 0.08 with step size 0.001)

5: Assign $d_n$ = Vector($d_{sc}$ to $d_{st}$ with step size 0.5)

6: For $i = 1 \rightarrow$ size of $\varepsilon_0$

7: For $j = 1 \rightarrow$ size of $d_n$

8: Calculate resulting forces using $\varepsilon_0(i)$ and $d_n(j)$ via equations (6-10)

9: $Err(j) =$ Error in force equilibrium.

10: End

11: $j^* = \min_j[Err(j)]$

12: $M(i) =$ Calculate moments using $\varepsilon_0(i)$ and $d_n(j^*)$ via equations (6-13)

13: $K(i) = \varepsilon_0(i)/d_n(j^*)$

14: End

15: Return $M, K$
The moment curvature curves produced by the above numerical method for both OPC and Geopolymer concrete beams are shown in Figure 10-13.

![Figure 10-13: Moment-curvature relationship of OPC and Geopolymer at 100 mm stirrup spacing](image)

Using the above Moment vs. curvature curve, the curvature at ultimate state ($K_u$) and curvature at yield ($K_y$) are calculated as follows: $K_u$ is the curvature of the beam when the load has dropped to 0.9 $M_{max}$ after reaching the peak moment $M_{max}$. $K_y$ is the deflection of the beam where the secant going through 0.75 $M_{max}$ (on the ascending branch of the moment-curvature curve) intersects the maximum moment $M_{max}$ [17].

Table 10-7 shows the calculated plastic hinge length values for the beams (Equations 6 and 7) using the curvature values from the model. In agreement with the physical observations (Figure 10-8), the calculations show that the plastic hinge length ($L_p$) of the geopolymer concrete beam (with same configuration) is significantly less than that of the OPC beam. As a result of larger plastic hinge length, OPC beam could undergo larger inelastic deflection compared to geopolymer concrete beam. Furthermore, the plastic hinge length for beams under 3-point loads was significantly higher than that of the beams under 4-point loading. The distance between the support and the load is higher in the 3-point test setup (1200 mm) than that of 4-point setup (800 mm). As a result, plastic hinge length of the beam and its rotation capacity is increased.

Table 10-7: The ultimate and yield curvature values for beams obtained via the model and the calculated plastic hinge lengths.

<table>
<thead>
<tr>
<th>Beam</th>
<th>Loading type</th>
<th>$K_y$</th>
<th>$K_u$</th>
<th>$L_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3Geo-250</td>
<td>3-point loading</td>
<td>0.000025</td>
<td>0.00039</td>
<td>55</td>
</tr>
<tr>
<td>3Geo-100</td>
<td>3-point loading</td>
<td>0.000025</td>
<td>0.00075</td>
<td>56</td>
</tr>
</tbody>
</table>
The plastic hinge length of a beam mainly depends on: reinforcement arrangement, cross sectional geometry, support condition, compressive strength of concrete and bond-slip characteristics between concrete and steel [20]. As the reinforcement design and other parameters for the beams are identical, this behaviour should be related to bond-slip characteristics (both geopolymer and OPC had similar 28 day compressive strength, section 10.3.1). Bond stress is the shear stress between the bar and concrete interface. If the maximum bond stress is exceeded under loading condition, the reinforcement can slip freely through the concrete creating significant reduction of stiffness of structures. The bonds-slip failure in concrete structure allows the structure to undergo large inelastic deformation [5, 12] and impedes sudden brittle failure. Previous studies (on OPC concrete) have shown that higher bond strength contributes towards limiting the crack width and plastic hinge rotation of a beam (and inelastic deflection) [21, 22]. Castel et al. [23] showed that the strength of bond between concrete and reinforcement is 10% stronger in blended fly ash and slag geopolymer compared to OPC due to high adhesion between geopolymer binder and steel. These results are in agreement with our observations and indicates that the higher bond strength in geopolymer concrete beams have contributed towards reducing the post-yield deflection.

### 10.3.6. Comparison of measured hinge length with existing hinge length prediction models

Several empirical methods have been proposed to determine the hinge length in OPC based beams. Most proposed methods only consider the geometry of beams which may lead to inaccurate calculations due to variations in parameters such as material properties, reinforcement etc. [14, 20].

In this study, the author used four existing methods listed in Table 10-8. The plastic hinge lengths predicted using these models are tabulated in Table 10-9. These predicted plastic hinge length values were then compared with the measured hinge length values and is shown Figure 10-14. The figure shows that the existing methods (Mattock, Corley and Sawyer) were only able to accurately predict hinge lengths of OPC beams.
The predicted hinge lengths for geopolymer concrete beams did not show high correlation with the measured values and the existing hinge length prediction models can overestimate the capacity of plastic hinge rotations in geopolymer concrete beams.

Table 10-8: Empirical expressions for plastic hinge length [14]

<table>
<thead>
<tr>
<th>Researcher (Model) name</th>
<th>$L_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Baker</td>
<td>$0.8k_1k_3(z/d)c$</td>
</tr>
<tr>
<td>(2) Sawyer</td>
<td>$0.25d + 0.075z$</td>
</tr>
<tr>
<td>(3) Corley</td>
<td>$0.5d + 0.2\sqrt{d}(z/d)$</td>
</tr>
<tr>
<td>(4) Mattock</td>
<td>$0.5d + 0.05z$</td>
</tr>
</tbody>
</table>

Where $d =$ effective depth of beam (258 mm), $z =$ distance from critical section to the point of support (3-point 1200 mm and 4-point 800 mm), $c =$ depth of neutral axis at ultimate moment (OPC 98.0 and Geopolymer 99.5 mm), $k_1 = 0.7$ and $k_3 = 0.9$ when the $f'_c = 11.7$ MPa and $k_3 = 0.6$ when $f'_c = 35.2$ MPa.

Table 10-9: $L_p$ of beams using different models

<table>
<thead>
<tr>
<th>Beam</th>
<th>Baker and Amarakone $L_{p,baker}$ (mm)</th>
<th>Sawyer $L_{p,sawyer}$ (mm)</th>
<th>Corley $L_{p,corley}$ (mm)</th>
<th>Mattock $L_{p,mattock}$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3Geo-250</td>
<td>122</td>
<td>154</td>
<td>153</td>
<td>189</td>
</tr>
<tr>
<td>3Geo-100</td>
<td>122</td>
<td>153</td>
<td>153</td>
<td>189</td>
</tr>
<tr>
<td>4Geo-250</td>
<td>81</td>
<td>124</td>
<td>145</td>
<td>169</td>
</tr>
<tr>
<td>4Geo-100</td>
<td>81</td>
<td>124</td>
<td>145</td>
<td>169</td>
</tr>
<tr>
<td>4OPC-100</td>
<td>70</td>
<td>124</td>
<td>145</td>
<td>169</td>
</tr>
</tbody>
</table>

Figure 10-14: Comparison between calculated and predicted plastic hinge length ($L_p$) (hatch angled line is for the 1:1 match)
10.4. Concluding remarks

1. For the same reinforcement configuration, the geopolymer concrete beam has lower ductility compared to OPC beam. However, the maximum load carrying capacity is the same.

2. The ductility differences cannot be explained by the moment curvature relationship of geopolymer and OPC because they are similar. They are similar because the stress verses strain curves of geopolymer and OPC concrete are similar.

3. This study found that the lower ductility of geopolymer concrete beam is due to the shorter hinge length. This is consistent the widely accepted view that the bond between geopolymer and steel is stronger than the bond between the steel and OPC. The higher bond in geopolymer decreases the hinge length and the ductility (This relationship between the bond and hinge length has been confirmed by previous studies).

4. The stirrups provide confinement and consequently ductility of geopolymer concrete beams is increased. The increase in ductility due to increased confinement is similar to OPC concrete beams.

10.5. References for chapter 10


11. Summary and Conclusions

Summary

This thesis presents an extensive study and development of an ambient cured geopolymer system.

Chapter 3 compared the characteristics of Australian brown coal fly ash, a widely available low rank coal fly ash in Victoria, with other class F fly ashes found in Australia. The chemical composition of (low SiO$_2$/Al$_2$O$_3$ SiO$_2$ and Al$_2$O$_3$ and high char content) brown coal fly ash suggested that the utilisation of 100% low ranked coal fly ash (brown coal fly ash) as geopolymer precursor material would be unsatisfactory. The research found that, blending of brown coal fly ash with other alumino-silicate precursor materials can alter the oxide composition of brown coal fly ash favourably, such that it can be used as feedstock for geopolymer. However, the high sulphate content (10-15%) in some brown coal fly ashes resulted in decomposition of geopolymer in high moist environment whereas, brown coal fly containing high aluminium content (>20%) produces enhanced microstructure leading to a stable binder in moist environments. Chapter 3 also revealed that the compressive strength of Australian class F fly ash based geopolymers mainly depends on the reactive SiO$_2$/Al$_2$O$_3$ and Na$_2$O/ (reactive SiO$_2$+Al$_2$O$_3$) molar ratios of the fly ash. In addition, when class F fly ash contains high amount of fine particles the amorphous content of oxides are distributed in a large area, in turn the reactivity of the fly ash is increased.

Chapter 4 shows that the properties of fresh blended fly ash and slag geopolymers can be influenced by the type of solid alkali activator used. Geopolymers synthesised using hydrated sodium metasilicate (PH) solid alkali activator has an initial endothermic reaction (heat absorption), whereas the geopolymer made using anhydrous sodium metasilicate solid alkali activator (AH) has an initial exothermic reaction (release of heat). The results indicate that the dissolution heat is the main factor contributing to the variations in the properties of fresh geopolymers made with AH and PH activators. In addition, usage of hydrated alkali solids enables the adjustment of properties of the fresh binder. The reaction kinetic upon alkali activation is retarded in hydrated solid activator (PH) based geopolymers (due to heat absorption) leading to a slow reaction mechanism, allowing a longer dissolution and better diffusion of ions from slag and fly
ash particles. The slower reaction kinetics leads to high strength development at later age.

Chapter 5 discusses the development of a geopolymer concrete with granular activator which is suitable for ambient temperature curing while chapter 6 investigates the long term engineering properties of ambient cured geopolymer concrete. All ambient cured geopolymer concrete gained compressive strength rapidly during the early age (<28 days). Fly ash blended and 100% slag based geopolymer did not show any strength regression after one year indicating high stability in the compressive strength for the test period of two years. Flexural strength of ambient cured geopolymer concrete is consistent with the heat-cured geopolymer concrete in literature. In addition, high slag based geopolymer concrete had slight flexural strength loss at later age which may associate with the micro-cracking in high slag based geopolymer concrete. Elastic modulus of ambient cured geopolymer concrete is slightly higher (32-34 GPa) than elastic modulus of previously reported heat-cured geopolymer concrete (less than 30 GPa). The disparity between ambient cured and heat-cured geopolymer may be attributed to slower reaction mechanism in the ambient cured geopolymer concrete which can be produced uniform and denser microstructure leading to high stiffness. Shrinkage of ambient cured geopolymer concrete is comparable with the heat cured geopolymer concrete. On the other hand, creep deformation of ambient cured geopolymer concrete is slightly higher than that of heat cured geopolymer concrete reported elsewhere. Most importantly, the study identified that addition of alkali in granular form is not affected the mechanical properties of geopolymers in early age as well as in later age where the properties are consistent with the geopolymer concrete containing alkali solutions in literature.

Chapter 7 investigates the Abrasion resistance of ambient cured geopolymer concrete using procedures in EN13892-4 standard. The results showed that the abrasion resistance of ambient cured geopolymer concrete is lower than that of OPC concrete. In addition, the slag content in the geopolymer binder does not influence the abrasion resistance of ambient cured geopolymer concrete. The abrasion resistance of geopolymer concrete does not improve with maturity. Dressing wheel method (EN13892-4 standard) creates highly abrasive conditions which may not be presented to concrete floors/pavements during their service life. Therefore, the result outcome does
not necessarily represent the expected abrasion during the service life of the concrete floors or pavements.

Chapter 8 studies the susceptibility of blended fly ash and slag geopolymer concrete to alkali aggregate expansive reaction in the presence of reactive aggregates. The rapid mortar bar test and concrete prism test results showed that blended fly ash and slag geopolymer show far less susceptibility to AAR than that of OPC concrete. The results also showed that, increasing the slag content of the geopolymer binder increased the susceptibility of geopolymer binders to alkali aggregate expansive reaction in the presence of reactive aggregates. Usage of at least 30% fly ash in the geopolymer composition can mitigate AAR expansion in geopolymer concrete. Geopolymers containing fly ash result in higher degree of cross linking in the structure inhibiting the re-organisation of the structure which causes high volume stability. AAR expansion obtained from the accelerated mortar bar test (AMBT) has high consistency with the AAR expansion from concrete prism test (CPT) for blended fly ash and slag geopolymer. On the other hand, 100% slag based geopolymers in combined with reactive aggregates showed significantly higher expansion from AMBT than that of CPT.

Chapter 9 presents the susceptibility of ambient cured geopolymer to chloride-induced corrosion. The results showed that the geopolymer concrete containing slag has higher resistance to the chloride ingress than OPC concrete. In addition, the chloride ingress is slower when slag content of the binder is higher leading to longer initiation times. Hydroalite phases formed in blended fly ash and slag geopolymers can bind the chloride ions preventing them reaching the level of rebar. Furthermore, geopolymer concrete containing slag provides greater protection against reinforced corrosion than that of OPC concrete when contaminated with chloride. This may be attributed to the reduction of oxygen availability around embedded rebar in geopolymer concrete as a result of consumption of oxygen by sulphide ions which are reported in the literature.

Finally, Chapter 10 highlights one disadvantage of high steel/concrete bond which is not generally understood or appreciated. The higher steel/concrete bond can leads to shorter hinge length resulting in lower ductility for the hinge (and the beam). The phenomenon is demonstrated in the OPC and geopolymer beam results presented in the thesis. According to the literature, the lower ductility of geopolymer beams compared to OPC
beam were known for some time. However, this study is the first one to provide an explanation for the lower ductility phenomenon.

**Conclusions**

1. Ambient cured geopolymer systems are possible for practical implementation. An ambient cured geopolymer mix was developed in this study and was shown that the fresh and hardened properties were suitable for practical implementation.

2. The study found that the geopolymers containing pentahydrate granular alkali activator have slower setting characteristics than anhydrous granular alkali activator. The reason for this was found to be the higher heat absorption during pentahydrate activator dissolution.

3. The ambient cured blended fly ash and slag geopolymer system was shown to have less chloride permeability, higher ageing factor and longer corrosion initiation time than ordinary Portland cement based concrete (OPC). Geopolymer concrete containing slag provides greater protection against reinforced corrosion than that of OPC concrete when concrete is contaminated with chloride.

4. Geopolymer concrete containing at least 30% fly ash, combined with reactive aggregates showed no alkali aggregate expansive reaction. When geopolymer contains high content of slag, susceptibility of geopolymer concrete to AAR is also high. Expansion results obtained for blended fly ash and slag geopolymer mortars are consistent with the expansion of geopolymer concrete.

5. The behaviour of reinforced geopolymer concrete beams was investigated. The study demonstrated that for the same reinforcement configuration, the geopolymer concrete beam has lower ductility compared to OPC beam as a result of stronger bond between steel and geopolymer.

6. Study on brown fly ash found it to be unsuitable for geopolymer production at this stage. The main issues were the disintegration of geopolymer in high moist environment and consumption of high amount of alkali solution.