Application of Spent Coffee Ground as a Road Subgrade Construction Material

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Teck Ang Kua

This thesis was prepared for the Degree of
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Declaration

I hereby declare that the contents written in thesis is original and bears no resemblance to any material accepted for the award of any degree or diploma of any universities. To the best of my knowledge, this thesis contains no materials previously published by other individuals or intellectuals except where acknowledgement has been explicitly made. The data published in this thesis was the result of laboratory experiments carried out throughout this degree.

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(Teck-Ang KUA)
Student ID: 4223713
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Refereed Papers

The following papers have been published and represents the results compiled during the conception of this thesis:


Abstract

Sustainability is becoming a pressing issue internationally and has since stimulated research in sustainable building technologies and design methodologies. As landfill space and non-renewable raw materials become scarcer due to rapid urbanisation, developing recycled construction materials has become an essential research field which improves wastes and resource management. Coffee is an internationally popular drink. Brewing coffee generates a water-insoluble granular waste which ends up in landfills. Spent coffee ground (CG) is granular and resembles sand, hence was selected to be geotechnically assessed for its suitability as a replacement material for subgrade fills. This research found that untreated CG has low shear strength and is easily compressible, hence the need for strength enhancement. Conventional soil stabilisers, Portland cement and Lime, were used to stabilise CG but the improvements in performance were minimal. Geopolymerisation, an alternative process which produces cementitious compounds with the alkaline activation of aluminosilicate-rich materials, was selected to treat CG as the process produces relatively low carbon emission. The geopolymeric precursors selected for this research, namely fly ash (FA), slag (S), rice husk ash (RHA), and bagasse ash (BA), are waste materials from industrial and agricultural sectors and are abundantly available. Factors found to affect the compressive strength of CG geopolymers were different curing temperatures, durations, and different concentrations of alkaline liquids. While all the precursors were found to successfully bind the CG to form a cemented compound material, only CG+FA and CG+S geopolymers possess sufficient compressive strength to be used as subgrade materials. These materials also meet the California Bearing Ratio (CBR) benchmarks set by the local state road authority to be used as a subgrade material. Recycled glass (RG) was found to enhance the strength of CG+FA and CG+S geopolymers due to its high friction angle. To further provide assess the feasibility of CG geopolymers to be used as a road construction material, Repeated Load Triaxial (RLT) tests were used to assess the flexibility and deformation patterns of these materials under simulated repeated traffic loadings. Leachate tests done on CG geopolymers indicate that the material meets hazardous material restrictions set by various environmental protection agencies. Commercially, while CG geopolymers were found to be costly compared to existing construction material, the utilisation of this green material may improve contemporary waste management and recycling practices.
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# Table of Contents

List of Figures   VIII  
List of Tables XIV  
Notations and Abbreviations XVI  

## Chapter 1 Introduction

1.1 Problem Statement 1  
1.2 Objective and Scope 3  
1.3 Research Approach 4  
1.4 Thesis Overview 5  

## Chapter 2 Literature Review

2.1 Recycling Practices in Civil Engineering 8  
   2.1.1 Overview on Sustainability 8  
   2.1.2 Contemporary Soil Stabilisation Methods 11  
   2.1.3 Geopolymerisation as an Emerging Green Technology 13  
2.2 Spent Coffee Ground 15  
   2.2.1 Production 15  
   2.2.2 Current Recycling Applications 16  
2.3 Soil Stabilisers and Geopolymeric Precursors 19  
   2.3.1 Fly Ash 19  
   2.3.2 Ground Granulated Blast Furnace Slag 21  
   2.3.3 Rice Husk Ash 22  
   2.3.4 Bagasse Ash 24  
2.4 Recycled Glass 25  
2.5 Summary 27  

## Chapter 3 Material Preparation and Test Methodologies

3.1 Material Procurement and Preparation 28  
3.2 Organic Content Test 31  
3.3 pH Test 32  
3.4 Moisture Content Measurement 33  
3.5 Particle Size Distribution Analysis 35  
3.6 Specific Gravity 37  
3.7 Compaction Effort 38  
3.8 Unconfined Compressive Strength Test 39  
3.9 California Bearing Ratio 42  

V
Chapter 4 Application of Orthodox Soil Stabilisation Methods on Spent Coffee Ground

4.1 Overview
4.2 Material Characteristics of Spent Coffee Ground
4.3 Stabilisation Methodology and Specimen Preparation
4.4 Stabilisation by Portland Cement and Lime
   4.4.1 General Characteristics
   4.4.2 Compaction Characteristics
   4.4.3 Unconfined Compressive Strength Development
4.5 Stabilisation by Fly Ash and Slag
   4.5.1 General Characteristics
   4.5.2 Compaction Characteristics
   4.5.3 Unconfined Compressive Strength Development
4.6 Summary

Chapter 5 Application of Geopolymerisation on Spent Coffee Ground

5.1 Overview
5.2 General Specimen Handling
5.3 Stabilisation by Fly Ash
   5.3.1 Testing Plan
   5.3.2 General and Compaction Characteristics
   5.3.3 Unconfined Compressive Strength Development
5.4 Stabilisation by Ground Granulated Blast Furnace Slag
   5.4.1 Testing Plan
   5.4.2 General and Compaction Characteristics
   5.4.3 Unconfined Compressive Strength Development
5.5 Stabilisation by Rice Husk Ash
   5.5.1 Testing Plan
   5.5.2 General and Compaction Characteristics
   5.5.3 Unconfined Compressive Strength Development
5.6 Stabilisation by Bagasse Ash
   5.6.1 Testing Plan
   5.6.2 General and Compaction Characteristics
<table>
<thead>
<tr>
<th>Section Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.6.3 Unconfined Compressive Strength Development</td>
<td>101</td>
</tr>
<tr>
<td>5.7 Crushed Glass as a Supplementary Filler</td>
<td>104</td>
</tr>
<tr>
<td>5.7.1 Testing Plan</td>
<td>104</td>
</tr>
<tr>
<td>5.7.2 General and Compaction Characteristics</td>
<td>107</td>
</tr>
<tr>
<td>5.7.3 Unconfined Compressive Strength Development</td>
<td>110</td>
</tr>
<tr>
<td>5.8 Microstructure Analyses</td>
<td>117</td>
</tr>
<tr>
<td>5.8.1 CG+FA and CG+S Geopolymers</td>
<td>117</td>
</tr>
<tr>
<td>5.8.2 CG+RHA Geopolymers</td>
<td>121</td>
</tr>
<tr>
<td>5.8.3 CG+BA Geopolymers</td>
<td>125</td>
</tr>
<tr>
<td>5.8.4 CG+RG Geopolymers</td>
<td>132</td>
</tr>
<tr>
<td>5.9 Summary</td>
<td>136</td>
</tr>
<tr>
<td>Chapter 6 Bearing Strength and Deformation Properties of Stabilised Spent Coffee Ground</td>
<td>138</td>
</tr>
<tr>
<td>6.1 Overview</td>
<td>138</td>
</tr>
<tr>
<td>6.2 California Bearing Ratio</td>
<td>138</td>
</tr>
<tr>
<td>6.2.1 Conventional Stabilisation of Spent Coffee Ground</td>
<td>138</td>
</tr>
<tr>
<td>6.2.2 Geopolymerisation of Spent Coffee Ground</td>
<td>140</td>
</tr>
<tr>
<td>6.3 Stiffness and Deformation Properties</td>
<td>143</td>
</tr>
<tr>
<td>6.3.1 Geopolymerisation of Spent Coffee Ground</td>
<td>143</td>
</tr>
<tr>
<td>6.3.2 RG as a Supplementary Filler</td>
<td>157</td>
</tr>
<tr>
<td>6.4 Summary</td>
<td>166</td>
</tr>
<tr>
<td>Chapter 7 Environmental and Economic Viability</td>
<td>168</td>
</tr>
<tr>
<td>7.1 Overview</td>
<td>168</td>
</tr>
<tr>
<td>7.2 Environmental Assessment</td>
<td>169</td>
</tr>
<tr>
<td>7.3 Cost Analysis</td>
<td>174</td>
</tr>
<tr>
<td>7.4 Summary</td>
<td>178</td>
</tr>
<tr>
<td>Chapter 8 Conclusions and Recommendations</td>
<td>179</td>
</tr>
<tr>
<td>References</td>
<td>184</td>
</tr>
</tbody>
</table>
List of Figures

CHAPTER 3

Figure 3.1 CG collected daily from cafes in Melbourne, Australia.

Figure 3.2 A tray of cleaned CG ready for drying.

Figure 3.3 Tablets of CG resulting from coffee brewing.

Figure 3.4 Bags of dried CG in air-tight zip lock tie-seals.

Figure 3.5 Furnace and crucible used to ignite organic materials.

Figure 3.6 Electronic Potentiometer with an electrode rinsed in distilled water.

Figure 3.7 Difference in colouration occurs with CG at different moisture contents.

Figure 3.8 Sieve set mounted on shaker apparatus.

Figure 3.9 CILAS 1190 Particle Size Analyser.

Figure 3.10 Apparatus setup for SG test. With flasks containing BA in the foreground and a mechanical vibrator and vacuum pump in the background.

Figure 3.11 (a) Apparatus configuration during a proctor compaction test, and (b) a compacted and trimmed specimen.

Figure 3.12 Mixing process of a CG+Stabiliser mix.

Figure 3.13 Apparatus setup showing (a) the split mould used to produce UCS samples; (b) LoadTrac II used to statically compress the material mixes; (c) a compacted specimen before extrusion; and (d) specimens wrapped in vinyl ready for curing.

Figure 3.14 A typical UCS specimen after failure.

Figure 3.15 Measuring linear swell on a soaked CBR specimen.

Figure 3.16 CBR test in progress.

Figure 3.17 Photographic documentation of a typical RLT test process.

Figure 3.18 An RLT specimen with excessively dried top layer.

Figure 3.19 EMITECH K975X sputter coating machine.

Figure 3.20 Gold-coated CG fragments fastened onto a copper plate with carbon tapes.
Figure 3.21 SEM unit used in this research.

Figure 3.22 INCA x-act EDS instrument.

CHAPTER 4

Figure 4.1 Comparison between the average PSD of CG used in this research and data obtained from Arulrajah et. al. (2014).

Figure 4.2 Particle size distribution of PC, and Lime compared to CG.

Figure 4.3 Dry unit weight vs. moisture content curves for CG+PC and CG+Lime (Kua et al., 2016a).

Figure 4.4 7 and 28 days UCS of CG+PC and CG+L (Kua et al., 2016a).

Figure 4.5 Particle size distribution of FA, and S compared to CG (Kua et al., 2016a).

Figure 4.6 Dry unit weight vs. moisture content curves for CG+FA and CG+S (Kua et al., 2016a).

Figure 4.7 Dry unit weight vs. moisture content curves for (a) CG+FA and (b) CG+S. (Kua et al., 2016a)

Figure 4.8 7 and 28 days UCS of CG+FA and CG+S (Kua et al., 2016a).

CHAPTER 5

Figure 5.1 Dry density vs. liquid alkali activator content for various Na$_2$SiO$_3$:NaOH ratios (Arulrajah, Kua et al., 2016).

Figure 5.2 Dry density vs. moisture content for various Na$_2$SiO$_3$:NaOH ratios (Arulrajah, Kua et al., 2016).

Figure 5.3 7 days UCS versus liquid content for various Na$_2$SiO$_3$:NaOH ratios (Arulrajah, Kua et al., 2016).

Figure 5.4 28 days UCS vs. liquid content for various Na$_2$SiO$_3$:NaOH ratios (Arulrajah, Kua et al., 2016).

Figure 5.5 7 days UCS vs. FA replacement ratio, with 8mol NaOH, and 50ºC curing (Arulrajah, Kua et al., 2016).

Figure 5.6 7 days UCS vs. NaOH molarity, with 30% FA replacement, and 50ºC curing (Arulrajah, Kua et al., 2016).
Figure 5.7 7 days UCS vs. curing temperature, with 8mol NaOH, and 30% FA replacement (Arulrajah, Kua et al., 2016).

Figure 5.8 SEM images of: (a) CG, (b) FA, and (c) S (Kua et al., 2016).

Figure 5.9 Compaction curves of different CG:S:FA mixes at different Na2SiO3:NaOH ratios (Kua et al., 2016b).

Figure 5.10 The effects of variations in Na2SiO3:NaOH ratios on achievable $\gamma_{\text{dmax}}$ (Kua et al., 2016b).

Figure 5.11 Average UCS of CG:S:FA mixes at different Na2SiO3:NaOH ratios for different curing periods of 7 and 28 days at a curing temperature of 50°C (Kua et al., 2016b).

Figure 5.12 The effects of S:FA ratio on average UCS at OLC at a curing temperature of 50°C (Kua et al., 2016b).

Figure 5.13 The effects of different curing temperature on 7 days UCS for 70CG:30S:0FA and 70CG:15S:15FA (Kua et al., 2016b).

Figure 5.14 SEM images of: (a) CG, (b) RHA, and (c) S.

Figure 5.15 Particle size distribution of CG, BA, and S.

Figure 5.16 7-days UCS of CG:RHA:S geopolymers at various L/P ratios

Figure 5.17 Effect of S on 7-days UCS for specimens produced at OLC.

Figure 5.18 Long-term strength development of CG:RHA:S geopolymers at OLC.

Figure 5.19 SEM images of: (a) CG, (b) BA, and (c) S.

Figure 5.20 Particle size distribution of CG, BA, and S.

Figure 5.21 Total density vs. L/P ratio for different CG:BA:S geopolymers

Figure 5.22 Bulk density vs. L/P ratio for different CG:BA:S geopolymers

Figure 5.23 7 days strength properties for various CG:BA:S geopolymers cured at (a) 21°C and (b) 50°C.

Figure 5.24 Strength development up to 90 days for different CG:BA:S geopolymers.

Figure 5.25 Particle Size Distribution of RG compared to other materials used.

Figure 5.26 SEM image of RG Particles (Arulrajah, Kua et al., 2016a).
Figure 5.27 OLC of CG geopolymers with different RG replacement ratios.

Figure 5.28 7-days UCS of various CG+RG geopolymer mixes at different L/P ratios.

Figure 5.29 28-days UCS of various CG+RG geopolymer mixes at different L/P ratios.

Figure 5.30 Long-term strength development of CG+RG geopolymers with FA as a precursor.

Figure 5.31 Long-term strength development of CG+RG geopolymers with S as a precursor.

Figure 5.32 SEM of (a) untreated CG and (b) CG geopolymer cured at 50°C for 7 days (Kua et al., 2016b).

Figure 5.33 SEM of 70CG:30S:0FA mixes at OLC, cured at 50°C for 7 days, with different L ratios at: (a) 90Na$_2$SiO$_3$:10NaOH (b) 70Na$_2$SiO$_3$:30NaOH (c) 50Na$_2$SiO$_3$:50NaOH (Kua et al., 2016b).

Figure 5.34 SEM of 70CG:30S:0FA mixes at OLC, cured at 21°C for 7 days, with different L ratios at: (a) 90Na$_2$SiO$_3$:10NaOH (b) 70Na$_2$SiO$_3$:30NaOH (c) 50Na$_2$SiO$_3$:50NaOH (Kua et al., 2016b).

Figure 5.35 SEM of 70CG:30S:0FA mixes at OLC, cured at 50°C for 28 days, with different L ratios at: (a) 90Na$_2$SiO$_3$:10NaOH (b) 70Na$_2$SiO$_3$:30NaOH (c) 50Na$_2$SiO$_3$:50NaOH (Kua et al., 2016b).

Figure 5.36 SEM of 70CG:15S:15FA mixes at OLC, cured at 50°C for 7 days, with different L ratios at: (a) 90 Na$_2$SiO$_3$:10NaOH (b) 50 Na$_2$SiO$_3$:50NaOH (Kua et al., 2016b).

Figure 5.37 SEM images of 7 days cured (a) 70CG:30RHA, (b) 70CG:20RHA:10S, (c) 70CG:10RHA:20S, (a) 70CG:30S specimens at various temperatures.

Figure 5.38 SEM images of 70CG:20RHA:10S specimens cured at (a) 21°C, and (b) 50°C at different curing durations.

Figure 5.39 SEM images of 70CG:10RHA:20S and 70CG:0RHA:30S specimens cured at 50°C for 60 and 90 days.

Figure 5.40 SEM of 7-days cured 70CG:10BA:20S specimens at L/P ratios of (a) 1.8, (b) 2.0, and (c) 2.2.

Figure 5.41 SEM of OLC specimens comparing geopolymeric development of 7-days-cured specimens for (a) 70CG:30BA, (b) 70CG:20BA:10S, (c) 70CG:10BA:20S, and (d) 70CG: 30S.
Figure 5.42 SEM of OLC specimens comparing geopolymeric development of 90-days-cured specimens for (a) 70CG:30BA, (b) 70CG:20BA:10S, (c) 70CG:10BA:20S, and (d) 70CG:30S.

Figure 5.43 Comparison of geopolymeric development in 70CG:20BA:10S and 70CG:10BA:20S specimens cured at 50°C for 7, 28, 60, and 90 days.

Figure 5.44 SEM of fungal growth in 70CG:30S specimens cured at 21°C for 90 days.

Figure 5.45 SEM of a 50CG:20RG:30S specimen cured for 7 days at 21°C, and EDS results on different areas of the geopolymeric formation.

CHAPTER 6

Figure 6.1 CBR values of CG stabilised with FA, S, PC, and L (modified from Kua et al. (2016a)).

Figure 6.2 CBR values for CG+FA and CG+S geopolymers.

Figure 6.3 CBR values for CG+RG geopolymers.

Figure 6.4 Swelling of CBR specimens corresponding to different design mixes.

Figure 6.5 $E_{50}$ versus UCS for all CG+P mixes.

Figure 6.6 $M_R$ results for untreated CG compared to CG+FA and CG+S geopolymers cured at 21°C for (a) 7 days and (b) 28 days (Kua et al., 2017).

Figure 6.7 $M_R$ results for untreated CG compared to CG+FA and CG+S geopolymers cured at 50°C for (a) 7 days and (b) 28 days.

Figure 6.8 $M_R$ versus bulk stress for specimens cured at 21°C for (a) 7 days and (b) 28 days (Kua et al., 2017).

Figure 6.9 $M_R$ versus bulk stress for specimens cured at 50°C for (a) 7 days and (b) 28 days (Kua et al., 2017).

Figure 6.10 Comparison of measured $M_R$ results versus predicted $M_R$ values for specimens cured at 21°C for (a) 7 days and (b) 28 days (Kua et al., 2017).

Figure 6.11 Comparison of measured $M_R$ results versus predicted $M_R$ values for specimens cured at 50°C for (a) 7 days and (b) 28 days (Kua et al., 2017).

Figure 6.12 Comparison of $M_R$ for CG+FA and CG+RG+FA geopolymers.

Figure 6.13 Comparison of $M_R$ for CG+S and CG+RG+S geopolymers.
Figure 6.14 Influence of RG on stress-strain behaviour of CG geopolymers.

Figure 6.15 $M_R$ versus applied bulk stress for (a) 7-days cured and (b) 28-days cured CG+RG geopolymers.

Figure 6.16 Comparison of measured $M_R$ results versus predicted Bulk Stress Model $M_R$ values for CG+RG geopolymers.

Figure 6.17 Comparison of measured $M_R$ results versus predicted 3-Parameter Model $M_R$ values for CG+RG geopolymers.

CHAPTER 7

Figure 7.1 Pavement cross section displaying proposed use of stabilized CG, depicting projected surface runoff and percolation flow (Kua et al., 2016a).
List of Tables

CHAPTER 2
Table 2.1 Engineering properties of coffee ground (Arulrajah et. al. 2014b).

CHAPTER 3
Table 3.1 Leachable heavy metal benchmarks in various fill materials.
Table 3.2 Leachable heavy metals from solid wastes, hazardous wastes, and allowable levels in potable water.

CHAPTER 4
Table 4.1 General Characteristics of CG, PC, and Lime
Table 4.2 General Characteristics of CG, FA, and S

CHAPTER 5
Table 5.1 UCS Testing Programme Summary (Arulrajah, Kua et al., 2016).
Table 5.2 Chemical composition of CG and FA by XRF analysis (Kua et. al. 2017).
Table 5.3 Strength Development in 7-Days and 28-Days cured specimens (Arulrajah, Kua et al., 2016).
Table 5.4 Summary of CG geopolymer testing program (Kua et al., 2016).
Table 5.5 Chemical composition of CG, FA, and S by XRF analysis (Kua et. al., 2017).
Table 5.6 Comparison of UCS at OLC, for different curing periods (Kua et al., 2016b).
Table 5.7 Chemical composition of CG, RHA, and S by XRF analysis.
Table 5.8 Summary of the compaction test results of CG:RHA:S geopolymers.
Table 5.9 Chemical composition of CG, BA, and S by XRF analysis.
Table 5.10 Comparison of 7-days UCS performance of various CG geopolymers

Table 5.11 Test plan for the strength assessment of CG geopolymers with RG supplementation.

Table 5.12 Chemical composition of RG by XRF analysis (Arulrajah, Kua et. al., 2016a).

Table 5.13 Comparison of EDS results done on 50CG:20RG:30P geopolymers cured for 7 days at different temperatures.

Table 5.14 Comparison of EDS results done on CG:RG:S geopolymers with 20, 30, and 50% of RG.

CHAPTER 6

Table 6.1 Material mix specifications for RLT test specimens.

Table 6.2 Empirical regression parameters of bulk-stress model for all material mixes (Kua et al., 2017).

Table 6.3 Empirical regression parameters of three-parameter model for all material mixes (Kua et al., 2017).

Table 6.4 Empirical regression constants of CG+RG geopolymers corresponding with the Bulk-Stress Model and 3-Parameter Model.

CHAPTER 7

Table 7.1 Heavy metal concentration in CG compared to relevant benchmarks (Kua et al., 2016a)

Table 7.2 Acidic and alkaline leachate test results of CG compared to relevant benchmarks (Kua et al., 2016a).

Table 7.3 ASLP test results for CG geopolymers compared to hazardous waste and potable water leachate thresholds.

Table 7.4 Cost estimation of producing CG Geopolymers.

Table 7.5 Cost estimation of producing CG Geopolymers supplemented with RG.
### Notations and Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASLP</td>
<td>Australian Standard Leaching Procedure</td>
</tr>
<tr>
<td>BA</td>
<td>Bagasse Ash</td>
</tr>
<tr>
<td>CBR</td>
<td>California Bearing Ratio</td>
</tr>
<tr>
<td>CG</td>
<td>Spent Coffee Ground</td>
</tr>
<tr>
<td>D&lt;sub&gt;50&lt;/sub&gt;</td>
<td>Cumulative 50% Particle Diameter Size</td>
</tr>
<tr>
<td>E</td>
<td>Young’s modulus</td>
</tr>
<tr>
<td>E&lt;sub&gt;50&lt;/sub&gt;</td>
<td>Secant Modulus</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy-dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>FA</td>
<td>Fly Ash</td>
</tr>
<tr>
<td>kPa</td>
<td>Kilo-Pascals</td>
</tr>
<tr>
<td>L</td>
<td>Alkaline Activator Liquid</td>
</tr>
<tr>
<td>MDD</td>
<td>Maximum Dry Density</td>
</tr>
<tr>
<td>MPa</td>
<td>Mega-Pascals</td>
</tr>
<tr>
<td>M&lt;sub&gt;R&lt;/sub&gt;</td>
<td>Resilient Modulus</td>
</tr>
<tr>
<td>P</td>
<td>Precursor</td>
</tr>
<tr>
<td>PSD</td>
<td>Particle Size Distribution</td>
</tr>
<tr>
<td>q&lt;sub&gt;u&lt;/sub&gt;</td>
<td>Unconfined Compressive Strength (geotechnical notation)</td>
</tr>
<tr>
<td>RHA</td>
<td>Rics Husk Ash</td>
</tr>
<tr>
<td>RLT</td>
<td>Repeated load Triaxial</td>
</tr>
<tr>
<td>S</td>
<td>Ground Granulated Blast Furnace Slag</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>UCS</td>
<td>Unconfined Compressive Strength (general notation)</td>
</tr>
<tr>
<td>USCS</td>
<td>Unified Soil Classification System</td>
</tr>
<tr>
<td>XRF</td>
<td>X-Ray Fluorescence</td>
</tr>
<tr>
<td>γ&lt;sub&gt;d&lt;/sub&gt;</td>
<td>Dry Unit Weight</td>
</tr>
<tr>
<td>γ&lt;sub&gt;dmax&lt;/sub&gt;</td>
<td>Maximum Dry Unit Weight</td>
</tr>
<tr>
<td>ε&lt;sub&gt;r&lt;/sub&gt;</td>
<td>Recoverable Strain</td>
</tr>
<tr>
<td>σ&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Confining Stress</td>
</tr>
<tr>
<td>σ&lt;sub&gt;atm&lt;/sub&gt;</td>
<td>Atmospheric Pressure</td>
</tr>
<tr>
<td>σ&lt;sub&gt;d&lt;/sub&gt;</td>
<td>Deviator Stress</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1 Problem Statement

The global community is increasingly aware of the importance of establishing a sustainable environment for future generations. Recent developments and innovations in sustainability have increasingly stimulated researches pertaining to novel and environmentally friendly construction materials by recycling waste materials contemporarily disposed into landfills. Current construction practices draw resources heavily from non-renewable raw materials (Danielsen and Kuznetsova, 2016) such as timber, limestone, sand and iron ore. Unmonitored urbanisation in the past decades has led to over-exploitation of natural resources (Rees, 2003). This unsustainable rate of material consumption is causing global construction As non-renewable raw materials and landfill space become increasingly scarce (Hoyos et al., 2011), utilizing recycled material derived from industrial wastes, which are normally disposed-off in landfills, solves two problems simultaneously. Moreover, provided that the waste material, which can be procured at low cost due to its near-zero commercial value (Tam and Tam, 2006), can be treated and re-processed properly, the end product can prove to be an economical alternative for urban developers and construction contractors. Therefore, construction and demolition materials such as recycled concrete aggregate (Arulrajah et al., 2015a; Kleijer et al., 2017), recycled glass (Biglarijoo et al., 2017), crushed brick (Mohammadinia et al., 2017), reclaimed asphalt pavement (Behroozikhah et al., 2017; Sangiorgi et al., 2017), and other industrial wastes such as fly ash (Dassekpo et al., 2017), slag (Hadi et al., 2017), calcium carbide residue (Jiang et al., 2015b) and waste-water biosolids (Arulrajah et al., 2013a) have been extensively tested for their suitability as recycled construction materials.

In Australia, the administration and public have, until recent years (Meyer, 2001; Sustainability-Victoria, 2010), been oblivious to the importance of recycling, due to the low population-to-resource ratio and abundance of land in the country (Disfani et al.,
However, the government has gradually realised the importance of sustainability, and Australia is now cooperating with various international organisations to better manage their resources and waste disposal protocols (Meyer, 2001). The reutilisation of organic wastes as a renewable material is still a relatively young and alien concept. Bioenergy contributes to only 6.9% of Australia’s renewable energy output (Edwards et al., 2015), implying that most organic waste materials are destined for landfills. The Australian government has since acknowledged the potential of reusing organic wastes to generate bioelectricity by supporting development of anaerobic digestion systems which feeds mainly on bio-waste and industrial organic wastes. The importance of organic waste management is further highlighted by the government’s ambitious goal to generate 55,815 GWh of bioelectricity by 2050 (Edwards et al., 2015). Although the concept of recycling CG into a construction material does not generate any bioelectricity, the notion of reusing an organic waste is present, hence lending credibility to the significance of this research.

Coffee is one of the most popular beverages in the world (Cornelis, 2015). Coffee is a staple beverage in Australia (Knox, 2016), and is particularly celebrated in the city of Melbourne. An estimate done in 2008 suggested that as a result of coffee brewing, the world produced 7.4 million tonnes of spent coffee ground (CG) (Kondamudi et al., 2008). This figure is projected to increase, particularly in developing nations, as the popularity of this beverage spreads across the globe (Butt and Sultan, 2011). CG is a water-insoluble and highly organic (Campos-Vega et al., 2015) waste which is known to be reused in the agricultural sector as a domestic fertiliser due to its nitrogen-rich composition (Gomes et al., 2013). On the other hand, researches have been done to develop a landfill leachate absorbent based on CG (Ching et al., 2011). Innovative entrepreneurs in Melbourne have started CG collecting initiatives in cafes across the city due to the abundance of CG generated daily (The-Canberra-Times, 2012), thus demonstrating the availability of CG and a means to harvest CG commercially. Nevertheless, the reutilisation of CG by these companies is limited to being used as agricultural fertilisers, and is a far cry from large-scale harvesting and processing of other recyclable materials such as glass and paper.

The concept of using CG as a recycled construction material stems from the observation that CG particles are granular and closely resembles sand, which is a key material used to form the bulk of embankment fills due to its high friction angle and shear strength. However, CG was found to possess little bearing strength even when the solid particles
are optimally compacted (Arulrajah et al., 2014b). Conventionally, weak and problematic soils such as peat and expansive clays require treatment by administering additives such as Portland cement and Lime into the soil (Akpongode, 1985; Holland and Griffin, 1980; Rogers and Glendinning, 1996). Hence by assuming that CG is a weak soil that requires stabilisation to achieve the required load bearing strength, additives possessing cementitious properties, namely Portland cement (PC) and Lime were mixed with CG to assess its resultant strength. On the other hand, these stabilizing agents are manufactured purposefully and the process furthermore results in a large carbon footprint (Sukmak et al., 2013a). Therefore, it is desirable to seek an alternative stabilizing method to create a green material with low negative environmental impact. Hence, an alternative treatment method employing Fly Ash (FA) and Slag (S) geopolymers was mixed with CG and compressed to produce a significantly strengthened product. This study further explored alternative geopolymers utilizing agricultural wastes, namely Rice Husk Ash (RHA) and Bagasse Ash (BA) to create a “green” CG geopolymer. Recycled glass (RG) was used as a supplementary material to further strengthen the CG geopolymer as medium and fine sized RG is known for high shear strength (Disfani et al., 2011). Furthermore, RG is also a recycled material, hence matches the notion of this research. The ultimate goal of the experiments conducted is to determine a suitable ratio of CG to stabiliser to produce a material strong enough to be considered a construction material.

1.2 Objective and Scope

This research aims to create a novel recycled material based on diverting wastes from the beverage and agricultural industries into an unrelated field: the construction industry. Apart from reducing the need of gradually scarce landfill spaces, this research suggests the possibility of channelling wastes from different industries into totally dissimilar fields, hence providing an alternative insight in waste management. Also, the materials involved in the synthesis of the recycled CG geopolymers were carefully selected to uphold the notion of creating a “green” material. FA and S are industrial wastes, RHA and BA are agricultural wastes, and RG is a construction and demolition waste. The objectives of this research are:

1) To use CG as a recycled construction material by reusing it as a pavement subgrade fill material.
2) To determine if contemporary soil stabilisation methods employing Portland cement and Lime can sufficiently strengthen CG to achieve the role as a subgrade fill material.

3) To determine if geopolymerisation is an effective way to sufficiently strengthen CG to achieve the role as a subgrade fill material.

4) To determine the optimum geopolymeric precursors to synthesize a CG geopolymer with maximum strength by testing different geopolymeric blends composed of different precursor ratios and liquid ratios.

5) To utilise RG as a supplement for CG geopolymers

6) To find an optimum curing condition by assessing the strength development of CG geopolymers under different curing conditions.

7) To run California Bearing Ratio (CBR) and Repeated load Triaxial (RLT) tests on selected CG geopolymers to determine their CBR and Resilient Modulus (MR) values, both which are needed in the mechanistic pavement design method proposed by the road authority in Victoria, Australia (Vicroads, 2013).

1.3 Research Approach

Firstly, the materials involved were subjected to experiments that determine their basic properties such as particle size distribution (PSD), inorganic chemical composition, specific gravity, and typical particle morphology. Then, CG was mixed with the stabilisers in different ratios and compacted to determine the variation of material density under various moisture contents. Using a trial and error approach by changing the CG, stabiliser, and liquid ratios, compacted specimens were then produced and left to cure for an arbitrary amount of time. The key parameter assessed in this research is the strengths of the compressed CG mixes corresponding with different additives types, concentrations, and curing environments. Specifically, strength assessment of these CG mixes is done via Unconfined Compressive Strength (UCS) tests. The interparticle interaction and development of bondings within the compressed material matrices were observed via Scanning Electron Microscopy (SEM).
From the many combinations of material blends, mixes that achieve high strengths in short curing periods are selected to undergo further geotechnical testings. California Bearing Ratio (CBR) tests were done to assess the load-bearing capacity of these mixes relative to standard pavement construction materials. As the materials become significantly cemented and stiff after the stabilisation process, tests were also required to assess the compressibility and flexibility of these geopolymers. The Repeated load Triaxial (RLT) test was used to simulate a CG subgrade under repeated traffic loading in which the deformation of the CG mix was recorded. Apart from assessing the geomechanical strength of the recycled CG material, several leachate tests were carried out on the CG geopolymers to ensure that the implementation of these materials as subgrade fills would not lead to hazardous leaching and pollution onto surrounding environments.

1.4 Thesis Overview

This thesis contains 8 chapters which essentially discusses the concept behind the research objectives, an in-depth presentation of background information regarding the materials and methods used in this research, and a progressive report of the experiments done on the parent material, spent coffee ground. A summary of individual chapter contents is provided below:

**Chapter 1: Introduction**

Chapter 1 highlights the problems and ideas that led to the conception of this research, and the significance of this research. A description is given on how the author attempt to address the research questions and problems. A summary of thesis content is also provided.

**Chapter 2: Literature Review**

While the utilisation of CG as a recycled construction material is a relatively new concept, many of the principles behind the methods used to process CG into a recycled material have been well established and extensively researched. This chapter provides an overview of the current global progress in promoting sustainability, past publications regarding soil stabilisation by PC and Lime, research findings on geopolymers, and the background
study of the four precursors (FA, S, RHA, and BA) and supplementary material (RG) used in this research.

**Chapter 3: Material Preparation and Test Methodologies**

This section provides the details regarding how CG is collected, and how the specimens used in the experiments are prepared. The standard laboratory test procedures and equipment used to assess the physical and geotechnical properties of the specimens are also described in this chapter.

**Chapter 4: Conventional Stabilisation of Spent Coffee Ground**

An attempt was made to stabilise CG via contemporary stabilisation methods because these are the simplest and most established methods in the geotechnical field. CG was mixed and compacted with water, PC and Lime and then cured for 7 days and 28 days. FA and S were also used in this simple hydration and compaction method to assess the UCS development of the stabilised CG mix.

**Chapter 5: Geopolymerisation of Spent Coffee Ground**

Geopolymerisation is an alternative process to the hydration of cement which also produces cementitious compounds. Many powdered material containing aluminosilicate can be mixed with alkaline liquids to form geopolymers. This chapter uses trial and error to determine the best precursor to form a strong geopolymer with CG. The precursors used were FA, S, RHA, and BA. UCS tests were done extensively on different material mixes cured at different ambient temperatures and durations. Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray Spectroscopy (EDS) was used to observe and explain the interaction between the granular particles and cementitious compounds in the material mixes.

**Chapter 6: Spent Coffee Ground as a Pavement Subgrade Fill Material**

Selected CG geopolymer mixes underwent CBR and RLT tests to determine their suitability to be used locally a recycled construction material. The results presented in this section give an insight on how strong and resilient the CG geopolymers are towards external traffic loadings. This chapter also discusses the limitations faced during the
laboratorial synthesis process of CG geopolymers and how these problems may manifest if the material is applied in the field.

Chapter 7: Environmental and Economic Viability

The environmental impacts of synthesizing CG geopolymers is determined and discussed. Also, a simple cost analysis was done to assess the economic feasibility of each CG +stabiliser mixes presented in this research.

Chapter 8: Conclusions and Recommendations

Concluding remarks were made to summarise the findings presented in this thesis. Suggestions were proposed for future research works.
2.1 Recycling Practices in Civil Engineering

2.1.1 Overview on Sustainability

A sustainable lifestyle is defined as one which consumes natural resources at a rate below the finite capacity of our planet. Sustainable development is widely quoted as a development that meets the demands of the present generation without compromising the resources of future generations for survival (Brundtland and Khalid, 1987). Throughout the history of mankind, great emphasis has been made to improve living standards by developing the environment in which we live in. Unfortunately, the many contemporary technological advancements which led to industrialisation and rapid urbanization are clearly unsustainable (Imperatives, 2016): The combustion of fossil fuel and coal for energy, the quarrying of valuable metals and minerals (Magnusson et al., 2015), and the harvesting of timber depletes non-renewable natural resources at alarming rates. The situation is worsened with the exponentially increasing human population which furthermore burdens the system by increasing the demand for resources.

A statement made by the World Wildlife Fund projects that the current population is overutilizing Earth’s resource capacity by 50%, and by 2030 “even two planets would not be sufficient” to sustain human life (Lee, 2017). The severity of destruction and pollution to the environment brought about by the industrial revolution eventually led scholars to coin terms such as “greenhouse gas” (Okoliša, 2009), “carbon footprint” (Kjerstadius et al., 2017), “emissions” (Rebolledo-Leiva et al., 2017), and “sustainability” as they begin to publish reports and statistics regarding the disparaging side-effects which followed human progress. As the global community began to realise the adverse effects brought about by the contemporary way of life, concepts such as the triple bottom line of sustainable development (Thabrew et al., 2017), carbon offsetting, industrial ecology, and zero emissions were increasingly assimilated into traditional industries and technologies to gradually reduce the harm done on the planet.
Recycling is one of the emerging technologies derived from the awareness that many resources that are currently tapped for development, including glass, iron, and carbon fuels are non-renewable. At the end of their design life, many consumer goods and man-made objects are traditionally disposed of in landfills (Little et al., 2017). Current technologies enable the extraction and processing of materials such as metals, glass, and paper to be reused as recycled materials to reduce dependency on extracting virgin resources from the environment. However, recycling is not widely practiced around the globe due to the relatively higher costs and additional technical expertise associated with collecting, segregating, and reprocessing waste products compared to the extraction and processing of raw materials (Hirota and Kawa, 1998).

Nevertheless, this does not deter researchers from improving and creating novel technologies associated with recycling. Recycling metal, polyethylene terephthalate, paper, and glass is now an integral part in the waste management system of highly developed countries like Japan (Sakai et al., 2017). On the other hand, governments in nations previously unfamiliar with sustainable practices, such as China and India (Awasthi and Li, 2017), are striving to indoctrinate their populace on the benefits of recycling while implementing prototypical recycling systems (Fan et al., 2017; Xiao et al., 2017) into their waste management systems. Recent advancements in recycling gave rise to the popularity of reutilising agricultural (Gumisiriza et al., 2017; Nikodinoska et al., 2017) and municipal wastes (Afolabi and Sohail, 2017; Aracil et al., 2017) to produce energy by biological processes such as anaerobic digestion and chemical processes such as combustion (Matsakas et al., 2017). These are prime indications that the globe is increasingly aware of sustainability and is gradually investing in creating a partially close-looped system that reduces raw material demand.

Post-consumer or post-municipal wastes are generated abundantly hence are widely studied for their reutilisation potentials. On the other hand, the construction industry, which is responsible for shaping the built environment, also generates a significant amount of wastes annually. Contemporary construction methods draw heavily from natural resources: the timber and steel required for structural components, limestone to produce cement, which in turn is used to produce concrete, and glass which is used as façade and architectural finishes. Particularly, the manufacturing of cement results is
responsible for 5-7% of the world’s carbon dioxide emission (Meyer, 2009; Worrell et al., 2001) due to the high energy required to process limestone into cement clinkers.

Apart from using non-renewable raw materials as the literal building blocks, a typical construction process usually results in wastage of material due to poor logistics, lack of waste segregation, and loose enforcement by government bodies and contractors alike in waste minimisation (Ajayi et al., 2017). However, it was found that the demolition of infrastructures, mostly due to unrepairable defects or end of design life, accounts for the largest source (Chen and Lu, 2017) of waste in the construction and demolition (C&D) waste stream. Surveys done in the last decade have reported that in Australia, C&D wastes accounts for up to 40% of annual solid waste generated (Yuan and Shen, 2011). In the UK, 70 million tonnes of C&D wastes were recorded annually, whereas in the USA this figure is almost double at 136 million tonnes (Yuan and Shen, 2011). Less than 30% of the wastes are recycled. The remainder is disposed of in landfills, which requires the continual partitioning of increasingly scarce land space (Poon et al., 2003). Civil engineers are increasingly conscious of these unsustainable practices hence are actively researching and adopting green materials and building technologies to create a sustainable man-made domain which co-exists in harmony with nature.

From 2000 to 2009, 87 publications in peer-reviewed journals discussed the managing and recycling of C&D wastes (Yuan and Shen, 2011). By observing recycling and reusing practices commonly applied in society, researchers have acknowledged the viability of reusing C&D wastes after proper treatment and stabilisation. Some materials like timber formworks and steel scaffolding can be reused occasionally. C&D wastes such as steel and glass can be melted and recast for further use. Other wastes which cannot be reused are subsequently studied for their potential to be recycled. Many crushed C&D materials, such as crushed brick (Poon and Chan, 2006), crushed concrete(Arulrajah et al., 2016c), crushed glass (Disfani et al., 2011), and reclaimed asphalt (Hoyos et al., 2011; Taha et al., 2002) have sufficient bearing strength to be used as recycled aggregates (Behera et al., 2014) in heavily bound construction materials. Other C&D wastes, such as pulverised glass powder, were studied for their chemical components which enables them to be potentially recycled as cementing agents. Generally, experimentations in recycling C&D wastes involves stabilising the wastes to produce bound materials (Mohammadinia et al., 2016; Puppala et al., 2011) and examining the resultant product for their strength and
durability characteristics. A common application of recycled construction wastes is as road construction materials, in which waste materials are stabilised and compared against the required strength benchmarks of road bases (Mohammadinia et al., 2016), subbases (Bradshaw et al., 2016), and subgrades (Kazmee et al., 2016).

This research is built on the concept of creating a recycled construction material by adopting the methods used in past literature. However, the novelty of this research stems from replacing C&D wastes with a beverage waste—spent coffee ground. The intended use for this material is as a road construction material. Therefore, this material was subsequently approached from a geotechnical point of view.

2.1.2 Contemporary Soil Stabilisation Methods

Geotechnical engineering is a branch of civil engineering which evaluates the strength of the underlying soil strata of designated building sites. Geotechnical engineers are responsible for ensuring a structurally stable foundation in which superstructures are built upon. Weak and problematic soils usually result in two general scenarios. Deep foundations in form of piles may be used to transfer building loads to a stable rock stratum beneath the weak layers. Otherwise, geotechnical engineers can employ compaction techniques to densify and consolidate the weak soil layers, or employ various chemical reactions to coagulate weak soils into denser and stronger matrices—in a process called ground improvement and soil stabilisation (Terzaghi et al., 1996). Soil stabilisation is conventionally done by mixing small amounts of chemicals into the soil strata to form relatively stiffer soil matrices. Additives seeing widespread use in the geotechnical field include Portland cement (PC) and lime (Akpokodje, 1985; Hagan, 1997; Jauberthie et al., 2010; Sirivitmaitrie et al., 2011). Typically, in the construction industry, the additives replace 3-5% of the raw material by mass in generic stabilisation processes practiced today (Holland and Griffin, 1980). In Melbourne, Australia alone, approximately 50,000 km of road network has one of their components cement-stabilised (Mohammadinia et al., 2016).

PC is derived mainly from limestone containing high levels of CaCO₃. Limestone mixed with clays containing alumina-silicate is heated in kilns under temperatures up to 1450 °C to form clinkers, which are then ground into a powdery form. This cement powder hardens in the presence of water via a chemical process known as hydration. The presence
of aluminate results in a highly exothermic reaction immediately after water is added. As the reaction progresses, the formation of calcium silicate hydrate (C-S-H) and calcium hydroxide results in a hardened matrix. Engineers have found that this simple reaction process results in good strength increase in many weak soils; however, soils with high acidity and sulphate content inhibits the PC hydration process hence are unsuitable to be PC-stabilised (Ismail et al., 2014a). A research done to assess the strength of cement-treat pavement base reports that soils with organic contents higher than 2% will also result in anomalies in the stabilisation process. Conversely, the research found that organic soils with high alkalinity exceeding pH 12 are favourable for cement reaction (Ismail et al., 2014a).

Lime used in soil stabilisation is manufactured by quarrying rocks rich in calcium carbonate (CaCO$_3$) and heating the material under temperatures up to 1000 °C to form calcium oxide, (CaO), also commonly known as quicklime. At this state, like PC, the reaction process in Lime can simply be activated by adding water, in which Ca$^{2+}$ ions are liberated. Lime is widely accepted as a soil stabiliser which improves soil stiffness, workability, and permeability. This additive works favourably when mixed with clayey soils rich in alumina and silica. These minerals react with Ca$^{2+}$ ions to form calcium silicate and aluminates, which in turn become cementitious compounds similarly to those found in PC. Sulphate rich soils are also known to inhibit soil stabilisation with Lime: the lime-sulphate reaction ironically causes soil expansion and reduced bearing strength. Carbonation, a lime-soil reaction which occurs when lime absorbs excess carbon dioxide in the atmosphere, slows the formation of cementitious compounds in the soil mixture, and typically occurs with hot-dry climates. Comparatively, lime-stabilised soils may require longer period to achieve maximum strength compared to the standard 28-day hydration time of PC (Consoli et al., 2001).

While PC and L are noted to be effective stabilising agents due to their rapid hydration and pozzolanic reactions (Croft, 1967; Rogers and Glendinning, 1996; Yoon and Abu-Farsakh, 2009), these materials must be purposefully manufactured at a significant cost. Moreover, the manufacturing process of PC also results in a large carbon footprint (Horpibulsuk et al., 2013), putting these solutions in conflict with current sustainable development doctrines. Due to the widespread use of concrete incorporating PC in constructions across the globe, which was recorded at a production rate of more 10 billion
tonnes in 2009 (Collins, 2013), the construction industry has been deemed as an anti-environment industry. Due to international pressure to overhaul the construction industry to be more environmental-friendly, researches focused on reducing the emissions associated with the manufacturing of PC. It was found that the demand and dependency on PC could possibly be reduced by partially replacing PC with industrial wastes possessing similar cementitious traits as PC, such as fly ash and ground granulated blast furnace slag (Meyer, 2009).

2.1.3 Geopolymerisation as an Emerging Green Technology

Geopolymerisation is a process that creates cementitious compounds by the dissolution of aluminosilicate compounds by highly alkaline liquids. After a prolonged period, the dissolved minerals reconstitute into calcium silicate hydrate (CSH) (Richardson et al., 1994) and aluminium-modified calcium silicate hydrate (CASH) gels (Garcia-Lodeiro et al., 2011), which are cementitious compounds found also in PC. Both the geopolymerisation of aluminosilicate-rich materials and the hydration of PC results in a strong cementitious compound, but the process involving the latter requires only water (H₂O) and PC, hence is simpler to employ, compared to geopolymerisation which requires an alkaline liquid to take effect. However, the key difference in geopolymerisation is that it results in virtually no carbon footprint compared to the manufacturing of PC (Turner and Collins, 2013). As ecological pollution increasingly becomes a pressing matter, civil engineers are opting for design and construction methods that are sustainable. Geopolymers can become an alternative cementing agent that can replace PC in the near future and furthermore substantially decrease carbon emissions from the construction industry.

Moreover, the process of geopolymerisation reuses waste materials from various industries, as the aluminosilicate required for geopolymerisation can be abundantly found in industrials wastes such as FA and S. FA is a by-product from the coal-combustion energy industry whereas S is generated from the iron-ore refinery industry. Both waste materials are abundantly available throughout the globe (Ahmaruzzaman, 2010; Yi et al., 2012a), and have been extensively researched for their role as precursors in geopolymerisation (Ismail et al., 2014b; Oh et al., 2010; Rangan et al., 2005; Wang et al.,
Researchers have also experimented with other aluminosilicate-rich materials including the clay mineral metakaolin (Clausi et al., 2016) and calcium-carbide residue, the by-product of acetylene gas production (Phetchuay et al., 2014). In addition, the studies on geopolymeric precursors are not confined to construction and industrial wastes: ashes derived from the combustion of agricultural wastes, for instance rice husk and sugarcane, were found to contain high percentages of silica, thus have been studied as geopolymeric precursors (Cordeiro et al., 2016; Mejia et al., 2016).

With the right ratio of precursor and alkaline liquid activator, geopolymers cured at elevated temperatures can substitute PC in producing concrete mixes with satisfactory compressive strengths (Srinivasan et al., 2015). Consequently, geopolymerisation can also be applied to greatly improve the unconfined compressive strength of unfavourable geo-materials (Phetchuay et al., 2014; Sukmak et al., 2013a). It is interesting to note that mixing Sodium Hydroxide (NaOH) and Sodium Silicate (Na$_2$SiO$_3$) to form a compound activator liquid is reported to augment the strength of geopolymers (Palomo et al., 1999; Wang et al., 2015). The increased level of silicates contributed by introducing Na$_2$SiO$_3$ into NaOH results in the increase of aluminosilicate-sodium silicate reaction (Xie and Xi, 2001), consequently promoting formation of the cementitious gel found in geopolymers.

Geopolymerisation has been found to be an effective method to stabilise problematic soils for geotechnical engineering purposes. This method has successfully increased the load bearing strength of weak clays in road applications (Du et al., 2014b; Du et al., 2016; Hoy et al., 2016; Jiang et al., 2015a; Phummiphan et al., 2016), and enhances stiffness in soil matrices to resist flexural deformation due to repeated traffic loading (Mohammadinia et al., 2016). Typical experiments involve mixing the weak soils with up to 30% of geopolymeric precursors (Horpibulsuk et al., 2012; Phetchuay et al., 2014; Sukmak et al., 2013a), but due to the low costs associated with procuring the waste materials used for geopolymerisation, replacement ratios up to 50% have been reported (Bernal et al., 2011; Rashad, 2013; Srinivasan et al., 2015). Then, geopolymeric reaction is induced by administering alkaline activators. This is followed by compaction of the treated soil to form a reinforced stratum. Geopolymerisation has been reported to provide good cementing strength and was found to successfully encapsulate even highly organic wastes such as biosolids (Arulrajah et al., 2013a; Disfani et al., 2013) and waste water treatment...
sludge (Suksiripattanapong et al., 2015a; Suksiripattanapong et al., 2015b) to form materials with high compressive strengths.

### 2.2 Spent Coffee Ground

#### 2.2.1 Production

Apart from bearing physical resemblance to sand, Spent Coffee Ground (CG) was chosen as a research material partly due to its popularity across the globe. Coffee is one of the most popular beverages in the world. It comes second as the world’s most important commodity, after fossil fuel (Marescotti and Belletti, 2016). Statistics gathered from the International Coffee Organisation (ICO) in early 2017 shows that the world consumed 9 million tonnes of coffee from year 2015 to 2016. Brazil was the world’s largest coffee exporter and was responsible for distributing 3 million tonnes of coffee beans, followed by Vietnam at 1.5 million tonnes of export. Records from the ICO also show that Brazilians ranked at the top of the annual coffee consumption statistics for 2015-2016, and is followed in descending order by Indonesia, Ethiopia, and the Philippines. Australia is considered as a coffee-importing country and in 2016 Australians were ranked the 8th heaviest coffee consumers in the world, preceded mainly by the European Union, USA, and Japan. A detailed statistical analysis has shown that in 2012, global consumption of coffee grew steadily by 1.9% annually for 50 years (ICO, 2014). Demands in coffee consumption is still projected to increase steadily, particularly in developing nations (Butt and Sultan, 2011). Moreover, the public opinion on coffee is increasingly positive, with current scientific publications widely reporting the benefits of coffee consumption (ICO, 2014). The rebranding of coffee, particularly in importing nations, as an exotic drink associated with high social positioning, coupled with extravagant brewing and drinking methods, has further propagated the interest of the younger generations in pursuing this beverage (Ponte, 2002).

CG is a waste material derived from the grinding and brewing of coffee from coffee beans. It is the solid granular residue of the ground beans which is disposed-off after the coffee-brewing process. Tsai et al. (2012) speculated that coffee producing countries generate residual coffee wastes amounting to more than 50% of the fruit mass. A survey done in 2015 projected that the world produced 8.6 million tonnes of CG (Phimsen et al.,...
2016), and this figure likely increased with annual growth in coffee demand. CG is increasingly becoming a significant waste stream hence gaining focus as a target for waste management. Nestle, the world’s biggest food company which owns the Nescafe brand of coffee, pledged to commit CG from more than 20 of their European coffee processing plants into biofuel development and implementation by 2020 (Campos-Vega et al., 2015).

2.2.2 Current Recycling Applications

CG is a waste material widely known as a nutrient rich organic compound. CG contains high levels of nitrogen hence is often used as an agricultural fertilizer (Gomes et al., 2013). However, the utilisation is strictly limited to domestic gardens and farms as a compost, because of the slow release of nutrients (Ciesielczuk et al., 2017; Hardgrove and Livesley, 2016). Research found that fresh CG is detrimental to plant growth due to reduced mineral availability and growth disruption due to bioactive residues such as caffeine. Even when introduced at small volumes as low as 2.5%, fresh CG was found to inhibit the growth of broccoli, sunflower, viola, leek, and radish (Hardgrove and Livesley, 2016). Also, while lettuce was observed to develop more vibrant colourations when their soil medium was added with 20-30% of CG, crop yield was reported to decrease (Cruz et al., 2015). About 15% of CG compost was found to optimally provide macronutrients to supplement plant growth (Cruz et al., 2014). Another study on basil and tomato done by Ronga et al. (2016) more positively reports that potted soil supplemented with CG compost by up to 40% resulted in enhanced yields. All literatures discussed the potential of reutilising CG compost as an economical fertiliser, but no documentation has been found to support any large-scale commercialisation of using CG as an agricultural fertiliser.

An alternative and relatively straight forward method to recycle CG is by utilising the organic waste as a biofuel. CG can be disposed of in anaerobic digestion tanks with other organic waste to produce methane (Kim et al., 2017). On the other hand, CG can also be refined to produce biodiesel. Kondamudi et al. (2008) successfully extracted highly efficient biodiesel equal to 15% of CG by weight, and estimated that 340 million gallons of biodiesel could be added to the global fuel supply if CG is fully utilised as a biofuel. Due to CG’s high antioxidant content, the biodiesel extracted from CG was deemed more
stable compared to those obtained from other sources (Yanagimoto et al., 2004). While many studies involved coffee oil extraction and esterification from CG to fuel, an innovative method was proposed to administer sulphuric acid into dried CG. The inclusion of an acid catalyst bypasses the tedious extraction process and was proposed by Liu et al. (2017) to further increase the efficiency of recycling CG into a biofuel.

The interesting biological configuration in CG enables this organic waste to be altered by various chemical activators to be reused in different fields. CG is also known to exhibit chemical properties suitable for a cationic dye removal agent (Franca et al., 2009). Studies done on the carbonisation of CG hints to potential reuse as a landfill leachate absorbent (Castro et al., 2011; Ching et al., 2011). CG was impregnated with different activating agents, including sulphuric acid and sodium carbonate, and subsequently carbonised. An activated carbon with high pore surface was synthesised and found to effectively absorb total iron and orthophosphate from landfill leachates. Composted CG mixed with soil was found to stall the leaching of methabenzthiazuron (Fenoll et al., 2014), a common herbicide used in agricultural applications, thus adding credibility to the potential of recycling CG as a leachate absorbent. On the other hand, CG was found to contain a substantial amount of antioxidant phenolics. These compounds play a positive role in health improvement and is a major component in pharmaceutical and nutritional food products. Since CG contain antioxidants, amino acids, low glycaemic sugars, and is composed of insoluble fibres which are resistant to thermal food processing and digestion, the waste was studied as a recycled food ingredient as a supplement for dietary fibre and low-calorie sweetener (Martinez-Saez et al., 2017). Innovative biscuits with high nutritional values and no adverse side effects to human health were formulated as a result.
Table 2.1. Engineering properties of coffee ground (Arulrajah et. al. 2014b).

<table>
<thead>
<tr>
<th>Engineering parameters</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
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<tr>
<td>D10 (mm)</td>
<td>0.153</td>
<td>0.65</td>
<td>0.182</td>
</tr>
<tr>
<td>D30 (mm)</td>
<td>0.252</td>
<td>0.25</td>
<td>0.3</td>
</tr>
<tr>
<td>D50 (mm)</td>
<td>0.349</td>
<td>0.332</td>
<td>0.351</td>
</tr>
<tr>
<td>D60 (mm)</td>
<td>0.427</td>
<td>0.4</td>
<td>0.42</td>
</tr>
<tr>
<td>Cu</td>
<td>2.79</td>
<td>2.42</td>
<td>2.31</td>
</tr>
<tr>
<td>Cc</td>
<td>0.97</td>
<td>0.95</td>
<td>1.18</td>
</tr>
<tr>
<td>Particle sizes between 0.075 mm and 2.36 mm (%)</td>
<td>99.5</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Particle size &lt; 0.075 mm (%)</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Specific Gravity, GS</td>
<td>1.36</td>
<td>1.37</td>
<td>1.36</td>
</tr>
<tr>
<td>Natural Moisture Content (%)</td>
<td>107</td>
<td>156</td>
<td>149</td>
</tr>
<tr>
<td>Organic Content (%)</td>
<td>86</td>
<td>89</td>
<td>88</td>
</tr>
<tr>
<td>pH</td>
<td>5.15</td>
<td>5.15</td>
<td>5.12</td>
</tr>
<tr>
<td>Maximum Dry Unit Weight (kN/m$^3$)</td>
<td>4.4</td>
<td>4.2</td>
<td>4.02</td>
</tr>
<tr>
<td>Optimum Moisture Content (%)</td>
<td>130</td>
<td>134</td>
<td>147</td>
</tr>
<tr>
<td>Initial void ratio, e$_0$</td>
<td>2.26</td>
<td>2.23</td>
<td>2.34</td>
</tr>
<tr>
<td>Preconsolidation pressure (kN/m$^2$)</td>
<td>118</td>
<td>126</td>
<td>90</td>
</tr>
<tr>
<td>Compression index, c$_c$</td>
<td>0.764</td>
<td>0.93</td>
<td>0.797</td>
</tr>
<tr>
<td>Recompression index,c$_r$</td>
<td>0.266</td>
<td>0.23</td>
<td>0.266</td>
</tr>
<tr>
<td>Coefficient of consolidation, c$_v$ (m$^2$/yr)</td>
<td>0.9</td>
<td>0.88</td>
<td>0.9</td>
</tr>
<tr>
<td>Coefficient of volume change, mv</td>
<td>0.43</td>
<td>0.42</td>
<td>0.44</td>
</tr>
<tr>
<td>Hydraulic conductivity, k (m/s)</td>
<td>1.19E-10</td>
<td>1.16E-10</td>
<td>1.31E-10</td>
</tr>
<tr>
<td>Triaxial test (CU): cohesion, c' (kPa)</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>Triaxial test (CU): friction angle, $\Phi'$ (degrees)</td>
<td>-</td>
<td>-</td>
<td>31.9</td>
</tr>
</tbody>
</table>

Studies on the “geotechnical properties” of CG was pioneered by Arulrajah et al. (2014b). A suite of geotechnical engineering tests designed for granular soils were applied on CG, and due to the physical similarities between granular CG and soil, a meaningful set of data were obtained. Table 2.1 shows the summary of results extracted from Arulrajah et
al. (2014b)’s findings, which tested 3 different sources of CG. CG are sand sized, with 99.5-100% of their particles falling in the range of 0.075 to 2.36 mm. According to the Unified Soil Classification System, it is uniformly graded, and resembles beach sand. A lack of interparticle cohesion renders Atterberg Limits unobtainable. CG have low specific gravity (1.3) and maximum dry density (4.2), indicating that it is a lightweight material close to the density of water. Fresh CG was found to contain high moisture due to the hydration process throughout the coffee brewing process. These range of moisture contents can be similarly found in marine clays. CG was found to be slightly acidic, which is typical for an agricultural waste. Low values of coefficient of consolidation indicates that CG is highly compressible. Triaxial shear test results revealed that CG has a practical friction angle that may potentially enable the usage of CG as a fill material to replace sandy soils.

Waste reduction initiatives are currently emerging in Melbourne, Australia, as the public becomes more aware of the importance of a sustainable environment (Sustainability-Victoria, 2010). A young company has organized the collecting, sorting and transportation of CG from various cafes, with the intention to divert the stockpiles of CG, from landfills and into sustainable practices (The-Canberra-Times, 2012). With the coffee generated in this city, it is estimated that 5 km of road can be constructed yearly (Arulrajah et al., 2014b). These initiatives may prove to be a valuable mode of logistic to transport CG for large scale commercial uses in the future.

### 2.3 Soil Stabilisers and Geopolymeric Precursors

Fly ash, slag, rice husk ash, and bagasse ash were selected and evaluated as precursors to stabilise CG by geopolymerisation, due to their availability and ease of procurement in Australia. FA and S are commercially available in Melbourne, whereas RHA and BA can be sourced from various agricultural sectors in Queensland. The background and basic properties of these materials were subsequently compiled and discussed.
2.3.1 Fly Ash

Fly ash (FA) is a by-product from the coal energy industry. Australia is one of the leading coal exporters in the world. It was the fourth largest producer and fifth largest resource of black coal in the world, according to a report by the Australian Department of Industry, Innovation and Science from year 2010 to 2011. The Bureau of Resources and Energy Economics estimated that Australia produced 401.4 million tonnes of commercial black coal from 2012 to 2013. In 2012 Australia contributed to 5% of global coal production. Coal combustion is a common method in many countries, including Australia, to generate energy. Incidentally, the ignition of coal produces aluminosilicate-rich FA as a residue, which has been reused extensively as a material in civil engineering applications. In Australia alone, 75% of the nation’s energy was reported to be drawn from coal power plants and 12 million tonnes of FA was accumulated as a by-product (Morrison, 2005). Statistics gathered in 2008 show that industries worldwide generated 900 million tonnes of FA in that year alone, and this figure is expected to increase up to a staggering 2000 million tonnes by 2020 (Malhotra, 2008).

Fly ash is a waste material produced from the combustion of pulverised coal in power plants. First, coal is fed into a pulveriser and finely ground, then blown into a furnace to be ignited. The resulting heat is used to power boilers, which in turn generates high pressure steam to move power turbines. FA would normally consist of 80-90% of the residue, whereas the remainder may be a distinctly different bottom ash (Ramme and Tharaniyil, 2004). According to ASTM (ASTM, 2012a), there are two major categories of FA, namely the Class F and Class C FAs. Class F contains less than 20% of free lime whereas Class C contains about 40% of lime. The high amount of lime causes Class C FAs to be partially self-cementitious in the presence of water. On the other hand, Class F FAs are highly pozzolanic, meaning they require alkaline activation to show any cementitious properties.

FA is commonly used to limit heat development during concrete hydration to prevent cracking associated with thermal expansion (Plowman and Cabrera, 1996). It can provide sulphide and sulphate resistance hence minimises the sulphate attack phenomenon experienced by concrete structures. In the geotechnical engineering sub-discipline, FA is used to stabilise problematic soils by increasing the shear strength (Ahmaruzzaman, 2010), and to reduce the moisture content of in-situ soil strata (Cristelo et al., 2013).
Literatures suggested that adding 20-25% of FA to supplement conventional PC and Lime stabilisation methods results in significant strength improvement in weak soils (Bai and Hou, 2006; Consoli et al., 2001; Kalita and Singh, 2010). FA can also partially replace natural soils as a load bearing material in pavement design (Rai, 2010). As early as 1979, FA was used as a backfill material behind retaining walls (Swain, 1979). Rai (2010) highlighted the viability of using FA as a replacement fill material due to its low unit weight and high shear strength, thus a lightweight, low-cost recycled material. FA was found to decrease the setting time of soil mixtures with the increase of ash-to-soil weight ratios. Due to the high concentration of silica in ash materials, FA is a suitable precursor that has been used to produce geopolymers- chemically cemented soils with elevated unconfined compressive strength (Phetchuay et al., 2014; Suksiripattanapong et al., 2015b). FA geopolymers have also been noted to produce high quality replacements for PC concretes, and are particularly favoured by researchers due to the abundance of FA as an industrial waste.

2.3.2 Ground Granulated Blast Furnace Slag

Slag, (S) is an industrial by-product from the blast-furnaces produced during the manufacturing of iron (Pavía and Condren, 2008). Manufacturing 1 tonne of steel produces 340-421 kg of blast furnace slag (Das et al., 2007). The ever increasing-demand for steel has generated a proportional amount of slag (Perná and Hanzlíček, 2015), but only a small fraction of this waste is reused while the remainder is destined for the landfill (Yi et al., 2012a). Australia is a leading steel exporter, with the majority, about 98%, of iron ore reserves located in Western Australia. While production has been declining since year 2010, in 2015 Australia produced 4.9 million tonnes of steel. Statistics obtained from the Australasian Slag Association in 2013 revealed that Australia and New Zealand utilises 80% of their iron and slag products and goods on various construction applications, including as replacement cements and fill materials.

Mined iron ore contains many impurities. The purification process to obtain iron involves melting the ores in blast furnaces. Molten iron ore undergoes reduction with the introduction of coke and lime, resulting in the denser pure iron sinking to the bottom while the residual impurities float onto the top. The impurities typically consist of four major chemical components: CaO, SiO$_2$, Al$_2$O$_3$ and MgO, segregated from iron and
oxides from the reducing agents (Snellings et al., 2012). The residue, when quenched, forms granular slag pellets. Air-cooled residue results in blast furnace rock slag which are lightweight, porous, and has high shear strength. This lock-like slag can be used as aggregates in pavement construction (Ahmedzade and Sengo, 2009). On the other hand, water-cooling results in an amorphous, coarse sand-sized slag, which is then ground to become ground granulated blast furnace slag (S). S can be used for many engineering applications such as cement replacement, and is one of the main soil stabiliser and geopolymeric precursors used in this research.

Due to the higher concentration of calcium oxide (CaO) in its material composition, S can manifest cementitious properties in the presence of water compared to the pozzolanic FA. S has a similar chemical composition to PC, but the proportion of compounds are different. S contain higher amounts of silica and lower amounts of ferric oxide. Therefore, during the hydration process, the cementitious properties of S manifests much slower compared to PC (Detwiler et al., 1996). Nevertheless, S can act as a substitute cementitious material that can reduce greenhouse gas emission by 47.5% in concrete manufacturing, improve the long term strength of concrete mixes, and is a suitable stabilising agent for soils (Yi et al., 2012b). S can replace up to 60% of PC in concrete without causing significant loss in long-term strength development (Khatib and Hibbert, 2005). S concretes may even outperform PC concretes in term of strength, but the major drawback is the long curing time (up to 28 days) required for S concretes (Kuder et al., 2012). S is a good replacement for Lime to stabilise sulphate-rich soils, because lime-sulphate reactions result in excessive expansion and reduce bearing strength. Swelling in expansive clays can be inhibited by administering a mix of PC and S (Cokca et al., 2009). S is commonly used as a precursor for geopolymerisation due to the high concentration of calcium and silica (Bernal et al., 2011; Ismail et al., 2014b; Oh et al., 2010; Perná and Hanzlíček, 2015; Puertas et al., 2000; Srinivasan et al., 2015).

2.3.3 Rice Husk Ash

The milling of rice in paddy field produces edible rice grains and results in rice husk, the natural shell encasing the grains at growth. Rice husk is generally considered as a waste material. According to information released by the International Rice Research Institute in 2017, the world produced 715 million tonnes of paddy in 2016. Out of the
yield, 480 million tonnes were estimated to be processed as milled rice, with the remained comprising of wasted or defective grains, and husk. Asian countries including China, India, Bangladesh, Thailand and Vietnam are major rice producers hence accounts for much of the global rice husk generated annually. Oceania, which includes Australia and New Zealand, recorded the smallest yield in paddy production among all regions across the globe. Rice husk is easily combustible, lightweight, but bulky hence requires large disposal areas. Moreover, it is prone to spontaneous combustion, resulting in the spreading of ash and causing harm to the environment (Aprianti S, 2017). Therefore, rice husk is used as a fuel in boilers and power generators, due to its high calorific value of approximately 16,720 kJ/kg. The residue of this contained combustion process is rice husk ash (RHA). Depending on the combustion process, the resultant RHA may contain up to 90% of silica (Zain et al., 2011), hence is a suitable precursor for geopolymerisation. RHA can be amorphous or crystalline depending on the calcination time and temperature (Geraldo et al., 2017).

Many studies have been done to divert this agricultural waste into the construction industries due to the cementitious and pozzolanic properties it possesses. RHA was studied as a supplementary cement (Zain et al., 2011) and replacement for PC in concretes. Replacing 40% of PC with RHA did not deteriorate concrete strength (Al-Khalaf and Yousif, 1984), thus implying that RHA can potentially minimise the carbon footprint resulting from the manufacturing of PC concrete. RHA geopolymers have been researched extensively due to the concept of creating a green cement. It is commonly used as a supplementary precursor for FA (Chaysuwan et al., 2014; Detphan and Chindaprasirt, 2009) and S (Venkatesan and Pazhani, 2016) geopolymers. FA concrete mixed with 10% of RHA were found to have enhanced mechanical strength, thermal properties, and acid resistance (Maulana et al., 2017). RHA is also an effective precursor when used independently: A mortar consisting of 33% alkaline-activated RHA and 66% of sand was found to outperform a PC-sand mortar, with the same material ratio, under elevated temperature curing at 60°C (Kim et al., 2014). 30% of RHA by weight was mixed with calcinated water treatment sludge and alkaline-activated to produce lightweight geopolymers with strengths also reported to be close to PC (Poowancum et al., 2015).
2.3.4 Bagasse Ash

Bagasse is the fibrous residue obtained when sugarcane is crushed to obtain sugarcane juice. 0.3 metric tonnes of bagasse are generated from each metric ton of sugarcane produced (Bezerra and Ragauskas, 2016). Australia’s sugarcane industry is centred at the tropical eastern coastline in Queensland. The Australian Sugar Milling Council estimates that the country’s sugarcane industry produces 4.5 million tonnes of raw sugar, 1 million tonnes of molasses, and 10 million tonnes of bagasse annually. The Council also states that Australian sugar mills are self-sufficient by tapping energy from the combustion of bagasse. Moreover, in 2014, it was reported that more than half of the energy generated (500GWh) was a surplus, which was then exported to the national grid to reduce greenhouse gas (GHG) emissions. Currently, this practice has reduced Australia’s GHG emissions by 1.5 million tonnes annually.

Bagasse is traditionally considered as a waste material, but concerns about the adverse effects of fossil fuels on GHG emissions have led to the utilisation of bagasse as a biofuel. Ethanol can be biologically extracted from bagasse in co-generation power plants that generate energy with relatively low GHG emissions compared to coal power plants (Kikuchi et al., 2016). Alternatively, bagasse can be burned to generate thermal energy. Interestingly, the amount of CO₂ generated from combusting bagasse is reported to be lower than the intake of CO₂ by sugarcane plants during photosynthesis, hence making this process carbon neutral (Acreche and Valeiro, 2013). The residue from the combustion, Bagasse Ash (BA), contains high levels of silica and is found to be pozzolanic (de Soares et al., 2016), hence has been actively studied as a supplementary cementitious material for concrete (Moretti et al., 2016), clay masonry units (Kazmi et al., 2016), and geopolymers (Noor ul et al., 2016). BA forms a steady stream of wastes easily obtainable from sugarcane producing countries such as Brazil, India, Thailand and Australia (Bezerra and Ragauskas, 2016). In the future, this residue from combustion may potentially be used as a ground improvement binder (Shen et al., 2013a; Shen et al., 2013b), embankment material (Zhang et al., 2015), and material of tunnel structures (Wu et al., 2015).
2.4 Recycled Glass

RG is the by-product of crushing mixed color bottles and other glass products collected from both municipal and industrial waste streams (Wartman et al., 2004). Glass is an amorphous solid which consists largely of silica (SiO₂) (Wartman et al., 2004). It is widely used to make containers, beakers, and bottles to hold liquid, and as a construction material in building facades, doors and windows due to its transparent property which allows maximum sunlight into a building. Glass is a recyclable product which can be crushed, melted and then remoulded into various shapes and sizes (Zolfagharinia et al., 2016). However, unlike biodegradable wastes such as paper, the chemical constituents in glass are inert and hard to decompose. Hence, glass is gradually becoming problematic in landfills across the globe. Moreover, glass requires additional energy to be broken down and melted (Ling et al., 2013). Care should also be taken to segregate glass with other wastes as contamination results in deterioration in recycled glass quality (Ling et al., 2013). Glass recycling practices require large efforts in instilling public awareness and even in developed countries, recycling efforts may vary: glass recycling has been assimilated into the Japanese culture for the past few decades (Usui et al., 2015), as opposed to being a relatively young concept in the USA (Meyer, 2001). Currently large quantities of used glass are either landfilled or stockpiled for future use because current logistics and recasting technologies do not result in a profitable glass recycling process (Maraghechi et al., 2012).

In Australia, approximately 1 million tonnes of waste glass is collected annually (Arulrajah et al., 2013b). Crushed glass obtained from municipal and industrial sources in Australia are all considered a construction and demolition (C&D) waste (Arulrajah et al., 2013b) and can be reused as recycled glass (RG). Medium and fine sized RG particles were found to possess high shear strengths (Arulrajah et al., 2014a), and can be used as a recycled material in construction applications such as embankment fills (Disfani et al., 2011; Disfani et al., 2012), masonry units (Biglarijoo et al., 2017; Kou and Poon, 2013; Liang et al., 2015), and earth retaining structures (Grubb et al., 2007). Sand-sized RG can also be used independently as a fine aggregate, and has been previously bound with a fly ash geopolymer to produce masonry units with a recorded 3-days UCS of 12 MPa (Arulrajah et al., 2016a). Powdered RG were found to be good pozzolans which may be used to potentially replace cement (Federico and Chidiac, 2009; Matos and Joana, 2016).
because of a large total exposed surface which enables silica to be readily leached by alkaline solutions. However, the main concern with using RG as a supplementary cementing agent or construction material altogether, is the alkali-silica reaction (ASR) between the alkali found in concrete and alkaline activator liquids and the silica in RG. ASR is an expansive reaction which cracks concretes and reduces mortar durability, but using ground or pulverized RG significantly minimizes the occurrence of ASR (Jin et al., 2000). The magnitude of ASR was reported to vary according to glass colour (Du and Tan, 2013; Topçu et al., 2008), due to the different compounds which results in colouration. Green and amber glass cullet were reported to result in least expansion due to ASR (Corinaldesi et al., 2016).

On the other hand, other wastes related to glass manufacturing are also widely recycled. Post-consumer glassware can be ground, mixed with foaming agents, and heated to produce a porous foamed-glass which is light-weight and possesses significant load-bearing strength (Arulrajah et al., 2015b). Researchers are exploiting the lightweight and freeze-resistant properties (Laakso and Engi, 2005) of foamed-glass and applying the material in roles such as aggregates in road construction (Fotiadou et al., 2004). Foamed glass has good water absorption capabilities and can possibly be used as a substrate to promote plant growth (Eksi and Rowe, 2016). Silica fume, the by-product of silicon and silicon-alloy manufacturing, is a waste product associated with glass and is used as a supplementary cementing agent for concrete due to its high silica content (Bajja et al., 2017). It is the residue from quartz reduction in a submerged electric arc furnace. It is a fine powder comprising of 80-85% of silica (Sudin and Swamy, 2006), hence possesses high pozzolanic capabilities and is suitable for the construction industry. The CSH compounds produced by a PC and silica fume mix were reported to be denser than conventional PC concrete (Baroghel-Bouny et al., 1999).
2.5 Summary

Literature shows that the global community is gradually realising the need to change the contemporary way-of-life in favour of a sustainable alternative. Researchers from the construction industry have tirelessly sought alternatives to reduce the carbon footprint of conventional construction methods, particularly brought about by the manufacturing of concrete. Therefore, geopolymerisation, which produces the same cementitious compounds as PC but adds virtually zero carbon footprint, is a plausible substitute. Moreover, with dwindling natural resources becoming an issue, recycling C&D wastes and the utilisation of alternative construction materials have become a priority in the construction industry. With the disposal of wastes such as CG, FA, S, RHA, BA, and RG becoming a problem due to increasingly scarce landfill space, a solution which enables the reusing of these wastes would be welcoming. Geopolymerisation has been documented to encapsulate organic wastes such as biosolids and wastewater sludge, hence is a viable approach to stabilising CG, an organic waste, into a construction material with high compressive strength. Across the world, CG has been acknowledged as an increasingly significant waste which is giving rise to various collecting and reusing efforts. Therefore, it is conceptually viable to collect CG for large scale construction projects as factories and cafes get accustomed to segregating CG for further use whereas businesses handling the collection and transportation of CG are deemed innovative and welcoming. With the help of FA, S, RHA, and BA, which are wastes easily obtainable from their respective industries in Australia, a green reprocessed CG product may be produced entirely from waste materials. The successful implementation of recycled CG for construction would provide an alternative method to dispose of industrial and agricultural wastes. On the other hand, RG may be added to supplement CG with the necessary shear and bearing strength it requires to be considered a construction material.
CHAPTER 3

MATERIAL PREPARATION AND TEST METHODOLOGIES

3.1 Material Procurement and Preparation

The parent material used in this research was CG. CG was collected daily from cafes near the vicinity of Swinburne University of Technology, Melbourne, Australia. As CG is a waste material, the acquired CG, shown in Figure 3.1, is usually mixed with other wastes such as paper towel, milk bottle caps, and serviettes used by the café operators, which must be removed. After the undesirable wastes inside the CG were removed by hand, the remaining CG was placed in trays as shown in Figure 3.2 and oven-dried in a controlled environment of 50°C to ensure that the bulk of the material, which is organic, is not lost by ignition- it was proposed that the scorching, irreversible dehydration, and oxidation of organic compounds start at about 60°C (Arulrajah et al., 2014a; Terzaghi et al., 1996). The drying process requires up to 5 days mainly due to the high natural moisture content in CG, and the relatively low oven temperature used. In this context, the natural moisture content of CG is defined as the as-is moisture content of CG collected after the coffee brewing process.

As shown in Figure 3.3, large coagulations of CG are commonly observed because as part of the brewing process, ground coffee powder is always compacted into tablets in coffee machines. However, when fully dried, these lumps can be easily fragmented with light abrasion by hand, indicating no chemical bonding. This observation was supported by results obtained from the PSD analysis done on CG. Hence, before being used as test specimens, dried CG was passed through a 2-mm sieve to filter out coagulated CG particles and to maintain a controlled particle consistency. Dried CG was then packed in vinyl bags and sealed with zip lock ties to create an air-tight environment that prevents moisture absorption, as shown in Figure 3.4. This measure ensures that CG can be kept for extended periods within developing fungus and decomposing. Australia not grow coffee on a large agricultural scale. Imported coffee beans from all over the world are used to sustain the high rate of domestic consumption, hence a large diversity in coffee...
bean types are present (Kua et al., 2017). However, the engineering properties of CG are similar, regardless of origin (Arulrajah et al., 2014a).

Figure 3.1 CG collected daily from cafes in Melbourne, Australia.
Figure 3.2 A tray of cleaned CG ready for drying.

Figure 3.3 Tablets of CG resulting from coffee brewing.

Figure 3.4 Bags of dried CG in air-tight zip lock tie-seals.
Many stabilising agents were used to treat CG. These agents are characterised as fine-grained solid granules. Commercially available PC, hydrated Lime, FA and S were used in this research. RHA and BA sourced from rice and sugar mills in Queensland, Australia were used in this study.

The alkaline liquid activators used to facilitate geopolymerisation was a mixture of Sodium Silicate, $\text{Na}_2\text{SiO}_3$ and Sodium Hydroxide, NaOH. Commercially available D-grade $\text{Na}_2\text{SiO}_3$ composed of 44.1% silicic acid, sodium salt ($1.6<\text{Molar Ratio}\leq2.6$) and 55.9% water, and reagent grade NaOH with 97% purity were used.

### 3.2 Organic Content Test

As CG is an organic waste derived from the blending of coffee beans, it is important to determine the organic content in the CG collected. Moreover, as RHA and BA are ash derived from the burning of organic wastes, it is essential to ascertain the amount of unburnt organic matter in the material gathered.

The percentage of organic content in CG was determined in accordance with ASTM D2974-14: Standard Test Methods for Moisture, Ash and Organic Matter of Peat and other Organic soils (ASTM, 2014c). Using this method, CG was first air-dried at room temperature, 21°C. After the mass of the air-dried material was recorded, the same specimen was oven dried at 50°C for 16 hours and then measured for its remaining mass. Subsequently the specimen was ignited in a high-temperature furnace where the temperature was brought up to a maximum of 440°C for about 10 hours to ensure that the CG is completely reduced to ash. The material was then cooled in a desiccator and the final mass was recorded. The mass of material which was lost on ignition (LOI) was assumed to be the organic compounds present in CG.

RHA, and BA were also tested in accordance with ASTM D2974 to determine the percentage of unburnt organic compounds present in these geopolymeric precursors. **Figure 3.5** shows the furnace and crucible used to house the CG used for ignition and organic content testing.
3.3 pH Test

CG and the stabilising agents used in this research consists of fine, granular particles, hence the pH value of these materials can be determined in accordance to ASTM D4972-13: Standard Test Method for pH of Soils (ASTM, 2013). The pH value is a parameter useful in determining the mobility of ions in the granular materials, and important for the assessment of any potential environmental risks posed by the leaching of these materials.

In this research, a potentiometer, as shown in Figure 3.6, was used to measure the pH value of these granular solids. pH measurements were taken on suspensions consisting of the granular materials mixed with water. To minimise error, the electrode on the potentiometer was first washed with distilled water, and then calibrated with standard buffers of known pH 4.0, 7.0, and 10.0. After every reading, the electrode was rinsed with distilled water to avoid contamination of subsequent test suspensions and results. Triplicate suspensions were made from each granular solid material and tested for their
pH. This thesis reports the minimum and maximum readings from the triplicates as a range of possible pH for all materials tested.

![Electronic Potentiometer with an electrode rinsed in distilled water.](image)

Figure 3.6 Electronic Potentiometer with an electrode rinsed in distilled water.

3.4 Moisture Content Measurement

As this research deals with creating design mixes with specific ratios of solid and liquid material contents, it is important to: 1) check and determine the moisture contents of the raw material obtained; 2) ensure that the granular solids used for mixing is completely dry; 3) determine the moisture contents of the material mixes before compaction to ensure no excess moisture was lost during mixing, and 4) check the moisture lost after curing, so that the reported final design mix has minimal error.

ASTM D2216-98 (ASTM, 2006) was used as a guideline to measure the moisture content of the CG collected. A tray of CG with known mass was oven-dried for 24 hours and then recorded for its new mass. The process was repeated daily until there was no difference
between two consequent measurements. The mass lost is assumed to be evaporated water hence the moisture content can be calculated.

CG is mixed with stabilising agents and water or alkaline liquid to form the many design mixes in this research. Immediately after putting all the solids and liquids in the mixing bucket, the total mass of the mix was recorded. The total mass was then recorded again after mixing to check if excessive evaporation occurred during mixing. On the other hand, although the compacted specimens were wrapped in vinyl to prevent moisture lost during curing in 50°C, the mass of specimens was measured before and after curing to check for discrepancies caused by faulty wrappings.

Interestingly, CG is dark brown when wet, but as this material becomes drier the brown colouration becomes lighter. This comparison is made in Figure 3.7, and is a quick and simple visual indication of whether the CG is dry, apart from the standard moisture content test used in this research.

Figure 3.7 Difference in colouration occurs with CG at different moisture contents.
3.5 Particle Size Distribution Analyses

In soil mechanics, it is important to determine the particle size distribution (PSD) of any given soil to predict how they behave under compaction and how they respond to fluctuations in moisture content. Since the intended use of CG is as a soil replacement which needed to undergo compaction, the granular CG was tested for its PSD with reference to ASTM D442-63 (ASTM, 2007a).

As reported previously, the waste CG obtained were compacted into tablets during the coffee brewing process. The PSD analysis of CG consisted of the material being first oven-dried, and then broken up using a mortar with a rubber-covered (ASTM, 2002). The dried material was then passed through a sieve set as shown in Figure 3.8. As all the tested portion passed through Sieve No. 10 (with 2 mm apertures), it was decided to agitate and sieve subsequent collected CG to maintain a consistent PSD for the
experiments of this research. Interestingly ASTM D442-63 was withdrawn in 2016, in accordance to ASTM’s policy to update a standard at the end of its eighth year of issue, with no replacement currently. By referring to other existing standards for PSD analysis, namely the Australian AS 1141.11-1996 and British BS 410-1:2000, it was found that the only differences are slight variations in sieve aperture size.

The stabilisers and precursors used in this research were fine powdered material deemed too fine for the standard sieve analysis testing. Instead, these materials underwent an automated particle analysis process utilising a CILAS 1190 device as pictured in Figure 3.9. The powdered materials were mixed with distilled water and run through the laser beam scanner of the device. Three separate sets of suspension were prepared and scanned for each stabilising agent. Every time prior to the scanning of a new material, distilled water was run thought the machine and scanned by the device to detect (and remove, on subsequent scans) any possible background noise readings due to the presence of water.

![CILAS 1190 Particle Size Analyser](image)

**Figure 3.9** CILAS 1190 Particle Size Analyser.
3.6 Specific Gravity

The specific gravity (SG) of a material is needed as it represents the relative density of a material against pure water. In geotechnical engineering, it is a parameter which influences compaction characteristics and shear strength development in a soil matrix. As all the granular solids, CG, PC, Lime, FA, S, RHA, BA, and fine RG passes through the 4.75-mm sieve, it was possible to determine the SG of all specimens using a water pycnometer subjected to vibration, in accordance with ASTM854-14 (ASTM, 2014a). The pycnometers used were first calibrated to remove any possible errors caused by the ambient temperature of the geotechnical lab.

![Apparatus setup for SG test. With flasks containing BA in the foreground and a mechanical vibrator and vacuum pump in the background.](image)

**Figure 3.10** Apparatus setup for SG test. With flasks containing BA in the foreground and a mechanical vibrator and vacuum pump in the background.
Figure 3.10 shows the set-up of apparatus with the sealed flasks placed on a mechanical vibrator, and connected to a vacuum pump. The granular materials were mixed with distilled water and carefully inserted into the flask, which was then vibrated to release air bubbles trapped within the suspension. The vacuum pump was used to extract air bubbles trapped in the suspension. The final mass was measured after all air bubbles were removed, and compared to a standard mass in which the flask is filled with only distilled water.

3.7 Compaction Effort

Compaction was carried out on stabilised CG to simulate compacted soil used for roadworks. After thorough mixing with the stabilisers and designated liquid content, the mixes were compacted using a mechanical compactor in an iron mould measuring 101.6 mm in diameter and 116.4 mm in height, as shown in the configuration of Figure 3.11 (a). The compacted specimens were trimmed to ensure a level surface as shown in 3.11 (b). Modified compaction method in accordance with ASTM D1557-12 (ASTM, 2012b) was selected to offset the high compressibility of CG.

Figure 3.11 (a) Apparatus configuration during a proctor compaction test, and (b) a compacted and trimmed specimen.
The proctor compaction method was used to determine the optimum moisture and liquid contents the CG+Stabiliser mixes by introducing different amounts of liquid content and measuring the post-compaction material density. After acquiring the material densities corresponding with the arbitrary moisture contents, a static compaction method, described in the next section, was employed to produce UCS samples.

3.8 Unconfined Compressive Strength Test

![Figure 3.12 Mixing process of a CG+Stabiliser mix.](image)

CG+stabiliser mixes were compacted into cylindrical samples and left to cure for a standard duration of 7 days, in either an ambient room temperature of 21°C, or an elevated curing temperature of 50°C for some geopolymeric mixes. Some portion of the experiments even required curing durations up to 90 days. To prepare the design mixes, dried CG was mixed with the stabilising agents in a pail, as shown in Figure 3.12, until an observable consistency in colouration could be observed. Controlled amounts of water or liquid were then introduced into the mixture by weight. The material was then kneaded
until consistency in texture and colour was observed again. In cases of geopolymeric mixes, the mixing process after L was introduced was limited to 10 minutes and compaction was done immediately afterwards to prevent liquid evaporation and flocculation of the geopolymer.

UCS specimens were prepared by statically compressing the mixtures in a 50 mm diameter by 100 mm height split-mould with 1-layer compression as done by Sukmak et al. (2013a); Sukmak et al. (2013b), to achieve target densities corresponding with different water or liquid contents, obtained prior under modified Proctor compaction. Triplicate samples were produced for all material combinations to minimize error margins. The specimens were all wrapped in clear vinyl to prevent surface moisture loss by evaporation. Figure 3.13 illustrates the apparatus used to produce the UCS specimens and also the wrapped specimens before curing. Specimens designated to cure at room temperature were placed in the geotechnical laboratory which has a regulated temperature of 21°C, whereas specimens cured at 50°C were left in a temperature-regulated oven. A maximum temperature of 50°C was selected because it was the highest temperature recommended to process CG and other organic materials without charring the organic contents (Arulrajah et al., 2014b). Although this temperature is difficult to achieve in regions with a temperate climate, it provides information on the upper limit of UCS that CG geopolymer can achieve.

The static compaction process utilises a compression rate of 1 mm/minute to minimise pore pressure resistance and maximise particle realignment. UCS tests were similarly done using a compression rate of 1 mm/minute. The LoacTrac II device was fitted with an electronic displacement sensor to record linear material strain per second under compressive stress. Figure 3.14 shows a specimen after a completed UCS test. A metal plate was used to evenly distribute the stress on the cylinder. UCS tests were carried out with reference to D1633-00 (ASTM, 2007b), in which specimens were ensured to have a height-to-diameter ratio between 2 to 1.
Figure 3.13 Apparatus setup showing (a) the split mould used to produce UCS samples; (b) LoadTrac II used to statically compress the material mixes; (c) a compacted specimen before extrusion; and (d) specimens wrapped in vinyl ready for curing (Arulrajah, Kua et. al. 2016).
3.9 California Bearing Ratio Test

The CBR test compares the bearing capacity of a material relative to well-graded crush rock with a reference CBR value of 100%. Originally intended as a parameter for flexible pavement design, it is also widely used and applied for the design of rigid pavements and embankment fills (Head, 1994). The test utilises a piston to penetrate a cylindrical specimen compacted and confined in an iron mould measuring 152.4 mm in diameter and 116.4 mm in height. The amount of force needed to penetrate the specimen
to a depth of 2.54 and 5.08 mm was recorded and compared to the standard value, hence the CBR ratio. Plates weighing 4.5 kg were placed on top of the compacted specimens throughout the soaking period to simulate overlaying pavement loading. Linear swell or shrinkage of the CBR specimen during the soaking period was recorded using a dial gauge.

The CG+stabiliser mixes were tested for their California Bearing Ratio (CBR) values in accordance with ASTM D1883-07 (ASTM, 2014b), as the CBR value is one of the key criteria used by the local road authority to assess the suitability of an embankment fill or subgrade materials (Vicroads, 2013). These specimens were compacted using the

Figure 3.15 Measuring linear swell on a soaked CBR specimen.
modified Proctor compaction energy for CBR specimens, and immersed fully in water for 4 days immediately after compaction, to simulate worst-case scenarios where full inundation of pavements occur in the open world environment. Figure 3.15 shows a configuration in which a soaked CBR specimen has been drained and measured for its linear swell, and Figure 3.16 shows a specimen undergoing the penetration test on a LoadTrac II. 3 specimens were prepared for each material combination, with the final assigned CBR taken as the average of the 2 lowest CBR results out of the 3 specimens (ASTM, 2014b).
### 3.10 Repeated load Triaxial Test

Resilient modulus ($M_R$), is the ratio of applied deviator stress over resilient or recoverable strain of a material (Du et al., 2016). $M_R$ reflects the stiffness of a road subgrade material and directly influences the required overlying pavement thickness (Suku et al., 2016). Many road authorities, including the American Association of State Highways and Transportation Officials (AASHTO), and the Roads Corporation of Victoria, Australia (VicRoads) consider $M_R$ to be a key design parameter in their road design guides. Past studies have demonstrated the viability of utilizing geopolymers to enhance the $M_R$ of road base, sub-base (Arulrajah et al., 2016c), and subgrade (Du et al., 2014b) materials.

Resilient modulus was determined by Repeated Load Triaxial (RLT) tests, in accordance to AASHTO T307-99 (AASHTO, 2007). The RLT equipment simulates vehicle dynamic load on different segments of the underlying soil by applying a sequence of cyclic loadings on specimens under different confining pressures. The cylindrical specimens used in the RLT tests were prepared in a split mold that produces samples with a diameter of 100 mm and a height of 200 mm. Compaction was done by Modified Proctor compaction effort with a mechanical compactor in 5 layers in accordance to T307-99 (AASHTO, 2007). Specimens were wrapped in clear vinyl wraps to prevent moisture loss, and cured in a temperature-regulated oven for the desired duration. Figure 3.17 shows the specimen preparation process of a typical RLT test in which: (a) the material mix was compacted into a cylindrical mould; (b) the specimens were trimmed to level, extruded, and wrapped in clear vinyl to facilitated curing; (c) the RLT specimen was sleeved and mounted onto an air-tight pressure cell; and (d) the cell was mounted onto a frame which housed a pneumatic actuator.
A prominent problem that occurred during the preparation of RLT specimens was the high flocculation rate of S geopolymer mix. If the mix was left uncompacted for too long, flocculation creates coagulations which resists compaction. The heat generated by the S geopolymer also causes rapid evaporation and prevents compaction at optimum liquid content as the mix dries out. Figure 3.18 shows a specimen that had a top layer which is dryer. This layer had a lighter colouration, was less dense relative to the bottom layer, hence compromised the structural integrity of the whole specimen.
To minimise error, compaction is done immediately after the granular solid is mixed for 5-10 minutes with the alkaline activator. The 5-layer compaction was done continually with minimal gap time in between layers. The total material used was weighed before compaction and compared to the final specimen mass to ensure that the specimens were prepared at the target OLC without significant moisture loss during compaction. Specimens were tested at ±5% of the target liquid content. This was checked again by measuring the post-curing specimen mass and comparing it to the pre-curing specimen mass. A duplicate specimen was also prepared for each mix to undergo the Unconfined Compressive Strength (UCS) test separately. This was done to check any difference between the small standard UCS specimens and large RLT cylindrical specimens.

Figure 3.18 An RLT specimen with excessively dried top layer.
3.11 Environmental Assessment

A common concern once CG is embedded into the soil strata would be adjacent soil or groundwater contamination. Before CG can be deemed as a “green” recycled material, it must be tested to ensure that CG as a fill material is not hazardous towards consumers and the surrounding environment alike. Australia’s Environmental Protection Agency (EPA), for example, has set up thresholds for detectable heavy metals in waste materials and industrial backfill materials intended to be buried underground. There is also a limit to the heavy metal present in industrial soils allowed to be embedded underground. These benchmarks, summarised in Table 3.1, were used as a guideline to ensure that the heavy metals found in CG do not exceed the requirements to be used as an underground fill material.

On the other hand, other aspects of environmental protection should also be considered. CG can be considered a solid waste. As there is a possibility that the liquid leached from CG is hazardous, it should be compared to the EPA’s standards of potable drinking water. Materials with toxic metal concentration levels exceeding 100 times the potable water standard would be considered hazardous (EPA, 1999). If the leachable contaminants in CG exceeds any of these benchmarks summarised in Table 3.2, it may become hazardous and unusable.

Total concentration (TC) and leachate tests are useful to determine the amount of heavy metal in a substance. Australia has an established standard protocol (AS, 1997) for testing the chemical constituents of wastes and contaminated soils. This Australian Standard Leaching Process, or ASLP, includes leachate extraction done in pH neutral water, and separate leachate tests conducted using slightly acidic (pH= 5.0) and alkaline (pH= 9.2) leaching buffers. Solid waste samples, such as CG in this context, are mixed with the leaching buffers and placed on a rotator to be agitated. After 19 hours on the rotator, liquid is extracted from the samples to be tested for their chemical content. Leaching a material with acidic and alkaline solutions may simulate different chemical attacks compared to pH-neutral water, and are good emulators of extreme environmental scenarios where the materials are exposed to acidic rainfall or alkaline substances leached from road pavement layers.
Table 3.1 Leachable heavy metal benchmarks in various fill materials.

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Soil (mg/kg) (Rahman et al., 2014)</th>
<th>Waste Material (mg/kg) (EPA, 2009)</th>
<th>Backfill Material (mg/kg) (EPA(AU), 2007)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>0.1-40</td>
<td>500</td>
<td>20</td>
</tr>
<tr>
<td>Barium</td>
<td>100-3000</td>
<td>6250</td>
<td>-</td>
</tr>
<tr>
<td>Cadmium</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chromium</td>
<td>5-1500</td>
<td>500</td>
<td>1</td>
</tr>
<tr>
<td>Copper</td>
<td>2-60</td>
<td>5000</td>
<td>100</td>
</tr>
<tr>
<td>Lead</td>
<td>2-100</td>
<td>1500</td>
<td>-</td>
</tr>
<tr>
<td>Mercury</td>
<td>10-150</td>
<td>75</td>
<td>1</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.01-0.5</td>
<td>3000</td>
<td>60</td>
</tr>
<tr>
<td>Selenium</td>
<td>0.1-5</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>Vanadium</td>
<td>3-500</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zinc</td>
<td>25-200</td>
<td>35000</td>
<td>200</td>
</tr>
</tbody>
</table>

Table 3.2 Leachable heavy metals from solid wastes, hazardous wastes, and allowable levels in potable water.

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Solid inert waste Threshold (mg/L) (EPA, 2009)</th>
<th>Hazardous waste designation (mg/L) (Wartman et al., 2004)</th>
<th>Potable Water Standard (mg/L) (EPA, 1999)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>0.35</td>
<td>5</td>
<td>0.05</td>
</tr>
<tr>
<td>Barium</td>
<td>35</td>
<td>100</td>
<td>2</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.1</td>
<td>1</td>
<td>0.005</td>
</tr>
<tr>
<td>Chromium</td>
<td>2.5</td>
<td>5</td>
<td>0.1</td>
</tr>
<tr>
<td>Lead</td>
<td>0.5</td>
<td>5</td>
<td>0.015</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.05</td>
<td>0.2</td>
<td>0.002</td>
</tr>
<tr>
<td>Selenium</td>
<td>0.5</td>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td>Silver</td>
<td>5</td>
<td>5</td>
<td>0.05</td>
</tr>
</tbody>
</table>
The environmental study compares the results of leachate testing of CG, done previously in compliance to this standard, with environmental benchmarks set by Environmental Protection Agencies (EPAs) in both USA and Australia.

3.12 Scanning Electron Microscope Imaging and Energy-dispersive X-ray Spectroscopy

Small fragments, with diameters less than 10 mm, yielded from crushed UCS specimens were used for SEM imaging to observe the geopolymeric matrices in treated CG before and after curing. The fragments were dried for 24 hours in a 50°C temperature-regulated oven to remove moisture, and then coated in gold using an EMITECH K975X unit (Figure 3.19) before scanning commenced because the specimens were electrically non-conductive. Before the gold coating process, the specimens were lined on a piece of copper plate and fastened with carbon tapes to the plate (Figure 3.20) to maximise material conductivity as suggested by the equipment supervisor.

The SEM machined used was a Zeiss-SUPRA 40VP, as shown on Figure 3.21. The voltage of the electron gun used was 5kV. The observation of specimens usually require magnification magnitudes of 1000 - 3000 times, but throughout the research it was found that at 1000 - 1500 times magnification levels a larger area can be better observed to get a clear visualisation of what is developing on the geopolymeric matrices.

The SEM unit was also fitted with an INCA x-act energy-dispersive X-ray spectroscopy instrument shown in Figure 3.22 which enabled the scanning of the same UCS fragments to obtain the element composition in targeted areas. A gun voltage of 20 kV and working distance of 15 mm was required for the EDS operation to run smoothly. EDS results indicated that during spectrum processing, no peaks were omitted. An average of 5 iterations were done for each scan.
Figure 3.19 EMITECH K975X sputter coating machine.

Figure 3.20 Gold-coated CG fragments fastened onto a copper plate with carbon tapes.
Figure 3.21 SEM unit used in this research.

Figure 3.22 INCA x-act EDS instrument.
CHAPTER 4

APPLICATION OF ORTHODOX SOIL STABILISATION METHODS ON SPENT COFFEE GROUND

4.1 Overview

Spent Coffee Ground (CG) is an insoluble waste material obtained from coffee brewing. Due to the brewing process that immerses ground coffee beans in hot water, the insoluble CG residue typically registers high moisture contents of 90-150%, depending on the handling methods of individual café operators. CG has a brown colouration and consists of fine granules that resemble sand. The resemblance led to the conception of this research, which studies the suitability of using CG as a construction material.

Melbourne has a strongly established coffee culture (Frost et al., 2010) hence produces a steady stream of CG annually. Moreover, there are initiatives in Melbourne functioning to collect CG from across different cafes in Melbourne for recycling purposes. In 2016, one of such company, Reground, has claimed to recycle 15 tonnes of CG since its establishment in 2015. CG has been used as a domestic agricultural fertiliser and landfill leachate absorbent due to its high organic content. Nevertheless, a large portion of CG produced by commercial coffee brewers are still disposed in landfills as waste materials (Kua et al., 2016a). Due to the high organic content in CG, this material is highly compressible and possesses low shear strength (Arulrajah et al., 2014b) hence must be appropriately stabilised before qualifying as a construction material.

4.2 Material Characteristics of Spent Coffee Ground

The moisture content of CG was obtained in accordance with ASTM D2216-98 (ASTM, 2006), and varies from 90 to 150%. The moisture content of CG varies according to the machine pressure used during the thermal extraction process of the coffee liquid (Kua et al., 2016a). Incidentally, machine pressure varies with different models and operator skills, hence resulting in a wide range of moisture contents for the residual CG.
Grinder efficiency of coffee machines are responsible for the particle size for ground coffee beans and the resultant CG, but the averaged gradation curve obtained in accordance with ASTM D442-63 (ASTM, 2007a) from oven-dried CG, as presented in Figure 4.1, is highly similar to the results obtained by Arulrajah et.al. (Arulrajah et al., 2014b) in a previous study, hence leading to the deduction that the difference in particle size of CG across Melburnian cafes are negligible from an engineering perspective. With particles in the range of 0.075 to 2.36 mm in size, the CG resembles poorly-graded sand, but due to its high organic content it is classified as an organic clay (OH). The average specific gravity of CG, obtained in accordance with ASTM D854-14 (ASTM, 2014a) was 1.35. Comparatively, previous works done by Arulrajah et.al. (Arulrajah et al., 2014b) reported the average specific gravity of CG to be 1.36. This further ascertains that regardless of source, the particle size distribution and particle density of CG is largely similar. The specific gravity of CG is half of typical soils: the specific gravity of most soils fall within the range of 2.4 to 3.0, with an average value approximated at 2.65 due to high quartz content in typical soils (Karol, 2003). CG collected throughout Melbourne has a high organic content of 88% on average.

Figure 4.1 Comparison between the average PSD of CG used in this research and data obtained from Arulrajah et. al. (2014).
4.3 Stabilisation Methodology and Specimen Preparation

In contemporary engineering practices, weak soils are excavated, mixed with stabilising additives, and recompacted in-situ to produce stabilised strata that have increased compressive strengths. The typical reactions between soil, stabilising agent, and water are cation exchange, flocculation and agglomeration, cementitious hydration, and pozzolanic reaction. Portland Cement (PC) and Lime, which are two traditional stabilising agents (Akpokodje, 1985; Du et al., 2014a; Hagan, 1997), rely heavily on these hydration processes to form cementitious compounds, which in turn binds weak soil particles to form denser soil matrices. In the industry, the amount of PC and Lime used in soil stabilisation varies from 3-5% (Holland and Griffin, 1980). While PC and Lime are abundantly available and relatively cheap and efficient, the manufacturing of these agents incur large carbon footprints (Phetchuay et al., 2014). Environment-conscious engineers and researchers have since discovered that Fly ash (FA) and Slag (S), both technically waste products from coal combustion and iron refining processes respectively, can be utilised as soil stabilizing agents by replacing PC and Lime.

The conventional stabilisation of CG assumes that CG is a weak soil that requires reinforcement. Firstly, the established industrial stabilisation method of replacing 3% and 5% of CG, by mass, with PC and Lime was explored. Subsequently, FA and S were introduced to replace the mass of CG by 3%, 5%, 10%, 20%, 30%, 40%, and 50%. The rationale behind the high replacement ratio of FA and S relative to PC and Lime is that both the former materials are waste products whereas the latter two have to be purposefully manufactured. Dry CG was first mixed with the desired stabilising agent in buckets, for a duration of 5 minutes, to ensure homogeneity. Water was then added and the mix was further mixed for 5 minutes to maximise homogeneity. After mixing, the mix is weighed to ensure that moisture was not lost due to evaporation during the mixing process. The bucket was then covered to prevent evaporation. Subsequently the mix was deemed ready to be used in different geotechnical tests.
4.4 Stabilisation by Portland Cement and Lime

4.4.1 General Characteristics

Commercially available PC and Lime were used. Figure 4.2 shows the particle size distribution of PC and Lime relative to CG, obtained by laser particle diffraction analysis using a CILAS 1190 device. The median particle diameter ($D_{50}$), specific gravity, and pH values of PC and Lime are summarised in Table 4.1. PC and Lime particles were significantly finer than CG. While CG was found to be mildly acidic, both PC and Lime are basic. The specific gravity of PC was highest at 3.1, whereas the specific gravity of Lime was 2.2.

![Figure 4.2 Particle size distribution of PC, and Lime compared to CG.](image)

<table>
<thead>
<tr>
<th></th>
<th>CG</th>
<th>PC</th>
<th>Lime</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{50}$ (mm)</td>
<td>0.35</td>
<td>$3.4\times10^{-4}$</td>
<td>$3.3\times10^{-4}$</td>
</tr>
<tr>
<td>pH</td>
<td>5.1- 5.2</td>
<td>11.0- 13.0</td>
<td>12.0</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.35</td>
<td>3.1</td>
<td>2.2</td>
</tr>
</tbody>
</table>
4.4.2 Compaction Characteristics

Modified Proctor Compaction effort was used to compact the CG+stabiliser mix. Water was added incrementally to separate bucket of mixes to observe the influence of moisture on the maximum achievable dry density. **Figure 4.3** was obtained by plotting all data points of dry unit weight versus moisture content, regardless of stabiliser type and percentage. Interestingly a parabolic best fit curve was obtained. The curve indicates that maximum dry density (MDD) can be achieved at the optimum moisture content (OMC) of 130%. The MDD corresponding with 100CG, 97CG+3PC, 95CG+5PC, 97CG+3Lime, and 95CG+5Lime were 4.45 kN/m$^3$, 4.49 kN/m$^3$, 4.54 kN/m$^3$, 4.47 kN/m$^3$, and 4.52 kN/m$^3$ respectively. Given ASTM’s allowance for a ±0.1 kN/m$^3$ margin of error (ASTM, 2012b), the effect of stabiliser type and replacement ratio on the MDD of CG is insignificant at this level. Moreover, the OMC also remains unchanged at 130%. This values is consistent with the OMC of untreated CG (Arulrajah et al., 2014b).

**Figure 4.3** Dry unit weight vs. moisture content curves for CG+PC and CG+Lime (Kua et al., 2016a).
4.4.3 Unconfined Compressive Strength Development

The effectiveness of PC and Lime on stabilising CG was monitored by Unconfined Compressive Strength (UCS) tests done on specimens cured under different conditions. Cylindrical specimens prepared according to ASTM D1633-00 (ASTM, 2007b) at OMC were done with a $9.92 \times 10^{-4}$ m$^3$ mould under modified Proctor compaction effort, using a mechanical compactor. Despite being cohesionless, the compaction and extrusion of cylindrical CG specimens was possible. This occurrence was observed to be the result of suction and interlocking of the irregularly shaped CG particles, which is distinct from true cohesion. Apart from the difference in stabiliser type and percentage of stabiliser used, two independent sets of each mix were produced and cured for 7 days and 28 days. The specimens were cured in an enclosed tank with 90% relative humidity to prevent moisture loss via evaporation. The ambient temperature in the enclosed tank was constant at 21°C throughout the curing period.

![Figure 4.4](image-url) 7 and 28 days UCS of CG+PC and CG+L (Kua et al., 2016a).

UCS tests were done on the cured specimens using an electronic loading machine with a force-measuring sensor. The specimens were compressed with a constant displacement rate of 1 mm/minute until failure occurs. Figure 4.4 shows the UCS of PC and Lime stabilised specimens after 7 days and 28 days of curing, as compared to untreated CG
specimens compacted and left to cure in the same manner. Untreated CG exhibits slight
decline in UCS from 7 days to 28 days. At 7 days curing, increasing the amount of
additives positively affect UCS development. Lime specimens were found to perform
better, albeit just slightly, than PC specimens, possibly due to the instantaneous cation
exchange and flocculation and agglomeration reactions associated with calcium-rich
Lime (Abu-Farsakh et al., 2015). On the other hand. PC dominantly gains strength from
the cementitious hydration of calcium-silicates and calcium aluminates, a process that
requires extended curing durations (Abu-Farsakh et al., 2015). Consequently, PC
specimens develop higher UCSs compared to Lime specimens after 28 days.

Practically, in typical soil treatment situations, an addition of 3-5% of PC and Lime would
result in exponential UCS growth for weak clays (Patel and Patel, 2012), marine clays
(Yi et al., 2015), or even gravels (Barišić et al., 2014). However, in these instances, the
importance of soil-and-stabiliser interaction were crucial in producing cementitious
compounds to strengthen the newly mixed and compacted soil matrices. Due to the deficit
of minerals in CG, the stabiliser cannot react with CG efficiently hence the lack of
cementation (Kua et al., 2016a). Nevertheless, data drawn from Figure 4.4 shows that the
additives act as retardants towards the biodegradation of CG as they help to improve the
UCS of CG over time.

4.5 Stabilisation by Fly Ash and Slag

4.5.1 General Characteristics

The FA and S used in this research were sourced locally in Melbourne, Australia.
Figure 4.5 compares the particle size distribution of FA and S, scanned similarly on a
CILAS 1190 device, to that of CG. FA and S are also finer than CG in particle size, but
on average are larger than PC and Lime particles. Nevertheless, FA registered the lowest
specific gravity out of all the stabilisers used, whereas S registered a specific gravity of
3.0, just slightly lower than PC. From the summary in Table 4.2, FA is mildly basic
whereas S is moderately basic compared to PC and Lime.
Table 4.2 General Characteristics of CG, FA, and S

<table>
<thead>
<tr>
<th></th>
<th>CG</th>
<th>FA</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{50}$ (mm)</td>
<td>0.35</td>
<td>0.036</td>
<td>0.021</td>
</tr>
<tr>
<td>pH</td>
<td>5.1- 5.2</td>
<td>7.1- 8.0</td>
<td>9.0- 10.0</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.35</td>
<td>2.1</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Figure 4.5 Particle size distribution of FA, and S compared to CG (Kua et al., 2016a).
4.5.2 Compaction Characteristics

Unlike PC and Lime, FA and S were added in large quantities to replace CG by up to 50%, as both FA and S are waste materials similar to CG hence conforming to the concept of green recycled material. At 3-5% replacement ratio, CG+FA and CG+S specimens behave similarly to the aforementioned PC and Lime specimens: as seen in Figure 4.6, the presence of the additives up to 5% do not significantly alter the OMC of CG. Respectively, the MDD corresponding with 97CG+3FA, 95CG+5FA, 97CG+3S, and 95CG+5S were 4.49 kN/m$^3$, 4.53 kN/m$^3$, 4.53 kN/m$^3$, and 4.55 kN/m$^3$.

![Figure 4.6: Dry unit weight vs. moisture content curves for CG+FA and CG+S (Kua et al., 2016a).](image)

However, as seen in Figure 4.7, as the percentage of FA and S were increased beyond 10%, the OMC of these newly formed CG mixes start to decrease. Essentially, increasing both FA and S by 10% intervals also resulted in approximately a 0.5 kN/m$^3$ increase in dry unit weight. This relationship is proportionate throughout 10-50% of additive content. The increase in MDD can be simply attributed to the FA and S particles that are finer but denser than CG. At contents greater than 10%, they significantly act as fillers for the inter-particle voids within the compacted CG mix. The highest recorded dry unit weight for
both FA and S mixes occurs at the additive content of 50% and 7.18 kN/m$^3$ for FA and 7.83 kN/m$^3$ for S. Nonetheless, even at 50% stabiliser content, these mixes still registered relatively low MDD compared to many naturally occurring soils reconstituted under Standard Proctor Compaction effort (from 13-22 kN/m$^3$) (Horpibulsuk et al., 2009), hence the potential to be utilised as a lightweight material.

Figure 4.7 Dry unit weight vs. moisture content curves for (a) CG+FA and (b) CG+S.

(Kua et al., 2016a)
4.5.3 Unconfined Compressive Strength Development

The addition of FA and S also improves the strength of CG after a sustained period of curing. As shown in Figure 4.8, at 7 days, CG+S specimens generally outperformed FA specimens. However, the increase in strength relative to untreated CG is minimal. While the more the additive content, the higher the UCS, the highest registered UCS at 7 days is by 50CG+50S at 52.1 kPa, which is only a 30 kPa increase from the 7 days UCS of untreated CG. Again this is highly likely due to the absence of minerals in CG which deters bonding between additive and parent material. The higher UCS recorded by CG+S specimens at 7 days were due to the class-F FA used in this research which possesses little self-cementing capabilities due to the absences of lime, whereas S undergoes a hydration process similar to PC and L due to its high calcium oxide content (Kua et al., 2016a). Given a prolonged curing period, the constituents in FA gradually react with the moisture in the mix hence the increase in UCS at 28 days. Still the increase in UCS is very small considering the large (up to 50%) additive content. Because of the inert CG, a large portion of strength increase of these specimens may be attributed to the increase in MDD as additive contents increases, which led to higher degrees of compaction and stronger inter-particle friction (Kua et al., 2016a).

![Figure 4.8 7 and 28 days UCS of CG+FA and CG+S (Kua et al., 2016a).](image-url)
4.6 Summary

CG is an organic waste from the food and beverage industry, which is destined for landfill. By stabilizing CG with industrial by-products using simple hydration, the following findings were obtained:

1) The MDD of unstabilised CG was unaffected when additives were added from 3-5%. When additives replacing CG exceeded 10%, a trend in which the higher the additive content the higher the MDD can be observed. Increasing the additive content also lowered the OMC of each mixes.

2) The presence of additives, namely PC, Lime, FA, and S enhances the UCS of CG, albeit just slightly. Additives were found to increase the UCS of CG after 28 days of curing. Due to the lack of mineral compounds in CG, conventional soil-stabilisation methods are not very effective towards increasing the compressive strength of CG. An alternative binding method can be explored.

Nevertheless, this research demonstrated that instead of disposing CG to increasingly scarce landfills, there is a potential to divert CG together with other industrial wastes such as FA and S to construction sites as fill materials, as these industrial wastes have been demonstrated to enhance the strength of CG. Alternative stabilisation methods may be employed to increase the efficiency of FA or S-stabilised CG until relevant strength benchmarks are met.
CHAPTER 5

APPLICATION OF GEOPOLYMERISATION ON SPENT COFFEE GROUND

5.1 Overview

The strength improvement of simply hydrated CG-stabiliser mixes proved to be small relative to the additive contents. Moreover, conventional soil-stabilisers, namely PC and Lime, are manufactured purposefully, and the process results in a large carbon footprint (Sukmak et al., 2013a). Therefore, it is desirable to seek an alternative stabilizing method to create a green material with low negative environmental impact. Geopolymerisation is a chemical bonding process, which uses highly alkaline solutions such as NaOH to dissolve aluminosilicate-rich materials to form polymers of alumina and silica. While creating a cementitious compound similar to Portland cement, the geopolymerisation process, comprising an inorganic polymeric material, leaves almost no carbon footprint compared to Portland cement (Turner and Collins, 2013). Geopolymerisation has been found to greatly improve the unconfined compressive strength of unfavourable geo-materials (Phetchuay et al., 2014; Sukmak et al., 2013a).

FA and S, both rich in alumina and silica, are commonly used as the precursors for geopolymerisation (Albitar et al., 2015; Castel and Foster, 2015). Researchers have also experimented with other aluminosilicate-rich materials including the clay mineral metakaolin (Clausi et al., 2016) and calcium-carbide residue, the by-product of acetylene gas production (Phetchuay et al., 2014). In addition, the studies on geopolymeric precursors are not confined to construction and industrial wastes: ashes derived from the combustion of agricultural wastes, for instance rice husk and sugarcane, were found to contain high percentages of silica, thus have been studied as geopolymeric precursors (Cordeiro et al., 2016; Mejia et al., 2016).
5.2 General Specimen Handling

The two main components involved in this study were the granular solids and liquid alkaline activators (L). The granular solids can further be distinguished into two components, namely the parent material, CG, and the geopolymeric Precursor (P), which reacts with L to form geopolymers. The P considered in this research were the industrial wastes FA and S, as well as the agricultural wastes Rice Husk Ash (RHA) and Bagasse Ash (BA). In general, the granular solids are first mixed in a pail until an observable consistency in colouration could be observed. Controlled amounts of L were then introduced into the mixture by weight. The material was then kneaded until consistency in texture and colour was observed again. The mixing process after L introduced was limited to 5 minutes and specimen preparation was done immediately afterwards to prevent liquid evaporation and hardening of the geopolymer (Kua et al., 2016b).

In the granular solid mix, CG generally comprised of 70% of the total dry mass, while the remaining 30% comprised of P, as literature reviews have suggested that a 30% precursor content was found to be efficient in waste treatment sludge (Horpibulsuk et al., 2015; Suksiripattanapong et al., 2015b), which is another organic material, and silty clays (Sukmak et al., 2013a; Sukmak et al., 2013b). The CG-Precursor mixes were compacted, subjected to different curing conditions, and then tested for their UCS to observe the influence of material composition and external curing conditions on the strength development of CG geopolymers. Specific preparation methods exclusive to each precursor material studied are further described in their respective chapters.

Locally available CG was obtained, processed, and stored similarly using the procedures described in Section 4.2. Commercially available Class-F FA and S, procured locally in Melbourne, Australia, were used. RHA and BA were sourced from rice and cane-sugar milling plants in Queensland, Australia. Commercially available reagent grade NaOH with 97% purity and D-grade Na$_2$SiO$_3$ composed of 44.1% silicic acid, sodium salt (1.6<Molar Ratio≤2.6) and 55.9% water were used as the liquid alkaline activators in this research.
5.3 Stabilisation by Fly Ash

5.3.1 Testing Plan

The experiments for this section consisted of 2 stages. In the 1st stage, a CG-FA mix was produced with the FA content fixed at 30% relative to the dry weight of CG. The L used to induce geopolymerisation was a NaOH+Na$_2$SiO$_3$ solution. Three ratios of Na$_2$SiO$_3$:NaOH, at 90:10, 70:30, and 50:50 by weight, respectively, were used in the CG-FA mixes. The concentration of NaOH was also initially fixed at 8 moles. The L solution was introduced into the CG-FA mixture at different percentages relative to the dry weight of the CG and FA. The optimum liquid activator content (OLC) of specimens produced at different activator L/FA ratios, under modified Proctor compaction effort according to ASTM (2012b), was determined. After the OLCs were obtained, UCS specimens were produced by varying the L contents from both the dry and wet side of the OLC. Triplicate specimens were produced for each mix by 1-layer static compression in a 50 mm diameter by 100 mm height split-mould to reach the target dry density previously obtained from the modified Proctor compaction method. This 1-layer static compression was previously performed on geopolymer stabilised soils (Sukmak et al., 2014; Sukmak et al., 2013a; Sukmak et al., 2013b; Suksiripattanapong et al., 2015b). The specimens were wrapped and sealed in transparent vinyl wraps to prevent moisture lost, and cured in temperature-regulated ovens.

In the 2nd stage, the Na$_2$SiO$_3$:NaOH ratio was fixed at 90:10 and the L/FA ratio at 1.8 to test the remaining variables under the following conditions: 1) The FA content was varied from 10%-30% relative to the dry weight of CG, with NaOH concentration fixed at 8 mol and curing temperature fixed at 50°C; 2) NaOH concentration was varied at 5, 8, 10, 12, and 15 mol, with FA content fixed at 30%; and lastly 3) Curing temperature was varied at 21°C (room temperature), 40°C (summer temperature), and 50°C (maximum workable temperature without burning and deforming the CG particles), with FA content fixed at 30% and NaOH concentration fixed at 8 mol.

All specimens in the 2nd stage were cured for a 7-day period. The Na$_2$SiO$_3$:NaOH ratio of at 90:10 was selected to assess the maximum achievable strength development when NaOH content is at a minimum. Emphasis was put on observing the effects of FA
replacement ratio, NaOH concentration, and curing temperature variations on the specimens. Table 5.1 summarises the different specimens generated for this research, with details regarding the fixed and modified parameters in each different mix.

Table 5.1 UCS Testing Programme Summary (Arulrajah, Kua et al., 2016).

<table>
<thead>
<tr>
<th>Stage</th>
<th>Modified Variable</th>
<th>CG:FA</th>
<th>Na₂SiO₃:NaOH &amp; L content</th>
<th>L/FA</th>
<th>NaOH Molarity (mol)</th>
<th>Curing Temperature (°C)</th>
<th>Curing Time (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na₂SiO₃:NaOH &amp; L content</td>
<td>70:30</td>
<td>90:10</td>
<td>1.5, 1.8, 2.2, 2.6</td>
<td>8</td>
<td>50</td>
<td>7, 28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70:30</td>
<td>70:30</td>
<td>1.2, 1.5, 1.8, 2.1</td>
<td>8</td>
<td>50</td>
<td>7, 28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70:30</td>
<td>50:50</td>
<td>1.2, 1.5, 1.8, 2.1</td>
<td>8</td>
<td>50</td>
<td>7, 28</td>
</tr>
<tr>
<td>2</td>
<td>FA Replacement Ratio</td>
<td>90:10, 85:15, 80:20, 75:25, 70:30</td>
<td>90:10</td>
<td>1.8</td>
<td>8</td>
<td>50</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>NaOH Concentration</td>
<td>70:30</td>
<td>90:10</td>
<td>1.8</td>
<td>5, 8, 10, 12, 15</td>
<td>50</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Curing Temperature</td>
<td>70:30</td>
<td>90:10</td>
<td>1.8</td>
<td>8</td>
<td>21, 40, 50</td>
<td>7</td>
</tr>
</tbody>
</table>

5.3.2 General and Compaction Characteristics

The compaction curves presented in Figure 5.2 indicate that the CG-FA mix is generally insensitive towards the change in L content from 0% to 60%. Within this range of L variation, the difference in dry density for each combination of mixes does not exceed 0.5 kN/m³. From Figure 5.2, the 50:50 Na₂SiO₃:NaOH ratio specimens achieved the highest maximum dry density (MDD) (8.6 kN/m³) relative to specimens compacted with the other ratios of Na₂SiO₃:NaOH (8.5kN/m³). However, ASTM (2012b) allows a measurement error of approximately ±0.1 kN/m³ hence making the difference barely significant. The MDD of CG-FA geopolymers is 8.6 kN/m³, which is almost two times higher than that
of unstabilised CG, which has an MDD of 4.4 kN/m³ (Arulrajah et al., 2014b). The MDD for CG-FA geopolymer is similar to the MDD of highly organic biosolids (8 kN/m³), which has been successfully studied in embankment fill applications (Arulrajah et al., 2013a). However, compared to many natural soils (Horpibulsuk et al., 2008; Horpibulsuk et al., 2009), the MDD of these new geopolymers are still very low. As L content of the CG-FA mix approaches 0%, the MDD of the 90:10 mix increases, resulting in a sinusoidal compaction curve. This can be related to a property observable in compaction curves for typical sands (Rollings and Rollings, 1996), where MDD typically occurs when moisture in the soil is close to 0%. This “bulking” behaviour may naturally occur in CG, but assigning an optimum liquid content of 0% to achieve MDD for this material would be meaningless because the activator liquid, Na₂SiO₃:NaOH, is needed to form the geopolymer.

Figure 5.1 and Figure 5.2 show the maximum dry density of the 70% CG + 30% FA mixes under the presence of the Na₂SiO₃:NaOH solution. In the case of Figure 5.1, activator liquid content is defined as the percentage of aqueous Na₂SiO₃:NaOH solution relative to the dry weight of the CG-FA mix. In Figure 5.2, the amount of pure water in the material was measured, while the dry density takes into account the solid Na₂SiO₃:NaOH trapped within the mix after all the water is evaporated. From Figure 5.2, all three mixtures exhibit a similar achievable MDD (10.5 kN/m³), but as the percentage of NaOH increases in the liquid alkali activator mix, moisture content in the mix where MDD is achieved increases as well, indicating the presence of high water content in the aqueous NaOH solution. Drawing conclusion from Figure 5.1, the OLC of all three L mixes was determined to be at 52% activator liquid content.

Table 5.2 compares the inorganic compounds found in CG and FA, obtained via X-Ray Fluorescence (XRF) tests. The results show that Al₂O₃ and SiO₂ in FA exceeds 70% hence it was a low-calcium Class F fly ash according to ASTM C618-12a (ASTM, 2012a).
Figure 5.1 Dry density vs. liquid alkali activator content for various Na$_2$SiO$_3$:NaOH ratios (Arulrajah, Kua et al., 2016).

Figure 5.2 Dry density vs. moisture content for various Na$_2$SiO$_3$:NaOH ratios (Arulrajah, Kua et al., 2016).
Table 5.2 Chemical composition of CG and FA by XRF analysis (Kua et. al. 2017).

<table>
<thead>
<tr>
<th>Chemical Composition (%)</th>
<th>CG</th>
<th>FA</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>N.D.</td>
<td>75.45</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>N.D.</td>
<td>12.01</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.61</td>
<td>3.96</td>
</tr>
<tr>
<td>CaO</td>
<td>33.99</td>
<td>2.72</td>
</tr>
<tr>
<td>MgO</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>SO₃</td>
<td>N.D.</td>
<td>0.78</td>
</tr>
<tr>
<td>K₂O</td>
<td>43.1</td>
<td>2.97</td>
</tr>
<tr>
<td>TiO₂</td>
<td>16.5</td>
<td>N.D.</td>
</tr>
</tbody>
</table>

Remark: N.D. = Not detected

5.3.3 Unconfined Compressive Strength Development

Initially, it was hypothesised that CG-geopolymers follow the trend in which maximum material compaction results in maximum UCS. To ensure that a curve with maximum value can be obtained for all 3 L mixes during UCS testing, L/FA ratios from both the dry and wet sides of the OLC pinpointed in Section 5.3.2 were selected for UCS testing, hence the 1.2, 1.5, 1.8, 2.1 ratios used for 70:30 and 50:50 specimens. As the ultimate goal is to obtain maximum strength, the L/FA ratio for 90:10 was adjusted more to the wet side to incorporate ratios of 1.5, 1.8, 2.2, and 2.6 to offset the hypothesised weaker geopolymer (relative to the 70:30 and 50:50 specimens) produced at low NaOH contents.

Table 5.3 shows the average achieved MDD and UCS values of the triplicate specimens tested in the 1st stage. The percentage in strength increase from 7 days of curing to 28 days of curing is also included for comparison.
Table 5.3 Strength Development in 7-Days and 28-Days cured specimens (Arulrajah, Kua et al., 2016).

<table>
<thead>
<tr>
<th>Na$_2$SiO$_3$:NaOH</th>
<th>L/FA</th>
<th>7 Days Curing</th>
<th>28 Days Curing</th>
<th>Strength Increase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\gamma_{dry max}$ (kN/m$^3$)</td>
<td>UCS (kPa)</td>
<td>$\gamma_{dry max}$ (kN/m$^3$)</td>
</tr>
<tr>
<td>90:10</td>
<td>1.5</td>
<td>7.98</td>
<td>353.2</td>
<td>7.96</td>
</tr>
<tr>
<td></td>
<td>1.8</td>
<td>8.01</td>
<td>658.5</td>
<td>8.13</td>
</tr>
<tr>
<td></td>
<td>2.2</td>
<td>7.81</td>
<td>1160.5</td>
<td>7.95</td>
</tr>
<tr>
<td></td>
<td>2.6</td>
<td>7.41</td>
<td>1091.9</td>
<td>7.78</td>
</tr>
<tr>
<td>70:30</td>
<td>1.2</td>
<td>7.79</td>
<td>368.7</td>
<td>8.07</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>8.08</td>
<td>633.3</td>
<td>8.13</td>
</tr>
<tr>
<td></td>
<td>1.8</td>
<td>8.26</td>
<td>779.3</td>
<td>8.35</td>
</tr>
<tr>
<td></td>
<td>2.1</td>
<td>7.95</td>
<td>679.9</td>
<td>8.07</td>
</tr>
<tr>
<td>50:50</td>
<td>1.2</td>
<td>7.92</td>
<td>354.2</td>
<td>8.27</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>8.28</td>
<td>650.1</td>
<td>8.45</td>
</tr>
<tr>
<td></td>
<td>1.8</td>
<td>8.10</td>
<td>956.3</td>
<td>8.43</td>
</tr>
<tr>
<td></td>
<td>2.1</td>
<td>7.95</td>
<td>821.8</td>
<td>7.93</td>
</tr>
</tbody>
</table>

The UCS values of geopolymer specimens with 30% FA cured at 50°C after 7 and 28 days are presented in Figures 5 and 6, respectively. By analysing Figure 5.3, it is of interest that the maximum 7 days UCS is found at L/FA ratio of 1.8 for Na$_2$SiO$_3$:NaOH ratios of 70:30 and 50:50 while it found at found at L/FA of 2.3 for Na$_2$SiO$_3$:NaOH ratios of 90:10. In other words, the maximum 7 days UCS for 70:30 is achievable at MDD but found on the wet side of the optimum L/FA content for 50:50 and 90:10. In practice, compaction is not always, but preferably undertaken at MDD, which is the workable state. By observing and comparing the points at the L/FA ratio of 1.8 (where the MDD for 90:10 and 70:30 was achieved), the effects of curing time on different mixes are evident. In the short term, mixes with a 50% Na$_2$SiO$_3$: 50% NaOH content result in the highest strength at L/FA = 1.8. A higher NaOH content results in a higher instantaneous reaction with the FA in the mix, hence a higher initial strength.
**Figure 5.3** 7 days UCS versus liquid content for various Na$_2$SiO$_3$:NaOH ratios (Arulrajah, Kua et al., 2016).

**Figure 5.4** 28 days UCS vs. liquid content for various Na$_2$SiO$_3$:NaOH ratios (Arulrajah, Kua et al., 2016).
For a long curing time of 28 days as shown Figure 5.4, the maximum UCS for 70:30 occurs at L/FA = 1.8, while 50:50 achieved maximum UCS at L/FA = 1.5. In the case of 90:10, a decrease in gradient starts to develop in the graph beyond L/FA = 1.8, indicating a saturation point. By comparing data obtained from both Figure 5.3 and 5.4, in scenarios where the least amount of chemical is required to provide the highest short-term strength, the 50% Na$_2$SiO$_3$:50% NaOH mix at a L/FA ratio of 1.8 would provide the most economic and efficient solution. It provides the highest UCS at early curing time (7 days) at 956.3 kPa. Albeit achieving the lowest UCS (1237.8 kPa) when compared to 90:10 (1332.5 kPa) and 70:30 (1281.2 kPa) at the same point of L/FA = 1.8 after 28 days of curing, the difference in value is less than 100 kPa.

By fixing 90% Na$_2$SiO$_3$:10% NaOH, L/FA of 1.8, and a 7-day curing period, the effects of various FA contents, NaOH concentrations, and curing temperatures were further studied. Figure 5.5 indicates that at a fixed curing temperature of 50°C, the higher the FA content, the higher the UCS of the specimens. Evidently, increasing FA content in the alkaline mix would increase dissolved silica and alumina to react with Na$_2$SiO$_3$, consequently strengthening the geopolymerisation products (sodium aluminosilicate hydrate) of the resulting geopolymer. However, at 25% FA content, the gradient of the curve decreases, indicating that the reaction is entering an inert zone.

Figure 5.6 illustrates that at a fixed FA content of 30% and curing temperature of 50°C, the UCS increases as the molarity of NaOH used in the mix is increased. The higher molarity can dissolve more silica and alumina from FA to react with Na$_2$SiO$_3$ and results in higher geopolymerisation products. The suitable NaOH molarity is between 8 mol to 12 mol where the small increase in molarity results in the significant increase in the UCS. Figure 5.7 illustrates that varying the curing temperature from room temperature to 40°C significantly increases the UCS, but from 40°C to 50°C the increase in UCS is relatively small. The increase in UCS is because the geopolymerisation reaction is accelerated by heat curing.
Figure 5.5 7 days UCS vs. FA replacement ratio, with 8mol NaOH, and 50°C curing (Arulrajah, Kua et al., 2016).

Figure 5.6 7 days UCS vs. NaOH molarity, with 30% FA replacement, and 50°C curing (Arulrajah, Kua et al., 2016).
Untreated CG is an organic material and subject to biodegradation. However, in this research, it is stabilised with the usage of FA as a precursor and with alkali activators. This approach will bind the organics within the geopolymer paste, thus rendering it as a non-biodegradable material. The strength development from the UCS tests demonstrates the binding properties of the CG-FA geopolymer. The $\text{Na}_2\text{SiO}_3:\text{NaOH}$ ratio of 50:50 is recommended as it provides the highest early UCS. Furthermore, construction of embankments utilising the CG-FA geopolymer should ideally be conducted in the summer seasons of temperate and tropical regions, when surface temperature can reach up to 40°C as the geopolymerisation reaction is accelerated at high temperature (Arulrajah, Kua et al., 2016). Stage 2 of the testings shows that there are other factors affecting strength development in this CG-FA geopolymer apart from $\text{Na}_2\text{SiO}_3:\text{NaOH}$ ratio, activator liquid content, and curing period. Fly ash content, curing temperature, and NaOH concentration all influence strength development in this CG-FA geopolymer. However, a saturation point exists where further increase in these parameters would yield little increase in geopolymer strength development.
5.4 Stabilisation by Ground Granulated Blast Furnace Slag

5.4.1 Testing Plan

Three ratios of \( \text{Na}_2\text{SiO}_3: \text{NaOH} \) - 90:10, 70:30, and 50:50 by weight, were used to produce three different L mixes used in this study. Palomo et al. (Palomo et al., 1999) experimented successfully with NaOH molarities from 8-12 M to produce geopolymers, hence the minimum value of 8 M was adopted for use in this study.

Dried CG was mixed with the precursor material (S or FA) in a pail until an observable consistency in colouration could be observed. Controlled amounts of L were then introduced into the mixture by weight. The material was then kneaded until consistency in texture and colour was observed again. The mixing process after L was introduced was limited to 5 minutes and compaction was done immediately afterwards to prevent liquid evaporation and hardening of the geopolymer. A wide range of L content from 30%-80% was introduced into the mix to pinpoint the optimum liquid content (OLC) of all material combinations under modified Proctor compaction effort according to ASTM D1557-12 (ASTM, 2012b). Subsequently, cylindrical UCS specimens were produced with L contents from both the dry and wet sides of the OLC.

UCS specimens were prepared by statically compressing the mixtures in a 50 mm diameter by 100 mm height split-mould with 1-layer compression as done previously, to achieve corresponding dry densities obtained prior under modified Proctor compaction. Triplicate samples were produced for all material combinations to minimize error margins. The specimens were all wrapped in clear vinyl to prevent surface moisture loss by evaporation. Specimens designated to cure at 50°C were left in a temperature-regulated oven. After the UCS results for these specimens were obtained, specimens from two different CG:S:FA ratios were replicated again and cured at room temperature (21°C) to study the effect of lower curing temperature on strength development. A maximum temperature of 50°C was selected because it was the highest temperature recommended to process CG and other organic materials without charring the organic contents (Arulrajah et al., 2014b). Although this temperature is difficult to achieve in regions with a temperate climate, it provides information on the upper limit of UCS that CG geopolymer can achieve. The maximum curing time studied was up to 28 days.
Table 5.4 Summary of CG geopolymer testing program (Kua et al., 2016).

<table>
<thead>
<tr>
<th>Test Type</th>
<th>CG:S:FA</th>
<th>Na$_2$SiO$_3$:NaOH Liquid Content (%)</th>
<th>Curing Temperature (°C)</th>
<th>Curing Time (Days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compaction</td>
<td>70:30:0</td>
<td>90:10, 70:30, 50:50</td>
<td>30-80</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>70:20:10</td>
<td>90:10, 70:30, 50:50</td>
<td>30-80</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>70:15:15</td>
<td>90:10, 70:30, 50:50</td>
<td>30-80</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>70:10:20</td>
<td>90:10, 70:30, 50:50</td>
<td>45-75</td>
<td>-</td>
</tr>
<tr>
<td>UCS</td>
<td>70:30:0</td>
<td>90:10, 70:30, 50:50</td>
<td>45-75</td>
<td>21 7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50 7, 28</td>
</tr>
<tr>
<td></td>
<td>70:20:10</td>
<td>90:10, 70:30, 50:50</td>
<td>45-75</td>
<td>50 7, 28</td>
</tr>
<tr>
<td></td>
<td>70:15:15</td>
<td>90:10, 70:30, 50:50</td>
<td>45-75</td>
<td>21 7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50 7, 28</td>
</tr>
<tr>
<td></td>
<td>70:10:20</td>
<td>90:10, 70:30, 50:50</td>
<td>45-75</td>
<td>50 7, 28</td>
</tr>
</tbody>
</table>

The CG:S:FA ratios used in this study were 70:30:0, 70:20:10, 70:15:15, and 70:10:20. Concurrently with three different ratios of Na$_2$SiO$_3$:NaOH, a total of 12 different material combinations were used. A mix of both S and FA was implemented on the basis that studies have indicated that S essentially increases the strength of FA geopolymers (Kumar et al., 2010; Rashad, 2013). Consequently, the UCS results obtained in this section were also compared with those obtained in Section 5.3. Table 5.4 summarizes the combination of mixes, and other controlled factors such as curing time and temperature used in this study.
5.4.2 General and Compaction Characteristics

Figure 5.8 shows the morphology of CG, FA, and S particles as determined via Scanning Electron Microscope (SEM) imaging. CG particles in Figure 5.8(a) are irregularly shaped, have jagged edges, and are highly porous. Figure 5.8(b) and Figure 5.8(c) on the other hand present the morphology of FA and S respectively. FA particles are smooth and spherical, while S particles also have smooth surfaces but are polygon-shaped. Table 5.5 compares the inorganic chemical composition of CG, FA, and S, obtained via XRF analysis.

Figure 5.8 SEM images of: (a) CG, (b) FA, and (c) S (Kua et. al., 2016).
Table 5.5 Chemical composition of CG, FA, and S by XRF analysis (Kua et al., 2017).

<table>
<thead>
<tr>
<th>Chemical Composition (%)</th>
<th>CG</th>
<th>FA</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>N.D.</td>
<td>75.45</td>
<td>35.21</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>N.D.</td>
<td>12.01</td>
<td>13.09</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>3.61</td>
<td>3.96</td>
<td>0.45</td>
</tr>
<tr>
<td>CaO</td>
<td>33.99</td>
<td>2.72</td>
<td>43.55</td>
</tr>
<tr>
<td>MgO</td>
<td>N.D.</td>
<td>N.D.</td>
<td>5.93</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>N.D.</td>
<td>0.78</td>
<td>0.85</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>43.1</td>
<td>2.97</td>
<td>0.92</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>16.5</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
</tbody>
</table>

Remark: N.D. = Not detected

Figure 5.9 presents the compaction curves of the CG:S:FA mixes under different L contents. For the Na$_2$SiO$_3$:NaOH ratio of 70:30 and 50:50, maximum dry unit weight ($\gamma_{d_{\text{max}}}$) is obtained at L= 55% while at the ratio 90:10, $\gamma_{d_{\text{max}}}$ occurs at L= 60%. As the ratio of S decreases (replaced by FA), the achievable dry unit weight ($\gamma_d$) of the specimens decreases, because the specific gravity of S is higher than that of FA. Figure 5.10 demonstrates that at fixed ratios of CG:S:FA, the higher the amount of Na$_2$SiO$_3$, the lower the $\gamma_{d_{\text{max}}}$. A similar observation where OLC and $\gamma_{d_{\text{max}}}$ decrease with increasing Na$_2$SiO$_3$ ratio has been reported by Phetchuay et al. (Phetchuay et al., 2014). Since NaOH contains water, a higher NaOH content may have increased inter-particle lubrication and subsequently enhanced the compaction effort.

Another observable trend in all the OLC curves is that $\gamma_d$ drops drastically as L content is increased to the wet side of the OLC. 90Na$_2$SiO$_3$:10NaOH specimens show a higher OLC which could be attributed to less water being present in the 90:10 mix, hence the need for a higher L content for optimum lubrication to achieve $\gamma_{d_{\text{max}}}$. Interestingly, changes of CG:S:FA ratio is not a factor altering the OLC of these mixes. This occurrence is probably due to the similar particle sizes of S and FA. The maximum recorded $\gamma_{d_{\text{max}}}$ is 8.86 kN/m$^3$, corresponding with 70CG:30S:0FA, with 50Na$_2$SiO$_3$:50NaOH, at L= 55%. Conversely, the lowest observed $\gamma_{d_{\text{max}}}$ is 8.39 kN/m$^3$, corresponding with 70CG:10S:20FA, with 90Na$_2$SiO$_3$:10NaOH, at L= 60%. This range of 8.39- 8.86 kN/m$^3$ is double the $\gamma_{d_{\text{max}}}$ of
untreated CG (4.4 kN/m$^3$) (Arulrajah et al., 2014b). The OLC range of 55-60% is also more than half the OMC of untreated CG (130%) (Arulrajah et al., 2014b).

The introduction of S and FA, which both have higher specific gravities, contribute to the rise in $\gamma_{dmax}$ and also drastically reduces the moisture needed to achieve $\gamma_{dmax}$. Comparatively, biosolids, another highly organic material being assessed as a recycled construction material, has a $\gamma_{dmax}$ of 8 kN/m$^3$ (Arulrajah et al., 2013a). Nevertheless, compared to naturally occurring soils (Horpibulsuk et al., 2008; Horpibulsuk et al., 2009), the $\gamma_{dmax}$ of these CG geopolymers are still very low.

**Figure 5.9** Compaction curves of different CG:S:FA mixes at different Na$_2$SiO$_3$:NaOH ratios (Kua et al., 2016b).
5.4.3 Unconfined Compressive Strength Development

Figure 5.11 shows the relationship between UCS values of specimens cured at 50°C and the variation in L content. A side-by-side comparison is made between the achievable UCS of 7 day and 28 day curing. All CG:S:FA combinations mixed with 50Na₂SiO₃:50NaOH of L exhibits highest UCS at OLC. The combination of 70CG:30S:0FA+ 70Na₂SiO₃:30NaOH also has a peak UCS at OLC, but the remaining combinations show inconsistencies in strength development relative to increase in L content. The plot in Figure 5.11 shows that most of them reach a “saturation point” at OLC, where further increase of L beyond the OLC would still yield an increase in strength, but the strength increase is disproportional compared to the increase in L. For a curing period of 7 days, the maximum UCS of 1406 kPa value is registered by specimens at 70CG:15S:15FA+ 90Na₂SiO₃:10NaOH at L= 75%. Subsequently, a UCS of 1241 kPa is attained at its OLC. Relatively, a 0.5 increase in L/P only results in a 200 kPa increase in strength. Comparatively, decreasing L/P by 0.5 from the OLC results in a 477 kPa loss in strength. This demonstrates that increasing L beyond the OLC would decrease the economic value and efficiency of the geopolymer, hence compaction at OLC is recommended.
Figure 5.11 Average UCS of CG:S:FA mixes at different Na$_2$SiO$_3$:NaOH ratios for different curing periods of 7 and 28 days at a curing temperature of 50°C (Kua et al., 2016b).
At 7 days of curing, by comparing only UCS values corresponding with specimens at OLC, 70CG:30S:0FA+ 50Na₂SiO₃:50NaOH yields a maximum UCS of 1338 kPa. Comparatively, the highest UCS at OLC achieved after 28 days of curing is 1729 kPa from the combination of 70CG:30S:0FA+ 70Na₂SiO₃:30NaOH. Interestingly the 7-day UCS value corresponding to this combination is 1304 kPa, which is only slightly lower than the aforementioned maximum value of 1338 kPa.

Table 5.6 summarizes the average UCS of the specimens at OLC, and shows the % increase in strength from 7 to 28 days curing at 50°C. Evidently, all specimens exhibit an increase in UCS with increasing curing time, but the rate of increase differs from each CG:S:FA mixes. Minimum variation in strength versus time is seen in the 70:30:0 mixes, where the increase ranges from 17.36-32.57%. 70CG:30S:0FA+ 50Na₂SiO₃:50NaOH develops the highest 7-day UCS. Results also indicate that mixes with a S-dominant precursor develop slightly high early strength when the proportion of NaOH increases. Inversely, as FA content increased, L ratios with larger Na₂SiO₃ proportions develop higher strengths. The 70:15:15 mix comparatively shows the largest strength increase of 31.89- 75.02% but with a relatively low early strength of 895- 1241 kPa.

Table 5.6 Comparison of UCS at OLC, for different curing periods (Kua et al., 2016b).

<table>
<thead>
<tr>
<th>CG:S:FA</th>
<th>Na₂SiO₃: NaOH</th>
<th>OLC (%)</th>
<th>7 Days Curing, 50°C UCS (kPa)</th>
<th>28 Days Curing, 50°C UCS (kPa)</th>
<th>Strength Increase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70:30:0</td>
<td>90:10</td>
<td>60</td>
<td>1114</td>
<td>1434</td>
<td>28.67</td>
</tr>
<tr>
<td></td>
<td>70:30</td>
<td>55</td>
<td>1304</td>
<td>1729</td>
<td>32.57</td>
</tr>
<tr>
<td></td>
<td>50:50</td>
<td>55</td>
<td>1338</td>
<td>1571</td>
<td>17.36</td>
</tr>
<tr>
<td>70:20:10</td>
<td>90:10</td>
<td>60</td>
<td>971</td>
<td>1244</td>
<td>28.08</td>
</tr>
<tr>
<td></td>
<td>70:30</td>
<td>55</td>
<td>1058</td>
<td>1293</td>
<td>22.25</td>
</tr>
<tr>
<td></td>
<td>50:50</td>
<td>55</td>
<td>1029</td>
<td>1494</td>
<td>45.13</td>
</tr>
<tr>
<td>70:15:15</td>
<td>90:10</td>
<td>60</td>
<td>1241</td>
<td>1636</td>
<td>31.89</td>
</tr>
<tr>
<td></td>
<td>70:30</td>
<td>55</td>
<td>919</td>
<td>1608</td>
<td>75.02</td>
</tr>
<tr>
<td></td>
<td>50:50</td>
<td>55</td>
<td>895</td>
<td>1382</td>
<td>54.32</td>
</tr>
<tr>
<td>70:10:20</td>
<td>90:10</td>
<td>60</td>
<td>1257</td>
<td>1411</td>
<td>12.25</td>
</tr>
<tr>
<td></td>
<td>70:30</td>
<td>55</td>
<td>1096</td>
<td>1499</td>
<td>36.70</td>
</tr>
<tr>
<td></td>
<td>50:50</td>
<td>55</td>
<td>1086</td>
<td>1688</td>
<td>55.35</td>
</tr>
</tbody>
</table>
Figure 5.12 illustrates the influences of variations in S:FA ratio on specimen strength. This figure compares the UCS of different Na$_2$SiO$_3$:NaOH specimens at OLC with varying S:FA contents in the 30% precursor replacement ratio, with CG fixed at 70%. At 7 days, specimens mixed with 70Na$_2$SiO$_3$:30NaOH and 50Na$_2$SiO$_3$:50NaOH show higher UCS values as the S content was increased. In contrast, 90Na$_2$SiO$_3$:10NaOH mixes display higher strength with increasing FA content. This trend is slightly distorted after 28 days of curing, where specimens with 50Na$_2$SiO$_3$:50NaOH show maximum UCS at 70CG:10S:20FA. Specimens with 70Na$_2$SiO$_3$:30NaOH still retain a maximum UCS at FA= 0%, while 90Na$_2$SiO$_3$:10NaOH specimens show peak UCS values at FA = 15%. It can be established that 70Na$_2$SiO$_3$:30NaOH mixes react best with 70CG:30S:0FA, with maximum S content; 90Na$_2$SiO$_3$:10NaOH mixes increase in strength as the FA content increases, but a saturation point at FA= 15% can be observed from both 7 days and 28 days curing. A similar fixation point of 15% was also reported by Phetchuay et. al. (Phetchuay et al., 2014), stating that excess FA particles obstruct dissociation of Ca(OH)$_2$, consequently slowing the process of silica and alumina breakdown in FA.

Figure 5.12 The effects of S:FA ratio on average UCS at OLC at a curing temperature of 50°C (Kua et al., 2016b).
Different reactions occur in a geopolymer mix depending on the dominant chemical composition. NaOH is essential for dissolving Si\(^{4+}\) and Al\(^{3+}\) ions for geopolymerisation (Somna et al., 2011). The reaction between CaO, Si, and Al with NaOH forms calcium silicate hydrate (CSH) (Richardson et al., 1994) and aluminium-modified calcium silicate hydrate (CASH) gels (Puertas et al., 2011) found similarly in Portland Cement (Garcia-Lodeiro et al., 2011). The S used in this study has a dominant CaO composition of 40\%. The increase in OH- ions as a result of increasing NaOH in the Na\(_2\)SiO\(_3\):NaOH ratio accelerates the formation of Si\(^{4+}\) and Al\(^{3+}\) ions, which readily react with the abundant Ca (dissolved from CaO) to form CSH (Wang et al., 2015). This enables mixes with a dominant S content to achieve high early (7 days) strength, a phenomenon also reported by Ismail et. al. (Ismail et al., 2014b), as observed in Table 5.6 and Figure 5.12.

On the other hand, a high level of silicate in a mix would also result in a high rate of geopolymerisation via the formation of a different silica-rich sodium aluminosilicate hydrate (NASH) gel (Oh et al., 2010). Mixes with a dominant silica-rich FA content underwent geopolymerisation under this reaction, as opposed to mixes with higher S content. FA-dominant mixes can therefore achieve high early (7 days) UCS values (Figure 5.12) with a 90Na\(_2\)SiO\(_3\):10NaOH solution due to additional silicate in the system (Ravikumar and Neithalath, 2012).

In the case of variations in Na\(_2\)SiO\(_3\):NaOH ratios, mixes with 50Na\(_2\)SiO\(_3\):50NaOH solutions have maximum UCS values corresponding with their OLC curves because minimizing inter-particle void by compaction is essential to ensure contact of CG particles, precursor, and alkaline liquid activator for maximum reaction and cementation to occur. On the contrary, it can be postulated that instead of relying on inter-particle contact to form dense matrices, mixes with 90Na\(_2\)SiO\(_3\):10NaOH and 70Na\(_2\)SiO\(_3\):30NaOH mainly draw strength from the coagulation of Na\(_2\)SiO\(_3\) into an amorphous product (Phetchuay et al., 2014; Phoo-ngernkhram et al., 2015a) due to a higher concentrations of silica (Ravikumar and Neithalath, 2012), incidentally originating from the activator liquid. Thus, increasing L content beyond the OLC for these mixes would generally still increase the UCS (Figure 5.11) due to the hardening and cementing of L, but this increase is limited because of high void ratio due to low material compactness.
Figure 5.13 The effects of different curing temperature on 7 days UCS for 70CG:30S:0FA and 70CG:15S:15FA (Kua et al., 2016b).

Figure 5.13 compares the UCS of specimens cured at room temperature (21°C) and at 50°C. Generally specimens cured at room temperature exhibit lower UCS values. While 90Na$_2$SiO$_3$:10NaOH specimens show increments of up to 400 kPa, other specimens show smaller variations in strength development, relative to the change of curing temperature. Puertas et. al. (Puertas et al., 2000) explained that curing done at high temperatures favour the dissolution of S and FA to some degree, but the consequent formation of dense and heterogeneous products deteriorates diffusion and reaction with age. This may clarify why 70CG:15S:15FA coupled with 70Na$_2$SiO$_3$:30NaOH or 50Na$_2$SiO$_3$:50NaOH does not show significant increments in strength; the simultaneous reaction of S and FA products ironically hinders the overall reaction process. On the contrary, specimens prepared with 90Na$_2$SiO$_3$:10NaOH show a higher increment in strength after heat treatment, implying that mixes with a dominant silica ratio have accelerated strength.
development under higher curing temperatures (Chindaprasirt, 2011). 70CG:20S:10FA activated with L ratios of 70Na$_2$SiO$_3$:30NaOH and 50Na$_2$SiO$_3$:50NaOH at OLC also show significant increase in strength after heat curing, confirming Puertas et al. (Puertas et al., 2000) observation that elevated temperatures favor dissolution of the reactive components in S. Interestingly, studies have indicated that S geopolymers cures adequately at ambient temperature (Bernal et al., 2012), and increasing the curing temperature excessively may even negatively impact the end strength of the product (Guo et al., 2010; Salih et al., 2015). Nevertheless, this study shows that even at ambient temperatures, CG geopolymers can achieve satisfactory compressive strengths.

5.5 Stabilisation by Rice Husk Ash

5.5.1 Testing Plan

Another geopolymer was synthesized by stabilizing CG with a Rice Husk Ash (RHA) precursor and Slag (S) as a supplementary material. At this stage, the liquid alkaline activator (L) consists only of NaOH. Na$_2$SiO$_3$ was excluded to observe the minimum achievable UCS of RHA geopolymers without additional silica the supplementation. This was also done as the level of SiO$_2$ in the RHA used was exceptionally high at 96.03%. The CG-to-additive ratio was fixed at 70:30 because a precursor composition of 30% was previously recommended for researches on water treatment sludge-fly ash geopolymers (Suksiripattanapong et al., 2015a; Suksiripattanapong et al., 2015b; Suksiripattanapong et al., 2015c) and lateritic soil-fly ash geopolymers (Phummiphan et al., 2016). The RHA:S, or precursor (P) ratios were 0:30, 10:20, 20:10 and 30:0. The L/P content was varied from 1.6 to 2.6.

The P and L were firstly mixed until an observable consistency in coloration could be observed. The CG was added and mixed for 5 minutes. Compaction was carried out immediately thereafter, under modified Proctor energy via an automated mechanical compactor, to prevent liquid evaporation and hardening of the geopolymer. The L/P content of 1.6 to 2.6 was added into the mix to obtain the optimum L content of all mix proportions according to ASTM (2012b). After obtaining the optimum liquid content (OLC) of all mixes, a set of specimens were reconstituted by statically compressing the mixtures in a cylindrical mold of 50 mm in diameter and 100 mm in height at the optimum
L content with a manual hydraulic jack. This set contains a range of specimens from both the dry and wet side of the OLC, and were designated different curing conditions to gauge their strength development in different environments.

Modified compaction was done using an automatic mechanical compactor whereas static compaction was done using a manual hydraulic jack. The specimens were wrapped in clear vinyl to prevent moisture loss throughout curing. Curing periods implemented were 7, 28, 60, and 90 days, at curing temperatures of both 21°C and 50°C.

5.5.2 General and Compaction Characteristics

Figure 5.14 shows the morphology of typical (a) CG, (b) RHA, and (c) S particles obtained via Scanning Electron Microscope (SEM) imaging. CG particles are irregular and porous. RHA particles are elongated and possess “wavy” corrugations throughout the external surface. Figure 5.14(b) also shows the internal configuration of a broken RHA particle, circled in red, which shows that it is very porous. S particles vary in size but are generally polygonal and smooth. Figure 5.15 shows the particle size distribution (PSD) of CG, RHA, and S particles. The curve for CG was obtained by testing dried CG in accordance to (ASTM, 2007a), while the PSD of RHA and S were undertaken using Laser Diffraction analysis due to their size being finer than detectable by sieve analysis (ASTM, 2007a). The D_{50} of CG, BA, and S are 0.35, 0.06, and 0.02 respectively. The specific gravity of CG, RHA, and S as obtained in accordance to (ASTM, 2014a), are 1.35, 2.05, and 3.23 respectively, indicating that S particles are densest whereas CG particles are the least dense. Table 5.7 summarizes the XRF results done onto CG, RHA and S. While the XRF analysis done on CG only represent a small inorganic portion in its composition, it does give an indication that CaO and K_{2}O are the major inorganic compounds found in CG. On the other hand, 96.08% of RHA is SiO_{2}, whereas S constitutes majorly of CaO (43.55%) and SiO_{2} (35.21%).
Figure 5.14 SEM images of: (a) CG, (b) RHA, and (c) S (Suksiripattanapong; Kua et.al. 2017).

Table 5.7 Chemical composition of CG, RHA, and S by XRF analysis (Suksiripattanapong; Kua et.al. 2017).

<table>
<thead>
<tr>
<th>Chemical Composition (%)</th>
<th>CG</th>
<th>RHA</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>N.D.</td>
<td>96.03</td>
<td>35.21</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>N.D.</td>
<td>N.D.</td>
<td>13.09</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>3.61</td>
<td>0.13</td>
<td>0.45</td>
</tr>
<tr>
<td>CaO</td>
<td>33.99</td>
<td>0.53</td>
<td>43.55</td>
</tr>
<tr>
<td>MgO</td>
<td>N.D.</td>
<td>N.D.</td>
<td>5.93</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>N.D.</td>
<td>0.20</td>
<td>0.85</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>43.10</td>
<td>1.67</td>
<td>0.92</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>16.51</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
</tbody>
</table>

Remark: N.D. = Not detected
Table 5.8 Summary of the compaction test results of CG:RHA:S geopolymers
(Suksiripattanapong; Kua et.al. 2017).

<table>
<thead>
<tr>
<th>CG:RHA:S</th>
<th>$\gamma_{t\text{max}}$ (kN/m$^3$)</th>
<th>L/P</th>
<th>$\gamma_{d\text{max}}$ (kN/m$^3$)</th>
<th>Liquid Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70:30:0</td>
<td>10.5</td>
<td>10.9</td>
<td>10.6</td>
<td>2.2</td>
</tr>
<tr>
<td>70:10:20</td>
<td>11.1</td>
<td>11.6</td>
<td>11.1</td>
<td>2.0</td>
</tr>
<tr>
<td>70:20:10</td>
<td>11.4</td>
<td>11.9</td>
<td>11.8</td>
<td>1.8</td>
</tr>
<tr>
<td>70:0:30</td>
<td>12.1</td>
<td>12.6</td>
<td>12.2</td>
<td>1.6</td>
</tr>
</tbody>
</table>

D.S = Dry Side; Opt = OLC; W.S = Wet Side.

Table 5.8 shows the summary of the compaction test result for CG:RHA:S geopolymers at different RHA and S contents. The maximum total unit weight ($\gamma_{t\text{max}}$) values of the mixes increased with an increase in S content, due to the specific gravity of S being higher than that of RHA (about 1.5 times). The optimum L/P ratios were 2.4, 2.2, 2.0 and 1.8 for RHA contents of 30%, 20%, 10% and 0% respectively. The CG:S ratio of 70:30 gave the
highest $\gamma_{\text{tmax}}$ whereas the lowest $\gamma_{\text{tmax}}$ was found at CG:RHA ratio of 70:30. The optimum liquid content (OLC) of the mixes increased as the RHA content increased. This increase in the amount of liquid needed to achieve OLC was due to the morphology of RHA, which contains high amounts of micro-pores and intra-particle voids, thus resulting in high liquid absorption.

5.5.3 Unconfined Compressive Strength Development

Figure 5.16 shows the 7-day strength of CG:RHA:S geopolymers at different RHA:S ratios and curing temperatures of 21$^\circ$C and 50$^\circ$C. The test result showed that for 70CG:30RHA, the 7-day UCS of the geopolymer decreased as L/P increased. This could be due to the excessive NaOH content which leached high amounts of SiO$_2$ from the RHA, hindering the reorganization of Si and Al polymers (Bui et al., 2012). With the introduction of S into the geopolymer, the 7-day UCSs of other CG:RHA:S geopolymers increased with increasing L/P ratios up to an optimum L/P value. The addition of S into the mix increased the percentage of Al$_2$O$_3$ and CaO, hence the NaOH at an optimum L/P ratio was significant for leaching SiO$_2$ and Al$_2$O$_3$ from the RHA and S in order to react with CaO to form calcium silicate hydrate (CSH) (Kua et al., 2016b), calcium aluminosilicate hydrate (CASH) gel and sodium aluminosilicate hydrate (NASH) gel in geopolymers. Beyond this optimum value, the 7-day UCS of the CG:RHA:S geopolymer decreased with increasing L/P values. The maximum UCS values of CG:RHA:S geopolymers at 70:20:10, 70:10:20 and 70:0:30 occurs at optimum L/P ratios of 2.2, 2.0 and 1.8 respectively.

The effects of elevated temperature curing on the 7-days UCSs of the CG:RHA:S geopolymers were studied. The 7-days UCS of the CG:RHA:S geopolymer cured at 50$^\circ$C was higher than that of the CG:RHA:S geopolymer cured at 21$^\circ$C, because the higher temperature accelerated geopolymerisation (Kumar et al., 2010). Comparatively, the 7-days UCS of 70CG:30S samples mixed with water and cured at 21$^\circ$C (room temperature) is shown in Figure 5.16 for comparison. The 7-day UCSs of CG:RHA:S geopolymer specimens were significantly higher than those of CG-S samples mixed with water. This comparison proves that alkaline activated aluminosilicate-rich materials are more effective in strengthening CG compared to those which are simply hydrated by water.
**Figure 5.16** 7-days UCS of CG:RHA:S geopolymers at various L/P ratios (Suksiripattanapong; Kua et.al. 2017).

**Figure 5.17** Effect of S on 7-days UCS for specimens produced at OLC (Suksiripattanapong; Kua et.al. 2017).
Figure 5.17 compares the influence of slag content on 7-days UCS of CG:RHA:S geopolymers compacted at OLC at different curing temperatures. At 21°C, the 7-days UCS of 70CG:30RHA geopolymers increased from 68.6 kPa to 265.4 kPa whereas at 50°C UCS increased from 220.5 kPa to 407.6 kPa when RHA is replaced with 10% S. It was previously reported that the compressive strength was improved by adding S, which contains a large amount of CaO, into the mixture (Kumar et al., 2010). This is because the presence of CaO improved the strength of the geopolymer by forming an amorphously structured Ca–Al–Si gel (Zhang et al., 2010). Beyond the optimum ratio, the UCS decreased when the S content increased because the excessive S creates an environment where SiO₂ is in excess, hence was insufficient to react with the CaO for CSH formation (Phoo-Ngernkham et al., 2015b). Therefore, the addition of S contents beyond the fixation point of 10% is not practical. The optimum mix for the CG:RHA:S geopolymer was therefore nominated to be CG:RHA:S of 70:20:10 at an optimum L/P ratio of 2.2. According to the Department of Highways, Thailand, the strength of stabilised subgrade material should be greater than 294.2 kPa (DH-S 102/2532) (Teerawattanasuk et al., 2015). Comparatively, from Figure 5.17, CG:RHA:S geopolymers with S>10% and a curing temperature of 50°C meet the requirements to be subgrade material.

![Graph showing long-term strength development of CG:RHA:S geopolymers at OLC](image)

Figure 5.18 Long-term strength development of CG:RHA:S geopolymers at OLC (Suksiripattanapong; Kua et.al. 2017).
Figure 5.18 shows the long-term UCS development in CG:RHA:S geopolymers compacted at OLC, at various curing temperatures. The UCS of CG:RHA:S samples cured at 21°C was almost constant with varying curing times for all mixes whereas the UCS of CG:RHA:S samples cured at 50°C increased up to 60 days after which the UCS remained constant with extended curing time. The combination of 70CG:20RHA:10S showed that UCS increased for up to 90 days. Figure 5.18 indicates that the elevated curing temperature of 50°C can stimulate long term geopolymerisation reaction in RHA geopolymers, resulting in continual strength developments of up to 60 days for 70CG:30RHA and 70CG:10RHA:20S specimens, and up to 90 days for the optimum 70CG:20RHA:10S specimens. The final achievable UCS for 70CG:20RHA:10S specimens at 90 days was 2 MPa.

5.6 Stabilisation by Bagasse Ash

5.6.1 Testing Plan

The main components involved in this study were the granular solids, namely dried CG, BA, S; and an alkaline Sodium Hydroxide (NaOH) liquid activator. These materials were blended and compacted to form a geopolymer in which CG was the parent material, BA and S were the precursors, and NaOH was the sole alkaline activator. In the granular solid mix, CG comprised of 70% of the total dry mass, while the remaining 30% comprised of BA:S with ratios of 30:0, 20:10, 10:20, and 0:30.

BA and S were first mixed with NaOH until an observable consistency in texture and coloration was observed. This paste was then mixed with CG for 5 minutes to form the geopolymer blend. Modified Proctor compaction effort (ASTM, 2012b) was used to compact the blend immediately to prevent excessive evaporation of moisture and the flocculation of geopolymeric substances. Different ranges of liquid contents were used to obtain the optimum liquid content (OLC) of all blends. After acquiring the wet density corresponding to each liquid content of different blends, static compression was used to produce geopolymers with a diameter of 50 mm and a height of 100 mm using a cylindrical split mould. Modified compaction was done using an automatic mechanical compactor whereas static compaction was done using a manual hydraulic jack. The
specimens were wrapped in clear vinyl to prevent moisture loss throughout curing. Curing periods implemented were 7, 28, 60, and 90 days, at curing temperatures of both 21°C and 50°C.

5.6.2 General and Compaction Characteristics

Figure 5.19 SEM images of: (a) CG, (b) BA, and (c) S (Arulrajah; Kua et. al., 2017).
Figure 5.19 shows the morphology of all three solids obtained using Scanning Electron Microscope (SEM) imaging. SEM images show that CG particles in Figure 5.19(a) appear to be irregular in shape, and have many intra-particle voids, giving them a sponge-like appearance. On the other hand, Figure 5.19(b) clearly shows an elongated BA particle. This particle is cellular-looking and has a rough surface, and is probably the result of partially burnt or unburnt bagasse. Two smaller particles with smooth surfaces (circled) are the quartz component or fully burnt bagasse (Cordeiro et al., 2016). On the other hand, S particles are all polygonal and smooth, as shown in Figure 5.19(c).

The particle size distributions (PSD) of all three materials are presented in Figure 5.20. The PSD curve of CG was undertaken on dried CG in accordance to (ASTM, 2007a), while the PSD of BA and S were undertaken using Laser Diffraction analysis. The PSD curves presented in Figure 5.20 shows that 80% of BA particles are >0.075 mm hence are fine-grained according to (ASTM, 2011), whereas the remainder 20% ranges from 0.075 mm to 0.3 mm. 97% of S particles fall into the category of fine-grained soils while the remaining 3% were between 0.075 mm and 0.13 mm hence considered as fine sand (ASTM, 2011). The \( D_{50} \) of CG, BA, and S are 0.35, 0.05, and 0.02 respectively. The specific gravity of CG, BA, and S as obtained in accordance to (ASTM, 2014a), are 1.35, 2.17, and 3.23 respectively. Interestingly, CG has the largest particle size but is least dense, whereas the inverse is true for S. BA also has larger particles compared to S but a lower specific gravity. This is attributed to the porous surface of both CG and BA particles, in which the intra-particle voids are present.

From the XRF results in Table 5.9, it can be seen that CG contains certain amounts of inorganic compounds, dominantly 43.10% of \( K_2O \) and 33.99% of \( CaO \). On the other hand, the major component in BA is 77.55% of \( SiO_2 \). S predominantly constitutes of 43.55% of \( CaO \) and 35.21% of \( SiO_2 \), both which are key compounds needed to form CASH and CSH gels.
Figure 5.20 Particle size distribution of CG, BA, and S
(Arulrajah; Kua et. al., 2017).

Table 5.9 Chemical composition of CG, BA, and S by XRF analysis
(Arulrajah; Kua et. al., 2017).

<table>
<thead>
<tr>
<th>Chemical Composition (%)</th>
<th>CG</th>
<th>BA</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>N.D.</td>
<td>77.55</td>
<td>35.21</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>N.D.</td>
<td>6.48</td>
<td>13.09</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>3.61</td>
<td>4.71</td>
<td>0.45</td>
</tr>
<tr>
<td>CaO</td>
<td>33.99</td>
<td>2.85</td>
<td>43.55</td>
</tr>
<tr>
<td>MgO</td>
<td>N.D.</td>
<td>4.19</td>
<td>5.93</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>N.D.</td>
<td>0.82</td>
<td>0.85</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>43.10</td>
<td>2.36</td>
<td>0.92</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>16.51</td>
<td>0.69</td>
<td>N.D.</td>
</tr>
</tbody>
</table>
Figure 5.21 shows the relationship between total density and the ratio between the mass of liquid NaOH (L), against the mass of precursor (P) used in each blend. The OLC for 70CG:30BA was L/P = 2.0, whereas the other blends had an OLC at L/P = 1.8. The maximum total density achieved by 70CG:30BA was 11.43 kN/m$^3$. The maximum total density achieved for 70CG:30S was 12.61 kN/m$^3$. This was directly influenced by the amount of S present in the blend: the higher the ratio of S, the higher the total density of the blend because S has the highest specific gravity among the three solid materials. Also more liquid was needed to achieve OLC for 70CG:30BA compared to the other mixes where S is present: This was due to the highly corrugated BA particles hence larger surface area of BA compared to the smooth surface of S particles as also shown in Figure 5.19, which led to higher liquid absorption.

Figure 5.22 presents the relationship between bulk density of each blend against L/P, acquired after crushing and drying the cylindrical specimen from the modified Proctor compaction tests until the moisture from NaOH was fully evaporated. The lowest maximum bulk density was 8.22 kN/m$^3$ which corresponded to 70CG:30BA. The 70CG:30S blend achieved the highest maximum bulk density at 9.48 kN/m$^3$. Comparatively, the maximum bulk density of unstabilised CG was obtained at 4.4 kN/m$^3$ (Arulrajah et al., 2016b). This implied that BA and S grains fill the inter-particle void between CG particles, hence the increased density. These CG:BA:S geopolymers were relatively lightweight and were comparable to ultra-lightweight geopolymer concretes with bulk densities less than 7.85 kN/m$^3$ (Huiskes et al., 2016).
Figure 5.21 Total density vs. L/P ratio for different CG:BA:S geopolymers

(Arulrajah; Kua et. al., 2017).

Figure 5.22 Bulk density vs. L/P ratio for different CG:BA:S geopolymers

(Arulrajah; Kua et. al., 2017).
5.6.3 Unconfined Compressive Strength Development

Figure 5.23 shows the strength performance of each blend after 7 days of curing, at both 21°C and 50°C. Evidently, the 70CG:30BA blend achieved the lowest UCS value. As the amount of S was increased, the UCS of the blend subsequently increased, due to the early manifestation of pozzolanic properties of the S geopolymers (Ismail et al., 2014b). Interestingly, the optimum precursor ratio at 7 days was found to be 70CG:10BA:20S, as increasing the S value to 30% results in lower UCS values. This indicates that, in the short term, a BA geopolymer is evidently weaker than an S geopolymer, but a mix of BA and S would result in a higher rate of geopolymerisation. Elevated temperature curing increases the UCS of all blends slightly. The highest UCS corresponds with the OLC. For specimens cured at 50°C, the UCS of all blends were similar as the L/P ratio was decreased to the dry side to the OLC, but experienced a significant drop as it was increased over the wet side of the OLC.

![Figure 5.23](image-url)

Figure 5.23 7 days strength properties for various CG:BA:S geopolymers cured at (a) 21°C and (b) 50°C (Arulrajah; Kua et. al., 2017).
Figure 5.24 shows the performance of the CG:BA:S polymers after an extended curing duration of up to 90 days. The 21°C-cured samples all showed a general trend, in which the 7 days UCS was the highest, followed by a drop in UCS values after 28 days of curing. However, the drop in UCS stabilised after 60 and 90 days. At 21°C, it was observed that the 70CG:30S samples performed better than the other geopolymers with BA, whereby the UCS achieved was maintained around 200 kPa throughout the 90 days curing duration. In contrast the 70CG:30BA: blend achieved the lowest UCS after 90 days at 72 kPa. This UCS value is similarly obtained in a study where CG stabilised with 30% FA and 30% S cured at 21°C by simple hydration, which produced UCS values of 76-78 kPa (Kua et al., 2016a). At 50°C curing, it can be observed that the 70CG:20BA:10S mix achieves the highest 90 days strength of 1482 kPa. This was followed in descending order by 70CG:0BA:30S (805 kPa), 70CG:30BA:0S (755 kPa), and lastly 70CG:10BA:20S (450 kPa). Elevated temperature curing was thus found to significantly improve the long-term strength of these geopolymers.

Figure 5.24 Strength development up to 90 days for different CG:BA:S geopolymers (Arulrajah; Kua et. al., 2017).
Among countries that use UCS values of soil materials as a benchmark for pavement design, the Department of Highway, Thailand nominated a minimum UCS of 294.20 kPa for road subgrade materials (Teerawattanasuk et al., 2015). On the other hand, Malaysia allows low-volume-traffic roads to be built on a subgrade with a UCS more than 800 kPa (Awg Shahminan et al., 2014). From this study, 70CG:10BA:20S can meet Thailand’s criteria after 7 days curing at 50°C. After 60 days and beyond, all specimens cured at 50°C meets Thailand’s benchmark except 70CG:30BA. On the other hand, using the Malaysian specifications, 70CG:20BA:10S cured for 90 days at 50°C meets the requirement to be used as a subgrade material.

From the 7 days UCS test results, it is evident that a geopolymer blend formed with 70CG:10BA:20S outperformed other geopolymers. As the strength development of geopolymers is directly influenced by its silica-to-alumina ratio (Noor ul et al., 2015; Phoo-ngernkham et al., 2015a), a geopolymer mix comprising BA and S precursors, was found to benefit from a balanced Si:Al ratio. While two BA:S ratios were tested in this study, the higher percentage of S in the 70CG:10BA:20S blend was probably responsible for early strength development due to its fast setting properties (Perná and Hanzlíček, 2015), hence had a notably higher UCS compared to the 20BA:10S blend at 7 days.

On the other hand, the 90-days strength development results showed that the geopolymers can gain increased strength only under continuous heat treatment. The key difference in room temperature and elevated temperature curing is the accelerated rate of geopolymerisation in the latter (Bakria et al., 2011), which was observed to inhibit organic content growth in specimens cured at 50°C. 21°C-cured specimens were observed to regularly develop mould. Thus, while the geopolymeric paste comprising of BA, S and NaOH reacted to form a binder material, the structural integrity of the geopolymer as a whole was negatively affected due to fungal growth developing on the parent CG material. Therefore the drop in UCS from 7 days to 28 days curing at 21°C can be attributed to the growth of fungus in CG, whereas the constant value of UCS was maintained from 28 days to 90 days due to strength development in the BA:S geopolymer.

For long-durations of curing at 50°C, the UCS of 70CG:30BA, 70CG:20BA:10S and 70CG:30S specimens were found to be increased with time, as presented in Figure 5.24. As discussed previously, a mix of BA:S results in an optimum Si/Al ratio hence maximum
UCS can be achieved in the 70CG:20BA:10S mix. Surprisingly, the 70CG:10BA:20S specimens displayed reduced UCS development compared to the other blends. In this case, curing the specimen with a higher S-to-BA ratio at 50°C mainly catalyses the dissociation of reactive compounds in S and to a lesser extent, the compounds in BA. The highly reactive process causes a “dense and heterogeneous” paste to form rapidly (Puertas et al., 2000), ironically slowing consequent diffusion processes at extended curing durations. This can be avoided by increasing the amount of silica in the mix (Chindaprasirt, 2011). As BA is composed predominantly of silica, this may explain why, for the long term, by adjusting slightly the BA:S ratio to 20:10 an optimum environment for geopolymerisation could be achieved.

5.7 Crushed Glass as a Supplementary Filler

5.7.1 Testing Plan

Medium and fine-grained recycled glass (RG) are materials with high shear strength (Arulrajah et al., 2014a) and have been proven to be good replacements for fine aggregates to produce masonry units with high UCSs (Arulrajah et al., 2016a; Kou and Poon, 2013). The amount of RG present in a design mix is reported to influence the workability, compressive strength, and elastic modulus of the mortar mix (Liang et al., 2015).

Comparing the full range of recorded 7-days strengths of the CG geopolymers obtained previously in this research reveal that CG+FA and CG+S geopolymers produces more reliable UCS results relative to CG geopolymers derived from the agricultural wastes RHA and BA. The results, displayed in Table 5.10, compares the 7-days UCS of CG geopolymers with that of FA+RG geopolymers cured at the same temperature for the same duration. The table also includes benchmarks given by official road authorities regarding the minimum UCS requirements for subgrade materials. By comparing these benchmarks with the maximum achievable UCS of the CG geopolymers, CG+FA and CG+S geopolymers comfortably meets the UCS benchmarks as all their maximum UCSs exceed 1 MPa.
CG+FA and CG+S geopolymers were therefore selected to undergo further enhancements with the supplementation of fine RG to produce a green material with high compressive strength. For the granular solids component, as per the experiments in previous sections, a ratio of 70% CG to 30% Precursor (P) was adopted for this trial. However, in these new mixes, within the 70% CG, RG arbitrarily replaced CG by 25%, 50%, and 75%. The alkaline liquid (L) component was fixed at 70Na$_2$SiO$_3$:30NaOH because it was found that FA and S geopolymers performed optimally with this L ratio (Arulrajah et al., 2016a; Kua et al., 2016b).

Table 5.10 Comparison of 7-days UCS performance of various CG geopolymers

<table>
<thead>
<tr>
<th>CG Geopolymer Design Mix</th>
<th>Recorded 7-days UCS at 50°C Curing (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70CG:30FA</td>
<td>0.4-1.0</td>
</tr>
<tr>
<td>70CG:30S</td>
<td>0.5-1.3</td>
</tr>
<tr>
<td>70CG:20RHA:10S</td>
<td>0.3-0.4</td>
</tr>
<tr>
<td>70CG:20BA:10S</td>
<td>0.1-0.2</td>
</tr>
<tr>
<td>70RG:30 FA masonry</td>
<td>4.8-16.1</td>
</tr>
</tbody>
</table>

Rural Highway Subgrade UCS Requirement, Thailand | 0.29 MPa | (Teerawattanasuk et al., 2015) |

Low-volume-traffic Road Subgrade UCS Requirement, Malaysia | 0.80 MPa | (Awg Shahminan et al., 2014) |

Oven-dried CG and RG were mixed with the desired precursor (FA or S) in a pail for a minimum of 5 minutes or until a consistent texture and colour can be observed. The homogenous dry mix was then separated into individual pails, in which L was introduced...
into each pail in controlled and different amounts. The solids and liquid were then blended until consistency in texture and colour was observed again. The mixing process after L was introduced was limited to 5 minutes and compaction was done immediately afterwards to prevent liquid evaporation and hardening of the geopolymer. First and foremost, the mixes were compacted under modified compaction effort (ASTM, 2012b) to determine the optimum liquid content (OLC) of all material combinations.

Table 5.11 Test plan for the strength assessment of CG geopolymers with RG supplementation.

<table>
<thead>
<tr>
<th>Test Type</th>
<th>CG:RG:P (by dry mass)</th>
<th>Na$_2$SiO$_3$:NaOH L/P (by mass)</th>
<th>Curing Temperature (°C)</th>
<th>Curing Duration (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Dry Density</td>
<td>50CG:20RG:30FA</td>
<td>70:30 0.8, 1.0, 1.2, 1.4, 1.6</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>35CG:35RG:30FA</td>
<td>70:30 0.4, 0.6, 0.8, 1.0, 1.2</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>20CG:50RG:30FA</td>
<td>70:30 0.2, 0.4, 0.6, 0.8, 1.0</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>50CG:20RG:30S</td>
<td>70:30 0.8, 1.0, 1.2, 1.4, 1.6</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>35CG:35RG:30S</td>
<td>70:30 0.4, 0.6, 0.8, 1.0, 1.2</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>20CG:50RG:30S</td>
<td>70:30 0.2, 0.4, 0.6, 0.8, 1.0</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>UCS</td>
<td>50CG:20RG:30FA</td>
<td>70:30 0.8, 1.2, 1.6, 2.0</td>
<td>21, 50</td>
<td>7, 28</td>
</tr>
<tr>
<td></td>
<td>35CG:35RG:30FA</td>
<td>70:30 0.6, 1.0, 1.4, 1.8</td>
<td>21, 50</td>
<td>7, 28</td>
</tr>
<tr>
<td></td>
<td>20CG:50RG:30FA</td>
<td>70:30 0.4, 0.8, 1.2, 1.6</td>
<td>21, 50</td>
<td>7, 28</td>
</tr>
<tr>
<td></td>
<td>50CG:20RG:30S</td>
<td>70:30 0.8, 1.2, 1.6, 2.0</td>
<td>21, 50</td>
<td>7, 28</td>
</tr>
<tr>
<td></td>
<td>35CG:35RG:30S</td>
<td>70:30 0.6, 1.0, 1.4, 1.8</td>
<td>21, 50</td>
<td>7, 28</td>
</tr>
<tr>
<td></td>
<td>20CG:50RG:30S</td>
<td>70:30 0.4, 0.8, 1.2, 1.6</td>
<td>21, 50</td>
<td>7, 28</td>
</tr>
</tbody>
</table>

Subsequently, L/P ratios from both the wet and dry sides of the OLC were selected to produce UCS specimens to check the correlation between L/P and strength development. UCS specimens were prepared by statically compressing the mixtures in a 50 mm diameter by 100 mm height split-mould with 1-layer compression as done previously.
Triplicate samples were produced for all material combinations to minimize error margins. Two sets of specimens were produced to cure at 1) 21°C, to simulate room temperatures and 2) 50°C, to compare the effects of heat treatment on the geopolymers’ UCS performance. A minimum curing period of 7 days was adopted. A separate set of specimens were also produced to cure for 28 days to observe and compare the long-term strength development of these CG+RG geopolymers. Moisture lost during the curing period was prevented by wrapping the cylindrical specimens in clear vinyl wraps after compaction. Table 5.11 summarizes the test plan for CG geopolymers supplemented with RG.

5.7.2 General and Compaction Characteristics

The RG used was sourced from a construction and demolition waste recycling plant in Melbourne, Australia. The RG have been sieved and graded prior to acquisition, and it was known that all particles are less than 2.36 mm in diameter. This source was categorized as fine recycled glass (FRG) which is suitable to be considered as a type of replacement fine aggregates (Disfani et al., 2011; Kou and Poon, 2013; Liang et al., 2015). Sieve analysis was done on oven-dried RG according to ASTM (2009) to determine its Particle Size Distribution (PSD). As glass is known to be brittle and will crack under high external pressure, a separate sieve analysis was done on dried RG impacted with modified Proctor compaction energy according to ASTM (2007a). The results presented in Figure 5.25 shows that RG particles are larger than CG. All the materials used were uniformly graded, but the fraction of smaller particles in RG is higher compared to the particle distribution of other materials.

Figure 5.26 shows the morphology of RG particles. RG particles have sharp edges, are polygonal, and have smooth surfaces without any observable pores. Fine RG particles can be observed to adhere to the surface of larger particles as highlighted in Figure 5.26 by a red circle. XRF analysis done on the RG particles used, presented in Table 5.12, shows that it is dominantly composed of 80% of SiO$_2$, with CaO being the second dominant compound at 13.6%. Theoretically, this means that the inorganic compounds found in RG are conducive for geopolymerisation as Si, Al, and Ca are required for the polymerisation process to take place.
Figure 5.25. Particle Size Distribution of RG compared to other materials used (Arulrajah; Kua et. al., 2017).

Figure 5.26. SEM image of RG Particles (Arulrajah, Kua et. al., 2016a).
Table 5.12 Chemical composition of RG by XRF analysis (Arulrajah, Kua et al., 2016a).

<table>
<thead>
<tr>
<th>Chemical composition (%)</th>
<th>RG</th>
<th>FA</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>80.12</td>
<td>75.45</td>
<td>35.21</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.98</td>
<td>12.01</td>
<td>13.09</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.69</td>
<td>3.96</td>
<td>0.45</td>
</tr>
<tr>
<td>CaO</td>
<td>13.58</td>
<td>2.72</td>
<td>43.55</td>
</tr>
<tr>
<td>MgO</td>
<td>N.D.</td>
<td>N.D.</td>
<td>5.93</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.44</td>
<td>0.78</td>
<td>0.85</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.56</td>
<td>2.97</td>
<td>0.92</td>
</tr>
</tbody>
</table>

N.D. = Not Detected

Figure 5.27 OLC of CG geopolymers with different RG replacement ratios (Arulrajah; Kua et al., 2017).
Modified Proctor compaction tests done on the CG:RG:P mixes, as shown in Figure 5.27, indicate that with the increase of RG, the L content required to achieve maximum dry unit weight after compaction decreased. Compared to CG geopolymers utilizing solely FA (L/P = 1.2 -2.6) (Arulrajah et al., 2016b) or S (L/P = 1.5-2.5) (Kua et al., 2016b), the range of L/P for CG+RG geopolymers to achieve maximum compaction is 0.2 -1.6. This is attributed to the porous CG being replaced by non-permeable RG particles. Also increasing the ratio of RG in the CG mix results in increased dry unit weight of the mix due to the significantly denser RG particles which replaces the lightweight CG. The maximum dry unit weight recorded by 50CG:20RG:30P specimens are 10.07 kN/m$^3$ for FA and 11.12 kN/m$^3$ for S, whereas the maximum dry unit weight recorded by 20CG:50RG:30P specimens are 13.87 kN/m$^3$ for FA and 14.92 kN/m$^3$ for S. Comparatively, the maximum dry unit weight of CG is 4.4 kN/m$^3$ and the maximum dry unit weight of 70RG:30FA geopolymers is 18.1 kN/m$^3$.

5.7.3 Unconfined Compressive Strength Development

Apparently, the UCS of CG geopolymers increased significantly after the introduction of RG. Compared to CG+FA and CG+S geopolymers, these supplemented geopolymers can easily gain compressive strengths of more than 1MPa, as seen in Figure 5.28. At 7 days, geopolymers at the dry side of the OLC are relatively inefficient, as the L/P ratio is too low to fully dissolve silica and alumina to form cementitious compounds. At the wet side of OLC, most mixes develop UCSs exceeding 1 MPa, except for the CG+RG+FA mixes cured at 21°C. CG+RG+FA specimens cured at 50°C gains strength with the increase of L/P because elevated temperature curing favours geopolymeric reactions in FA geopolymers (Bakria et al., 2011) due to the fact that FA is high in silica content (Chindaprasirt, 2011). On the other hand, without catalysation of geopolymeric reaction by heat treatment, the excess Al-Si cementitious compounds. At the wet side of OLC, precipitation in CG+RG+FA geopolymers hinders geopolymeric reactions by preventing contact between reactive materials (Villa et al., 2010). Hence it is important for CG+RG geopolymers with FA as a precursor to be heat treated for proper strength development. On the other hand, S specimens do not show much variance in strength gain regardless of curing temperature, confirming that geopolymers with S as a precursors can cured adequately without elevated curing temperatures (Bernal et al., 2012).
Figure 5.28 7-days UCS of various CG+RG geopolymer mixes at different L/P ratios (Arulrajah; Kua et. al., 2017).
Figure 5.29 28-days UCS of various CG+RG geopolymer mixes at different L/P ratios (Arulrajah; Kua et. al., 2017).

At 28-days, as seen in Figure 5.29, the trend of strength development relative to the change in L/P is like that of the 7-days specimens. At 21°C, with FA as a precursor, the increase of L/P does not cause any significant variation in UCS. Mixes with high L/P
content have begun developing geopolymeric compounds in contrary to the 7-days specimens, resulting UCS values similar to specimens with lower L/P values. At 50°C, like 7-days specimens, the UCS of 28-days specimens increased when L/P increased. However, as the geopolymeric reactions at 28-days had manifested, the geopolymers have saturation points in which the increase of L/P still may result in UCS increase, but the increment is not proportionate to the increase of L/P. These saturation points are 1.2, 1.0, and 1.2 for 50CG:20RG:30P, 35CG:35RG:30P, and 20CG:50RG:30P respectively regardless of precursors used. Compared to the OLC of these mixes, which are 0.4, 0.6, and 1.0 for 50CG:20RG:30P, 35CG:35RG:30P, and 20CG:50RG:30P respectively, the saturation points are situated at much higher L/P ratios. This indicates that for these geopolymers, a good balance between L/P is more important than the maximum compaction of the granular solids, and that the geopolymeric bonds are the dominant contributors to UCS compared to the interparticle friction created from maximum material compactness. A balanced L/P ratio ensures that the aluminosilicate in the mixes is fully utilised in the chemical reaction to produce desirable calcium silicate hydrate (CSH) and aluminium-modified calcium silicate hydrate (CASH) gels required for geopolymerisation (Hoy et al., 2016; Sukmak et al., 2013a).

Generally, the UCS of CG:RG geopolymers increased with the increase of RG in the mix. This can be attributed to the shear strength provided by RG particles (Arulrajah et al., 2014a; Disfani et al., 2011). Interestingly, 20CG:50RG:30S specimens gain tremendously high UCS values which exceeds 10 MPa at L/P > 1.2 after 7 days of curing. Referring to Table 5.11, XRF results showed that the S used in this study has a dominant CaO composition of 43.55%. OH- ions readily react with the abundant Ca (dissolved from CaO) to form CSH (Wang et al., 2015), enabling the mix to achieve high early (7 days) strengths. This observation is consistent with findings by Ismail et al. (2014b). Mechanical strength provided by the RG particles and additional Si leached from fine RG particles provided elevated compressive strength performance and supplements the formation of geopolymers.
Figure 5.30 Long-term strength development of CG+RG geopolymers with FA as a precursor (Arulrajah; Kua et. al., 2017).
Figure 5.31 Long-term strength development of CG+RG geopolymers with S as a precursor (Arulrajah; Kua et. al., 2017).
**Figure 5.30** shows the difference in UCS of specimens cured for 7 and 28 days obtained from FA geopolymers. Evidently FA geopolymers cured at room temperature exhibits decrease in UCS when the L/P ratio goes beyond the optimum ratio. Alkaline activation causes FA particles to dissolve and form NASH gels, which should merge into larger masses with time (Khan et al., 2016). However, due to excess Si in the mix which excessively increased the Si/Al ratio (Duxson et al., 2005), and without the help of elevated temperature curing, the process is hindered as seen in **Figure 5.30**. Moreover, with the addition of Si-rich RG further increases the Si/Al ratio, FA geopolymers cured at room temperature performed poorly at 7 days. However, there are large improvements in UCS after 28 days. With 50°C curing, FA specimens develop higher overall UCS, and the difference between the 7-days and 28-days specimens’ UCS was smaller.

On the other hand, in **Figure 5.31** it can be seen that S geopolymers develop high early strengths regardless of curing temperature. Only 20CG:50RG:30S specimens cured at 21°C at high L/P ratios showed a significant difference in UCS between 7-days and 28-days. As explained earlier, S geopolymers gain early strength mainly by the formation of CSH, which is independent of the Si/Al ratio. However, at 20CG:50RG:30S the high amount of Si may start to hinder the geopolymerization process due to excess unreacted compounds. This problem was not present in 50°C-cured S geopolymers. On the other hand, comparing all 7-days and 28-days UCS results show that the UCSs are increased or maintained after prolonged curing.

Interestingly, at low L/P values of 0.4 to 0.8, all the geopolymers perform relatively poorly, with UCS ranging from 500-800 kPa. This is attributed to insufficient L content which results in poor dissociation of precursor material to form cementitious compounds, regardless of heat treatment or prolonged curing. After reaching the optimum L/P ratio it is especially evident at 21°C curing that, S geopolymers outperforms their FA counterparts. In short, FA geopolymers require heat treatment to develop high UCS, whereas S geopolymers develop relatively high UCS values regardless of curing temperature.
5.8 Microstructural Analyses

While the correlation between material mixes, curing conditions, and UCS developments can be empirically determined via experimental data, it is also important to further understand the interactions between the many compounds in the material mixes, as many different solids and liquids were interacting to form the CG geopolymers described in this research. Scanning Electron Microscopy (SEM) imaging is a useful tool to observe the development of inter-particle bondings after a designated curing period. Similarly, Energy-dispersive X-ray Spectroscopy (EDS) can be used to determine the chemical composition of bonds formed by the alkaline activation of the many precursors used in this research.

5.8.1 CG+FA and CG+S Geopolymers

SEM imaging was used to observe the effects of alkaline activation on the cementitious matrices generated on a microstructural scale. Figure 5.32 demonstrates that prior to geopolymerisation, untreated CG particles (Figure 5.32a) have porous and jagged surfaces. The addition of S and FA strengthens the material by filling up the voids present and forming a solid matrix (Figure 5.32b). CG itself contains little to no cohesion (Arulrajah et al., 2014b), hence cementation is contributed by the chemical reactions between S and FA with the alkaline liquid activators. In the context of CG-geopolymers, CG can be considered as the material that forms the physical bulk of the mix, whereas S and FA act as chemical binders to hold the CG particles together. As S and FA interact differently with Na$_2$SiO$_3$ and NaOH, SEM was used to observe various CG-geopolymer samples. Figure 5.33 presents the 70CG:30S:0FA specimens produced at OLC. Figure 5.33(a) has an L ratio of 90Na$_2$SiO$_3$:10NaOH, Figure 5.33(b) 70Na$_2$SiO$_3$:30NaOH, and Figure 5.33(c) 50Na$_2$SiO$_3$:50NaOH. While the formation of cementitious materials can be observed in all three images, Figure 5.33(a) shows a smoother texture compared to Figure 5.33(b) and Figure 5.33(c). This is due to the gel produced by the relatively higher amount of Na$_2$SiO$_3$, while Figure 5.33(b) and Figure 5.33(c) have more corrugated matrices resulting from the dissolution of S by NaOH. There is also an abundance of unreacted S particles in Figure 5.33(a), implying that the matrix formed is not mainly from the breaking-down of S particles.
Figure 5.32 SEM of (a) untreated CG and (b) CG geopolymer cured at 50°C for 7 days (Kua et al., 2016b).

Figure 5.33 SEM of 70CG:30S:0FA mixes at OLC, cured at 50°C for 7 days, with different L ratios at: (a) 90Na$_2$SiO$_3$:10NaOH (b) 70 Na$_2$SiO$_3$:30NaOH (c) 50 Na$_2$SiO$_3$:50NaOH (Kua et al., 2016b).
Figure 5.34 presents the SEM results for the 70CG:30S:0FA specimen cured at room temperature (21°C) for 7 days while Figure 5.35 presents the SEM results for the 70CG:30S:0FA specimen but cured at 50 °C for 28 days. The effect of elevated curing temperature is evident when comparing Figure 5.34 to Figure 5.33. Both were made with the same mixes and compacted at OLC, but there are significant amounts of unreacted S present in the material in Figure 5.34 where the specimens were cured in room temperature (21°C) as opposed to 50°C. The effect of prolonged curing can be observed by comparing Figure 5.35 to Figure 5.33, where larger and defined matrices have formed as a result of extended reaction time.

Figure 5.34 SEM of 70CG:30S:0FA mixes at OLC, cured at 21°C for 7 days, with different L ratios at: (a) 90Na$_2$SiO$_3$:10NaOH (b) 70Na$_2$SiO$_3$:30NaOH (c) 50Na$_2$SiO$_3$:50NaOH (Kua et al., 2016b).
At 7-days curing, 70CG:15S:15FA mixes for 70Na$_2$SiO$_3$:30NaOH and 50Na$_2$SiO$_3$:50NaOH specimens display the lowest UCS values in their subset. **Figure 5.36(a)** was a 70CG:15S:15FA specimen stabilised with 90Na$_2$SiO$_3$:10NaOH while **Figure 5.36(b)** was a specimen stabilised with 50Na$_2$SiO$_3$:50NaOH. Strength development in **Figure 5.36(b)** might have been hindered by the simultaneous reaction of S and FA, whereby it is apparent that S particles are cemented to a FA particle. This supports Puertas et al. (2000)’s postulation that the coagulation resulting from many concurrently occurring reactions hinders diffusion hence reducing the reaction between the cementing agents and CG. On the other hand, it is apparent in **Figure 5.36(a)** that a relatively consistent matrix can be observed. This may be associated with the high amount of Na$_2$SiO$_3$ present in the mix, hence contributing to the increased UCS for 70CG:15S:15FA + 90Na$_2$SiO$_3$:10NaOH samples.

**Figure 5.35** SEM of 70CG:30S:0FA mixes at OLC, cured at 50°C for 28 days, with different L ratios at: (a) 90Na$_2$SiO$_3$:10NaOH (b) 70Na$_2$SiO$_3$:30NaOH (c) 50Na$_2$SiO$_3$:50NaOH (Kua et al., 2016b).
Figure 5.36 SEM of 70CG:15S:15FA mixes at OLC, cured at 50°C for 7 days, with different L ratios at: (a) 90 Na$_2$SiO$_3$ : 10NaOH (b) 50 Na$_2$SiO$_3$ : 50NaOH (Kua et al., 2016b).

5.8.2 CG+RHA Geopolymers

Figure 5.37 shows 3000×-magnified SEM images of CG-RHA-S geopolymers with different S contents, cured at different temperatures for 7 days. Figure 5.37(a) shows 70CG:30RHA samples cured at 21°C and 50°C. The formation of geopolymeric material could be observed in both specimens. However, at 21°C, RHA particles were found to be intact within the sample, meaning the RHA was not dissolved completely to form a geopolymeric material under this curing condition. On the other hand, elevated temperature curing catalyzed the dissociation of RHA particles to form a consistent
matrix. With the introduction of S in Figure 5.37(b), (c), and (d), under the same curing conditions of 21°C and 7 days, the development of denser geopolymeric matrices compared to 5.37(a) is observable. Side-by-side comparisons made with samples cured at 50°C indicated that at 21°C, partially reacted S could still be observed. Also, samples cured at 50°C developed denser geopolymeric matrices compared to their 21°C counterparts. This phenomenon is obvious in Figure 5.37(d), for the 70CG:30S mix, in which the sample cured at 21°C exhibited higher porosity compared to a separate specimen cured at 50°C.

Figure 5.38 shows 1000×-magnified SEM images of CG:RHA:S geopolymers and compares with the mixtures which achieve the lowest and highest UCS at 90 days respectively: 70CG:30RHA:0S (21°C) and 70CG:20RHA:10S (50°C). Figure 5.38(a) shows the surface of 70CG:30RHA:0S samples with different curing times. RHA particles could be abundantly found throughout the samples regardless of curing duration, indicating inefficient alkaline activation. A geopolymeric matrix could be seen from 60 days onwards which developed into a denser formation at 90 days, indicating an ongoing but slow geopolymerisation process. The geopolymeric material was also unable to fully coat the CG particle. On the other hand, in Figure 5.38(b), the strength development of 70CG:20RHA:10S as shown in Figure 6 was clearly reflected in the evolution of the geopolymeric formations captured throughout the designated curing durations. The amount of voids evidently diminished, and comparing the SEM images taken at 7 days and 90 days showed almost complete reduction of loose RHA and S particles to form a dense geopolymeric matrix. This highlights the importance of elevated temperature curing in promoting geopolymerisation in CG:RHA geopolymers by effectively dissociating the RHA particles.

70CG:10RHA:20S and 70CG:0RHA:30S samples showed slight drops in their UCS values from 60 days to 90 days. However, SEM images presented in Figure 5.39 showed that there were no significant differences between the geopolymeric matrices of both mixtures at 60 days and 90 days. As S was the dominant precursor in these mixtures, it was highly likely that S had fully dissociated hence any significant reactions cease to occur after 60 days. Therefore, the geopolymers displayed a near constant UCS value from 60 to 90 days.
Figure 5.37 SEM images of 7 days cured (a) 70CG:30RHA, (b) 70CG:20RHA:10S, (c) 70CG:10RHA:20S, (a) 70CG:30S specimens at various temperatures (Suksiripattanapong; Kua et. al. 2017).
Figure 5.38. SEM images of 70CG:20RHA:10S specimens cured at (a) 21°C, and (b) 50°C at different curing durations (Suksiripattanapong; Kua et. al. 2017).
5.8.3 CG+BA Geopolymers

The geopolymeric reactions occurring throughout the curing of the CG:BA:S geopolymers were observed by SEM to further understand the mechanical strength development in this material. Figure 5.40 displays specimens from the 70CG:20BA:10S blend, cured for 7 days under different L/P ratios. Figure 5.40(a), (b), and (c) have L/P ratios of 1.8, 2.0, and 2.2 respectively. By comparing the specimens cured at 21°C and 50°C, the 50°C samples evidently had more defined matrices. The geopolymeric material formed in Figure 5.40 (a) was inadequate to fully coat the CG particle, indicating that the L/P ratio was too low. The formations in Figure 5.40(b) and (c) were quite similar, indicating that the liquids were sufficient to react with the precursors. The drop in strength for specimens on the wet side of the OLC was caused by excessive pore pressure that hindered the compaction of the solid particles.
Figure 5.40 SEM of 7-days cured 70CG:10BA:20S specimens at L/P ratios of (a) 1.8, (b) 2.0, and (c) 2.2 (Arulrajah; Kua et. al., 2017).
Figure 5.41 SEM of OLC specimens comparing geopolymeric development of 7-days-cured specimens for (a) 70CG:30BA, (b) 70CG:20BA:10S, (c) 70CG:10BA:20S, and (d) 70CG:30S (Arulrajah; Kua et. al., 2017).
Figure 5.42 SEM of OLC specimens comparing geopolymeric development of 90-days-cured specimens for (a) 70CG:30BA, (b) 70CG:20BA:10S, (c) 70CG:10BA:20S, and (d) 70CG:30S (Arulrajah; Kua et. al., 2017).
Figure 5.43 Comparison of geopolymeric development in 70CG:20BA:10S and 70CG:10BA:20S specimens cured at 50°C for 7, 28, 60, and 90 days (Arulrajah; Kua et. al., 2017).
Figure 5.41 shows all four blends prepared at OLC and cured for 7 days at different temperatures. 50°C curing evidently created a geopolymeric material with a larger surface area. The geopolymers appear denser and had significantly less voids compared to the formations produced at 21°C. For the 50°C-cured specimens, note that relative to other specimens, there were many loose particles around the formations in Figure 5.41(a), which was the 70CG:30BA blend. This means the BA has not fully dissociated.

These observations can also be seen in Figure 5.42, which shows the specimens of the same blends cured for 90 days. 21°C samples appear to have rougher surfaces and many unreacted particles, particularly on Figure 5.42(a) and (b). This implies that at OLC, BA cannot dissociate adequately at 21°C. S does not require high curing temperatures to achieve accelerated geopolymerisation hence denser formations can be found from Figure 5.42(c) and (d) at 21°C. While the surfaces of the 50°C formations are similarly rough, the amount of observable loose particles and voids were evidently fewer. Figure 5.42(a) and (d) shows wide formations covering the whole image frame of the 50°C specimens, but voids were still present, hence their relatively mediocre UCS. Figure 5.42(b) shows a dense formation at 50°C, in contrast to the rough and cracked surface of the formation at 50°C for Figure 5.42(c).

Referring to Figure 5.43, which compared the 50°C samples of 70CG:10BA:20S and 70CG:20BA:10S at 7 and 90 days, the formations in the 70CG:10BA:20S specimens had relatively rougher surfaces, more obviously seen in Figure 5.43(c) and (d) in which the 70CG:20BA:10S specimens had relatively smoother surfaces. The rough surface may be the result of formation of a dense and heterogeneous paste as reported by Puertas et al. (2000) which deterred the formation of larger and denser geopolymeric substances.

Figure 5.44 shows the growth of fungus found throughout many samples cured at 21°C. These fungi typically grow in the voids where the geopolymeric substance cannot fully encapsulate the CG particles. Figure 5.44(a) and (b) shows the small patches of fungi (circled) growing on a 70CG:30S specimen cured for 90 days at 21°C. As S is an inorganic precursor, this demonstrates that the fungal growth only required exposed surfaces on the CG particles, even without the introduction of BA (which may contain trace amounts of unburnt organic cellulose). Figure 5.44(c) shows the typical fungus species growing on inadequately developed CG:BA:S geopolymers.
Figure 5.44 SEM of fungal growth in 70CG:30S specimens cured at 21°C for 90 days (Arulrajah; Kua et. al., 2017).
5.8.4 CG+RG Geopolymers

Energy-dispersive X-ray Spectroscopy (EDS) was used in conjunction with SEM imaging to analyse the geopolymeric reactions which occurred in the CG:RG geopolymers. While the geopolymeric interactions between FA, S, and the alkaline liquids have been discussed via SEM previously, it is important to ascertain how RG affects the geopolymeric mixes. While it has been established that introducing RG into the CG geopolymer resulted in an increase in UCS, it is important to determine if RG only contributed to the material strength mechanical via friction, or if the alkaline liquid leached silica from RG to form geopolymeric compounds.

EDS was used to scan the geopolymeric bonds occurring within the CG:RG geopolymers. **Table 5.13** compares the EDS results of 50CG:20RG:30P specimens cured for 7 days. The carbon content represents CG: if the detectable percentage of carbon is large, it means the geopolymeric material was not effective in encapsulating the CG particles. FA specimens contain trace amount of iron, whereas S specimens contain trace amounts of magnesium.

**Table 5.13** Comparison of EDS results done on 50CG:20RG:30P geopolymers cured for 7 days at different temperatures (Arulrajah; Kua et. al., 2017).

<table>
<thead>
<tr>
<th>Element</th>
<th>50CG:20RG:30FA, 7 days, 21°C</th>
<th>50CG:20RG:30FA, 7 days, 50°C</th>
<th>50CG:20RG:30S, 7 days, 21°C</th>
<th>50CG:20RG:30S, 7 days, 50°C</th>
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<tbody>
<tr>
<td>C</td>
<td>45.64 56.03 32.83 42.67 29.91 39.9 18.49 26.39</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>38.95 35.89 47.15 46.01 47.11 47.19 52.72 56.49</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>2.3 1.48 4.16 2.82 6.13 4.27 6.5 4.85</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>N.D. N.D. N.D. N.D. 0.66 0.43 1.03 0.73</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>2.98 1.63 3.82 2.21 1.25 0.74 1.99 1.26</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
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<tr>
<td>K</td>
<td>0.54 0.2 0.64 0.25 0.57 0.23 0.55 0.24</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>0.89 0.33 0.97 0.38 5.7 2.28 7.55 3.23</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.45 0.12 0.54 0.15 N.D. N.D. N.D. N.D.</td>
<td></td>
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<tr>
<td>Totals</td>
<td>100 100 100 100 100 100 100 100</td>
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</tr>
</tbody>
</table>
From Table 5.13, the percentage of carbon in FA geopolymers was higher than S geopolymers. However, at 50℃ the percentage of carbon is significantly reduced. Sodium, Aluminium, Silica, and Calcium levels in the geopolymeric compounds all showed increase at 50℃ curing, with the increase more prominent in FA mixes, thus validating that elevated temperature curing aids the formation of geopolymeric substances. The level of Na, Si and Ca are significantly higher in S geopolymers, indicating that the geopolymeric compound possesses a higher concentration of CSH and CASH gels. It can also be deduced that the geopolymeric formation in FA mixes rely on Al and Si whereas in S mixes, Ca and Si are the main components in geopolymerization.

Table 5.14 Comparison of EDS results done on CG:RG:S geopolymers with 20, 30, and 50% of RG.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
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<td>O</td>
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<tr>
<td>Mg</td>
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<td>Si</td>
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<td>N.D.</td>
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</table>

Table 5.14 shows that with the increase of RG in the dry material ratio, geopolymeric activities increased, as indicated by the increase in Na, Si, and Ca and the decrease of carbon percentage in the geopolymeric formation. A geopolymer without RG consisted of 8% of Si. This doubled to 16% when CG is replaced by 75% RG. An SEM image of an S geopolymer specimen in Figure 5.45 shows a large polygonal particle cemented by geopolymeric substances. The corresponding EDS results show significant difference in Silica concentration at (a) a large area of geopolymeric formation encompassing voids,
(b) a smaller area of relatively denser geopolymeric formation, and (c) an embedded particle. With the presence of voids in the geopolymer in (a), exposed CG are prone to detection. A concentrated scanning area as shown in (b) may better represent the typical element ratio in a geopolymeric compound. The polygonal particle in (c) does not contain carbon, and is largely composed of Si and O. RG and S are both polygonal but due to the trace amount of detectable Ca, it can be deduced that the particle is RG.

From the EDS results, it can be deduced that a fractional amount of RG dissolves and contributes to the formation of geopolymeric substances, but large RG particles can be found cemented by the geopolymeric compounds. The RG used in this study has particle sizes from 0.075–4.5 mm, and fine RG particles contain easily dissolvable Si which are highly pozzolanic (Corinaldesi et al., 2016). In a past study, fine RG particles less than 0.1 mm were found to be effective pozzolans with properties similar to FA (Carsana et al., 2014), whereas another report considered RG finer than 0.3 mm to be an effective precursor for geopolymerization (Corinaldesi et al., 2016). 10% of the RG used in this study is less than 0.3 mm in diameter, and hence acts to supplement the formation of geopolymeric substances, as shown in the difference of Si concentration in the geopolymeric formations with different percentages of RG in Table 5.12. The embedded glass particle supports Arulrajah et. al.’s (2016a) observation that in an RG geopolymer, the geopolymeric formation acts as a cementing agent that encapsulates and bonds RG particles together. Thus, the addition of RG in CG geopolymers creates a highly favourable environment for UCS development in which geopolymeric reaction is enhanced by the supplementation of Silica whereas large RG particles provide the mechanical strength to the mix by acting as an aggregate.

Due to the porous surface of CG particles, it is much more water absorbent whereas RG particles are smooth and non-porous hence reducing the overall water absorption rate of the mix (Corinaldesi et al., 2005). Hence with the reduction of CG in the geopolymer mix, the amount of free alkaline liquid which can react with the precursor increased dramatically hence the increase in UCS due to effective geopolymerization. Coupled with the high shear strength that characterizes fine RG, the addition of RG into CG geopolymers led to the increased UCS in the resultant material.
Figure 5.45 SEM of a 50CG:20RG:30S specimen cured for 7 days at 21°C, and EDS results on different areas of the geopolymeric formation (Arulrajah; Kua et. al., 2017).
5.9 Summary

The geopolymerisation of spent coffee ground (CG) essentially creates a CG geopolymer cement with high unconfined compressive strength (UCS). A 30% precursor replacement ratio produced CG geopolymers with good UCS. This chapter concludes that geopolymers derived from the industrial wastes fly ash (FA) and slag (S) were more effective in encapsulating CG, compared to the agricultural wastes rice husk ash (RHA) and bagasse ash (BA). CG+FA and CG+S geopolymers were found to produce high 7-days UCS under 50°C curing. By using S as a precursor, ambient curing temperatures produce specimens with UCS comparable to those cured at 50°C. On the contrary, CG+FA geopolymers cured at ambient temperature require long curing durations because of the high amount of silica present in these materials. This property is similarly shared by other ash precursors, namely CG+RHA and CG+BA geopolymers, in which elevated curing temperatures and a curing duration of 90 days were necessary to ensure proper strength development. Tentatively, S is a better precursor due to the high amounts of fast-reacting calcium oxide present in the material.

The requirement for elevated heat treatment for extended periods, especially for geopolymers utilising ash precursors, may be hard to replicate in real life scenarios. However, in Australia this may be achieved if construction is done in summer, where temperatures may reach 40°C continually. Tropical countries such as Thailand, or hot and arid countries such as the UAE may also consider the use of CG geopolymers for construction. Based on this chapter, the geopolymer mix design with 70CG:30S + 70Na₂SiO₃:30NaOH and L/P = 1.8 is recommended for subgrades, because it produces high strength with a relatively low L content. This mix design also has the potential to achieve high early strength due to the alkaline activation of S, and no heat treatment is required for this formula to achieve the required strength after 7 days of curing to meet performance benchmarks in terms of UCS.

The Na₂SiO₃:NaOH ratio is an interesting parameter in which the higher the NaOH in the mix, the faster the reaction which occurs in the geopolymer. This should be taken into consideration during real life scenarios, in which CG geopolymers may be batched in large mixing tank. A high input of NaOH may cause rapid flocculation of uncompacted materials, creating low-density materials with low cementitious properties, thus weakening the mix and decreasing the workability. Na₂SiO₃ not only supplements silica,
but acts as a retardant for excessive flocculation due to the elevated silica content which slows the geopolymerisation process. In this chapter, it was found that 70Na₂SiO₃:30NaOH is a good ratio for efficient geopolymerisation, thus validating many previous literatures that recommend a similar alkaline liquid composition.

RG was found to reduce the L/P ratio of CG geopolymers to achieve the saturation points for maximum UCS development. However, the dry unit weight of CG geopolymers increased proportionately along with the strength increase following the replacement of CG by RG. Experiments done in this chapter ascertained that RG not only provided mechanical strength to CG geopolymers due to high inter-particle friction, but also supplemented the formation of geopolymeric substances by providing readily dissolvable Si into the mix. The highest recorded UCS at 7 days is 10.86 MPa and corresponds with 20CG:50RG:30S at L/P =1.2 cured at 50°C.

This chapter demonstrated that CG+FA and CG+S geopolymers continually gain strength up to 28 days of curing. The successful implementation of a CG geopolymer mix would no doubt contribute to streamlining waste management efforts as large volumes of fill material are required annually to construct roads and highways across the globe. A green geopolymer encompassing waste materials CG, RG, FA, and S may no doubt promote a sustainable future.
CHAPTER 6

BEARING STRENGTH AND DEFORMATION PROPERTIES OF STABILISED SPENT COFFEE GROUND

6.1 Overview

California Bearing Ratio (CBR) is an important parameter for subgrade soils as it directly influences the thickness of overlaying pavement materials. The higher the subgrade CBR, the lower the construction cost of the overlaying pavement. On the other hand, resilience modulus (MR), is used to measure the resistance of a pavement material to compression and permanent deformation. A stiff material can distribute external force onto a large area of effect. Rutting easily occurs when the pavement material used have low MR, and may result in high maintenance costs. The road authority governing Victoria, Australia, uses CBR and MR as design parameters in their mechanistic pavement design method. Hence, recycled CG should undergo these tests to gain further insight on the viability of using these materials as a pavement fill. Ideally, these materials should replace aggregates as a subgrade material. Therefore, the benchmarks nominated by local road authorities were used to assess the suitability of using these recycled materials in construction. CG stabilised with FA and S up to 50% were tested for their CBR values. Additionally, CG+FA and CG+S geopolymers were selected to undergo further geotechnical testings due to the high 7-days UCS produced. Also, CG+RG geopolymers utilising FA and S as precursors were evaluated with the same suite of geotechnical tests to compare and assess the effects of RG on CG geopolymers.

6.2 California Bearing Ratio

6.2.1 Conventional Stabilisation of Spent Coffee Ground

Figure 6.1 summarizes the CBR values recorded in this study. CBR samples of unstabilised CG yielded an average value of 1.2%. Subsequently, CBR specimens were prepared for all mixes with 5% additive content based on the observation from the UCS
tests. However, all 5% mixes attain CBR values in the range of 1.2-1.4% only, and are below the value of 2% allocated by local road authorities as the design CBR value for materials at or below subgrade level (Vicroads, 2013). Since the amount of PC and L were limited to 5%, further stabilisation with higher contents of PC and L was deemed impractical due to the associated high economical costs for practical implementation in the field. Consequently, CBR specimens were prepared with high volumes of FA and S. Increasing the additive content to 10% for both FA and S results in elevated CBR values exceeding 2%, albeit marginally. Subsequent sets of specimens show that as FA and S increases, the CBR value increases as well. The highest achievable CBR value is 3.9% by 50CG+50S, which met the CBR > 2% requirements to qualify as a road subgrade fill. By further observing the results in the 10-50% additive content range, CG+S mixes exhibit higher CBR values compared to CG+FA mixes. For CG stabilised with orthodox geotechnical methods, by comparing the CBR values to their corresponding UCS values a relationship can be seen in which CBR increases with UCS.

![Figure 6.1](image_url) Figure 6.1 CBR values of CG stabilised with FA, S, PC, and L (modified from Kua et al. (2016a)).
To gauge the potential of CG geopolymers to be used practically, CBR tests were done in accordance with the worst-case scenario proposed in ASTM D1883-14, in which the specimens are immersed in water for 4 days and tested for their CBR values. Moreover, the specimens were soaked immediately after compaction to simulate the unlikely, but possibly scenario, in which flooding occurs directly after construction. The 4-days soaked test simulates severe pavement inundation by heavy rain, and measures the effects of prolonged exposure to water on pavement material strength. CG+FA and CG+S mixes at optimum L/P ratios were tested for their CBR values. A summary of results is shown in **Figure 6.2**. The CBR results further confirm the phenomenon that FA geopolymers require longer curing time compared to S geopolymers for proper strength development. NaOH also accelerates material strength gain, as administering 50Na$_2$SiO$_3$:50NaOH into
the CG+FA mix results in a CBR value of 12%, while the CBR value for specimens mixed with a 90Na$_2$SiO$_3$:10NaOH solution is only 4%.

On the other hand, CG+S geopolymers developed CBR values in the range of 18-30%. Australian pavement design guides recommended by Austroads and VicRoads stress the importance of subgrade CBR in influencing the overlaying pavement thickness, as stronger subgrades would typically require thinner pavement layers hence lower cost (Vicroads, 2013). Typically, subgrade strength is considered poor (2-4%), moderate (5-9%), or high (>10%) depending on the CBR values (ABC, 2006). Therefore CG+S geopolymers and the 50Na$_2$SiO$_3$:50NaOH CG+FA mix can be considered as strong subgrade materials, whereas the remaining CG+FA geopolymers can be categorised as moderately strong subgrade materials. Interestingly however, regardless of the ratio used, based on road authority specifications in the state of Victoria, Australia, all specimens pass the minimum acceptance requirement of 2% (Vicroads, 2013) for their usage as an embankment structural fill or subgrade material.

![Figure 6.3 CBR values for CG+RG geopolymers.](image-url)
The effect of RG on CG geopolymers can also be reflected by the high CBR values obtained by CG+RG geopolymers. **Figure 6.3** shows that FA mixes achieve improved CBR after the introduction of RG. CG supplementation resulted in all mixes achieving CBR values >10% hence considered strong subgrade material. Note that all design mixes shown in **Figure 6.3** used an alkaline liquid ratio of 70Na$_2$SiO$_3$:30NaOH after drawing rationale from Chapter 5 that this ratio provided a balance between strength development and geopolymeric reaction speed.

Additionally, the supplementation of RG not only increased material bearing strength, but also improved material quality by reducing linear swell after 4-days soaked conditions. At the alkaline liquid ratio of 70Na$_2$SiO$_3$:30NaOH, **Figure 6.4** shows the comparison between the recorded swell for CG geopolymers compared to CG+RG geopolymers compacted under modified Proctor energy. Evidently, increasing RG resulted in less material swell, with 50% RG specimens recording the lowest change of 0.08-0.30%, in contrast to CG+FA and CG+S mixes, which swelled by 5.57-5.92%. This can be likely attributed to the sponge-like morphology of CG particles which easily absorbs water, leading to pore pressure build-up and subsequent expansion of the material mix., which contrasts the dense RG particles.

**Figure 6.4** Swelling of CBR specimens corresponding to different design mixes.
### 6.3 Stiffness and Deformation Properties

#### 6.3.1 Geopolymerisation of Spent Coffee Ground

Table 6.1 Material mix specifications for RLT test specimens.

<table>
<thead>
<tr>
<th>Material Mix</th>
<th>Curing Temperature</th>
<th>Curing Period</th>
<th>Na$_2$SiO$_3$ :NaOH</th>
<th>L/P</th>
<th>Target bulk unit weight (kN/m$^3$)</th>
<th>UCS (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70CG+30FA</td>
<td>21°C</td>
<td>7 Days</td>
<td>90:10</td>
<td>1.9</td>
<td>12.0</td>
<td>616</td>
</tr>
<tr>
<td>70CG+30FA</td>
<td>21°C</td>
<td>7 Days</td>
<td>70:30</td>
<td>1.7</td>
<td>12.3</td>
<td>634</td>
</tr>
<tr>
<td>70CG+30FA</td>
<td>21°C</td>
<td>7 Days</td>
<td>50:50</td>
<td>1.7</td>
<td>12.1</td>
<td>576</td>
</tr>
<tr>
<td>70CG+30FA</td>
<td>21°C</td>
<td>28 Days</td>
<td>90:10</td>
<td>1.9</td>
<td>12.0</td>
<td>1040</td>
</tr>
<tr>
<td>70CG+30FA</td>
<td>21°C</td>
<td>28 Days</td>
<td>70:30</td>
<td>1.7</td>
<td>12.3</td>
<td>829</td>
</tr>
<tr>
<td>70CG+30FA</td>
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<td>28 Days</td>
<td>50:50</td>
<td>1.7</td>
<td>12.1</td>
<td>876</td>
</tr>
<tr>
<td>70CG+30FA</td>
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<td>7 Days</td>
<td>90:10</td>
<td>1.9</td>
<td>12.0</td>
<td>659</td>
</tr>
<tr>
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<td>50°C</td>
<td>7 Days</td>
<td>70:30</td>
<td>1.7</td>
<td>12.3</td>
<td>779</td>
</tr>
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<td>50°C</td>
<td>7 Days</td>
<td>50:50</td>
<td>1.7</td>
<td>12.1</td>
<td>956</td>
</tr>
<tr>
<td>70CG+30FA</td>
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<td>1.9</td>
<td>12.0</td>
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<tr>
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<td>28 Days</td>
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<td>1.7</td>
<td>12.3</td>
<td>1281</td>
</tr>
<tr>
<td>70CG+30FA</td>
<td>50°C</td>
<td>28 Days</td>
<td>50:50</td>
<td>1.7</td>
<td>12.1</td>
<td>1237</td>
</tr>
<tr>
<td>70CG+30S</td>
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<td>7 Days</td>
<td>90:10</td>
<td>2.0</td>
<td>13.8</td>
<td>775</td>
</tr>
<tr>
<td>70CG+30S</td>
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<td>7 Days</td>
<td>70:30</td>
<td>1.8</td>
<td>13.1</td>
<td>1096</td>
</tr>
<tr>
<td>70CG+30S</td>
<td>21°C</td>
<td>7 Days</td>
<td>50:50</td>
<td>1.8</td>
<td>12.5</td>
<td>1097</td>
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<tr>
<td>70CG+30S</td>
<td>21°C</td>
<td>28 Days</td>
<td>90:10</td>
<td>2.0</td>
<td>13.8</td>
<td>995</td>
</tr>
<tr>
<td>70CG+30S</td>
<td>21°C</td>
<td>28 Days</td>
<td>70:30</td>
<td>1.8</td>
<td>13.1</td>
<td>1282</td>
</tr>
<tr>
<td>70CG+30S</td>
<td>21°C</td>
<td>28 Days</td>
<td>50:50</td>
<td>1.8</td>
<td>12.5</td>
<td>1482</td>
</tr>
</tbody>
</table>

Remark: OLC = Optimum Liquid Content; UCS = Unconfined Compressive Strength

Table 6.1 summarizes the Optimum Liquid Content (OLC), target density, and the corresponding UCS of the selected mixes. UCS development observed during the current tests followed the trend reported previously in (Arulrajah et al., 2016b) and (Kua et al., 2016b). Regardless of curing temperature and duration, CG+S geopolymers show higher
UCS compared to CG+FA mixes. This is due to the higher amount of CaO in S, which reacts readily with Si$^{4+}$ and Al$^{3+}$ ions to form CSH (Wang et al., 2015), enabling mixes with S to achieve high early strengths. Mohammedinia et al. (Mohaddadinia et al., 2016) also reported a similar occurrence where S geopolymers outperform FA geopolymers. On the other hand, geopolymers cured at 50°C have higher strengths compared to those cured at 20°C, confirming that elevated curing temperatures increase the strengths of geopolymers with time (Chindaprasirt, 2011; Puertas et al., 2000), particularly in FA geopolymers with higher silica contents. The strengths of these geopolymers can be compared to UCS benchmarks set by various road authorities for subgrade materials. All selected mixes cured for 7 days met the Thailand Department of Highways’ minimum specification for subgrade materials, nominated at 294.20 kPa (Teerawattanasuk et al., 2015). S geopolymers cured for 7 days at 50°C and all 28 days-cured mixes fulfil the 800 kPa requirement set by Malaysia for low-volume-traffic roads (Awg Shahminan et al., 2014).

Figure 6.5 $E_{50}$ versus UCS for all CG+P mixes (Kua et al., 2017).
The secant modulus ($E_{50}$) of a material is defined as the ratio between 50% of material strength ($0.5 q_u$) and the corresponding strain percentage. In other words, it is the slope of the line between the origin and the point $0.5 q_u$ on the stress-strain curve (Lee et al., 2014). Geotechnical numerical analyses incorporating Hooke’s stress and strain laws commonly require soil stiffness parameters such as $E_{50}$ to simulate in-situ conditions and predict soil responses to variations in confining pressures (Cox and Mayne). The $E_{50}$ values of all mixes were calculated from their respective stress-strain curves obtained from the UCS tests. **Figure 6.5** presents the $E_{50}$, in MPa, of all the 24 CG-geopolymer specimens described in **Table 6.1**, versus their corresponding UCS. A linear relationship can be approximated to $E_{50} = 30UCS$. The low $E_{50}$ to UCS ratio of CG-geopolymers indicates that these materials have very low stiffness relative to other geopolymer-stabilised materials (Mohammadinia et al., 2015). It is also an indication that geopolymerisation drastically increases the UCS of CG-geopolymers compared to a relatively small enhancement in material stiffness.

**Figures 6.6 and 6.7** illustrate the results of RLT tests undertaken on the 24 specimens with different material mixes and curing conditions. **Figure 6.6** compares the resilient modulus of specimens cured at 21°C whereas **Figure 6.7** compares that of specimens cured at 50°C. In accordance to (AASHTO, 2007) a confining pressure of 41.4 kPa was applied to the first 5 stages, followed by 27.6 kPa for the next 5 stages, and finally 13.8 kPa for the remaining 5 stages. These different confining pressures are meant to simulate different stress states at varying depths. Within each 5 stage, axial stress values of 13.8 kPa, 27.6 kPa, 41.4 kPa, 55.2 kPa, and 68.9 kPa were applied for 100 cycles in each individual stage to simulate dynamic and cyclic traffic loadings.

The $M_R$ of untreated CG, compacted in the same manner as the geopolymer specimens, ranged from 4.8 to 8.2 MPa, implying very high compressibility. From both **Figures 6.6 and 6.7**, it is evident that geopolymerisation dramatically increases the $M_R$ of CG. The increase $M_R$ varies from mix to mix, and ranges from 48 to 150 MPa for 21°C-cured specimens as shown in **Figure 6.6**. All mixes cured at 21°C display a general trend, where S samples cured for 7 days have higher $M_R$ compared to FA samples cured under the same condition. As curing period is extended to 28 days, FA samples display relatively minimal change in $M_R$ whereas S samples show increased $M_R$. On the contrary, 50°C-cured specimens in **Figure 6.7** indicate that FA and S have almost similar $M_R$ as early as
7 days, implying that at an elevated curing temperature, FA specimens gain increased material stiffness. 50°C-cured specimens have M_R values from 56 to 123 MPa, which is a narrower range compared to the M_R of 21°C-cured specimens. The hydration process in FA geopolymers is accelerated by heat treatment, whereas S geopolymers can cure adequately at an ambient temperature and heat treatment is relatively ineffective towards S compared to FA.

Fascinatingly, at 50°C after 28 days of curing, the 70CG:30FA +90Na_2SiO_3:10NaOH, 70CG:30S +90Na_2SiO_3:10NaOH, and 70CG:30S +50Na_2SiO_3:50NaOH mixes have noticeably lower M_R as compared to the same specimen cured at 50°C for 7 days; Another observation was that the 70CG:30S +70Na_2SiO_3:30NaOH specimens registered the highest M_R regardless of curing temperature, but 50°C curing decreased the M_R of the mix in question slightly. The above findings show that while CG undergoing geopolymerisation increase in strength over time, their stiffness will not increase proportionately hence may maintain a certain degree of ductility, depending on the geopolymeric mix used. Some CG-geopolymers may even gain increased ductility over time, as seen from mixes with lower M_R but higher UCS after 28 days of curing. Evidently, geopolymerisation improves the strength properties of a parent material greatly, but the development of material stiffness does not necessarily increase proportionately with material strength (Mohammadinia et al., 2016).
Figure 6.6 $M_R$ results for untreated CG compared to CG+FA and CG+S geopolymers cured at 21°C for (a) 7 days and (b) 28 days (Kua et al., 2017).
Figure 6.7 $M_R$ results for untreated CG compared to CG+FA and CG+S geopolymers cured at 50°C for (a) 7 days and (b) 28 days (Kua et al., 2017).
External stress conditions also affect the $M_R$ of the geopolymers. Generally, the effect of confining pressure on $M_R$ is small: Throughout the stress stages, confining pressure decreases gradually after every 5 stage, but the graph readings in Figure 6.6 & 6.7 do not decline downwards, mostly maintaining a horizontal trend. However, $M_R$ is sensitive to the change in applied axial stress for most specimens: The higher the axial stress, the higher the $M_R$. By referring to the stress-strain relationship used to derive $M_R$ (Huang, 1993):

$$M_R = \frac{\sigma_d}{\varepsilon_r} \quad (1)$$

where $\sigma_d$ is the deviator stress applied on the sample and $\varepsilon_r$ is the recoverable strain experienced by the sample, this means that the recoverable strain remains almost constant while the applied axial stress increases. On the other hand, some mixes, such as 70CG:30FA +70Na$_2$SiO$_3$:30NaOH cured for 7 days at 21°C are not sensitive to changes in axial stress, indicating that the recoverable strain of these materials varies proportionately to axial stress, in which the higher applied stress results in the higher recoverable strain. Specimens manifesting the latter property for their $M_R$ are consequently more ductile and compressible, regardless of material strength.

Bulk stress can be defined as the sum of all normal inward forces acting on an object. Figures 6.8 and 6.9 show the relationship between bulk stress ($\theta = \sigma_1 + \sigma_2 + \sigma_3 = 2\sigma_3 + \sigma_d$) and resilient modulus at 21°C and 50°C respectively. By referring to the best-fit curves, many specimens showed a trend in which $M_R$ increases with bulk stress, but some specimens showed an inverse relationship. Specimens with the former property behave similarly to soils (Han and Vanapalli, 2016b) and stabilised road construction materials (Puppala et al., 2011), in which the increase in bulk stress results in more compression and hence development of a denser and stiffer material. The latter trend is reported in fine-grained soils (Ng et al., 2013). Factors that usually contribute to reduction $M_R$ include decrease in inter-particle suction and breakage of inter-particle bonds due to the increased exertion of external pressure (Sivakumar et al., 2013).
Figure 6.8 $M_R$ versus bulk stress for specimens cured at 21°C for (a) 7 days and (b) 28 days (Kua et al., 2017).

In the context of this experiment, CG-geopolymers experiencing increased $M_R$ with increased bulk stress (i.e., steeper slopes) have become stiffer, whereas those experiencing negative slopes display highly increased recoverable strain (hence the low $M_R$) as bulk stress increases, hence are relatively elastic. The resilient modulus-bulk stress relationships for specimens shown in Figure 6.9(b) developed relatively gentle-sloping best-fit curves that almost approach horizontal. These specimens have $M_R$ values that are insensitive to the increase in bulk stress, also implying higher ductility and
compressibility, as recoverable strain is proportional to variations in externally exerted stresses. Comparing the curves in Figure 6.9(b), where steeper gradients can be found, to Figure 6.9(b), it is evident that heat treatment improves the ductility of CG-geopolymers tentatively in the long term.

**Figure 6.9** $M_R$ versus bulk stress for specimens cured at 50°C for (a) 7 days and (b) 28 days (Kua et al., 2017).

The collection of empirical experiment data would optimally result in the most accurate readings, but in scenarios where cost and time are limited, predictions of material properties, given a set of easily obtained yet limited data, would be economical, provided
that the prediction is close to field values. The best-fit curves in Figures 6.8 and 6.9 are derived from the Bulk Stress Model proposed by AASHTO to predict the $M_R$ of granular materials (AASHTO, 2007), as shown in equation (2):

$$M_R = k_1 \times \theta^{k_2} \quad (2)$$

where $M_R$ is resilient modulus, $\theta$ is bulk stress, and $k_1$ and $k_2$ are regression constants. This model, along with the 3-Parameter Model, is an empirical formula (Han and Vanapalli, 2016a) used to predict the $M_R$ for base, sub-base (Puppala et al., 2011), and subgrade materials (Sadrossadat et al., 2016). From Figure 6.8, 21°C-cured specimens follow the Bulk Stress Model prediction more closely compared to the 50°C-cured samples in Figure 6.9. While the projection for the 70CG:30S + 70Na$_2$SiO$_3$:30NaOH specimen in Figure 6.8(a) is highly inaccurate, the Bulk Stress Model projections for remaining specimens in Figure 6.9(a) and (b) are relatively close to measured values. On the contrary, the 50°C specimens in Figure 6.9(a) have a wide range of $M_R$ that is badly represented by the best-fit curves. However, referring to Figure 6.9(b), long-term elevated temperature curing slightly brings the range of $M_R$ closer to the best-fit curves.

The Bulk Stress Model’s limitation is that it does not differentiate confining stress with deviator stress whereas there are sequences in (AASHTO, 2007) that has the same bulk stress but with different confining and axial stresses. Also, the isotropy of the CG-geopolymers varies as curing temperature increases, hence differentiation between confining stress and axial stress is critical in prediction of $M_R$ for CG-geopolymers with high anisotropy, because the deviator stress acts on only one axis of the specimen. Many sequences in (AASHTO, 2007) yield the same bulk stresses, but at earlier stages, the confining stress is higher than the axial stress, while at later stages the inverse occurs. In these two scenarios the bulk stress would be the same but result in very different $M_R$ readings as the major axis of the cylindrical specimens is subject to different axial stresses, as seen in many specimens in Figure 6.9(a) where one bulk stress value may have two different $M_R$ with a large range of difference.

The previously mentioned 3-Parameter Model, proposed by Puppala et al. (Puppala et al., 2011), addresses this problem by differentiating confining stress and axial stress. This model, written as Equation (3) considers atmospheric pressure ($\sigma_{atm}$), confining stress ($\sigma_3$), and deviator stress ($\sigma_d$):

$$M_R = k_1 \times \theta^{k_2} \quad (2)$$
\[
\frac{M_R}{\sigma_{atm}} = k_1 \times \left(\frac{\sigma_3}{\sigma_{atm}}\right)^{k_2} \times \left(\frac{\sigma_6}{\sigma_{atm}}\right)^{k_3}
\]  

(3)

By determining the constants \(k_1\), \(k_2\), and \(k_3\) using the least-squares method, prediction of \(M_R\) can be made. Figures 6.10 and 6.11 compare the laboratory-measured \(M_R\) to the \(M_R\) obtained from the Bulk Stress Model and the 3-Parameter Model, showing that the 3-Parameter Model can more accurately predict the \(M_R\) of these geopolymers. Figure 6.10(b) shows that the Bulk Stress Model predicts the \(M_R\) of the specimens with higher accuracy compared to the other group in Figures 6.10 and 6.11, but the 3-Parameter Model still performs slightly better. Figure 6.11 indicates that the 3-parameter model greatly improves prediction accuracy for 50°C-cured samples. As seen in Figure 6.10, the Bulk Stress Model performs more acceptably for specimens cured at 21°C whereas in Figure 6.11, applying the Bulk Stress Model to 50°C-cured specimens results mainly in overestimation of the resilient modulus. Hence, in scenarios where limited data is available, the Bulk Stress Model can still be used to predict the \(M_R\) of 21°C-cured CG-geopolymers with relatively good accuracy. Overall, the 3-Parameter Model provides a more accurate prediction for these CG-geopolymers, regardless of curing conditions.

Figure 6.10 Comparison of measured \(M_R\) results versus predicted \(M_R\) values for specimens cured at 21°C for (a) 7 days and (b) 28 days (Kua et al., 2017).
Table 6.2 lists the Bulk Stress Model constants $k_1$ and $k_2$ for all material combinations. Table 6.3 displays the constants $k_1$, $k_2$ and $k_3$ of each material for the 3-Parameter Model. The least-squares method was used in both cases to find the regression constants. Although they have the same material composition and curing temperature, the 7 days-cured specimens have different constants compared to the 28 days-cured specimens, indicating that the same constants cannot be used to predict the $M_R$ of a material at different curing durations and temperatures. Currently, researchers still find $M_R$ to be highly unpredictable (Han and Vanapalli, 2016a; Han and Vanapalli, 2016b; Sadrossadat et al., 2016) and this parameter needs to be considered on a case-by-case basis. Note that Equations (2) and (3), which were used in this study to predict the $M_R$ of CG-geopolymers, were developed empirically from data gathered from a large number of soil specimens (Han and Vanapalli, 2016a).
Table 6.2 Empirical regression parameters of bulk-stress model for all material mixes (Kua et al., 2017).

<table>
<thead>
<tr>
<th>Material Mix</th>
<th>( k_1 \times 10^3 )</th>
<th>( k_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CG</td>
<td>1.641</td>
<td>0.274</td>
</tr>
<tr>
<td>7 days, 21°C, 70CG:30FA, 90Na₂SiO₃:10NaOH</td>
<td>20.457</td>
<td>0.271</td>
</tr>
<tr>
<td>7 days, 21°C, 70CG:30FA, 70Na₂SiO₃:30NaOH</td>
<td>29.703</td>
<td>0.145</td>
</tr>
<tr>
<td>7 days, 21°C, 70CG:30FA, 50Na₂SiO₃:50NaOH</td>
<td>37.837</td>
<td>0.093</td>
</tr>
<tr>
<td>7 days, 21°C, 70CG:30S, 90Na₂SiO₃:10NaOH</td>
<td>36.762</td>
<td>0.164</td>
</tr>
<tr>
<td>7 days, 21°C, 70CG:30S, 70Na₂SiO₃:30NaOH</td>
<td>56.467</td>
<td>0.143</td>
</tr>
<tr>
<td>7 days, 21°C, 70CG:30S, 50Na₂SiO₃:50NaOH</td>
<td>40.559</td>
<td>0.219</td>
</tr>
<tr>
<td>7 days, 50°C, 70CG:30FA, 90Na₂SiO₃:10NaOH</td>
<td>29.736</td>
<td>0.215</td>
</tr>
<tr>
<td>7 days, 50°C, 70CG:30FA, 70Na₂SiO₃:30NaOH</td>
<td>20.936</td>
<td>0.316</td>
</tr>
<tr>
<td>7 days, 50°C, 70CG:30FA, 50Na₂SiO₃:50NaOH</td>
<td>36.086</td>
<td>0.226</td>
</tr>
<tr>
<td>7 days, 50°C, 70CG:30S, 90Na₂SiO₃:10NaOH</td>
<td>111.517</td>
<td>-0.051</td>
</tr>
<tr>
<td>7 days, 50°C, 70CG:30S, 70Na₂SiO₃:30NaOH</td>
<td>50.128</td>
<td>0.155</td>
</tr>
<tr>
<td>7 days, 50°C, 70CG:30S, 50Na₂SiO₃:50NaOH</td>
<td>45.499</td>
<td>0.174</td>
</tr>
<tr>
<td>28 days, 21°C, 70CG:30FA, 90Na₂SiO₃:10NaOH</td>
<td>59.287</td>
<td>0.029</td>
</tr>
<tr>
<td>28 days, 21°C, 70CG:30FA, 70Na₂SiO₃:30NaOH</td>
<td>129.652</td>
<td>-0.159</td>
</tr>
<tr>
<td>28 days, 21°C, 70CG:30FA, 50Na₂SiO₃:50NaOH</td>
<td>25.367</td>
<td>0.227</td>
</tr>
<tr>
<td>28 days, 21°C, 70CG:30S, 90Na₂SiO₃:10NaOH</td>
<td>45.143</td>
<td>0.190</td>
</tr>
<tr>
<td>28 days, 21°C, 70CG:30S, 70Na₂SiO₃:30NaOH</td>
<td>51.623</td>
<td>0.197</td>
</tr>
<tr>
<td>28 days, 21°C, 70CG:30S, 50Na₂SiO₃:50NaOH</td>
<td>71.374</td>
<td>0.072</td>
</tr>
<tr>
<td>28 days, 50°C, 70CG:30FA, 90Na₂SiO₃:10NaOH</td>
<td>45.014</td>
<td>0.163</td>
</tr>
<tr>
<td>28 days, 50°C, 70CG:30FA, 70Na₂SiO₃:30NaOH</td>
<td>27.136</td>
<td>0.270</td>
</tr>
<tr>
<td>28 days, 50°C, 70CG:30FA, 50Na₂SiO₃:50NaOH</td>
<td>48.749</td>
<td>0.070</td>
</tr>
<tr>
<td>28 days, 50°C, 70CG:30S, 90Na₂SiO₃:10NaOH</td>
<td>60.057</td>
<td>0.038</td>
</tr>
<tr>
<td>28 days, 50°C, 70CG:30S, 70Na₂SiO₃:30NaOH</td>
<td>46.598</td>
<td>0.164</td>
</tr>
<tr>
<td>28 days, 50°C, 70CG:30S, 50Na₂SiO₃:50NaOH</td>
<td>37.353</td>
<td>0.116</td>
</tr>
</tbody>
</table>
Table 6.3 Empirical regression parameters of three-parameter model for all material mixes (Kua et al., 2017).

<table>
<thead>
<tr>
<th>Material Mix</th>
<th>k₁ ($\times 10^3$)</th>
<th>k₂</th>
<th>k₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>CG</td>
<td>0.083</td>
<td>0.326</td>
<td>-0.120</td>
</tr>
<tr>
<td>7 days, 21°C, 70CG:30FA, 90Na₂SiO₃:10NaOH</td>
<td>1.032</td>
<td>0.084</td>
<td>0.217</td>
</tr>
<tr>
<td>7 days, 21°C, 70CG:30FA, 70Na₂SiO₃:30NaOH</td>
<td>0.698</td>
<td>0.124</td>
<td>0.001</td>
</tr>
<tr>
<td>7 days, 21°C, 70CG:30FA, 50Na₂SiO₃:50NaOH</td>
<td>0.616</td>
<td>-0.046</td>
<td>0.117</td>
</tr>
<tr>
<td>7 days, 21°C, 70CG:30S, 90Na₂SiO₃:10NaOH</td>
<td>0.952</td>
<td>0.022</td>
<td>0.149</td>
</tr>
<tr>
<td>7 days, 21°C, 70CG:30S, 70Na₂SiO₃:30NaOH</td>
<td>1.263</td>
<td>0.006</td>
<td>0.125</td>
</tr>
<tr>
<td>7 days, 21°C, 70CG:30S, 50Na₂SiO₃:50NaOH</td>
<td>1.516</td>
<td>0.052</td>
<td>0.207</td>
</tr>
<tr>
<td>7 days, 50°C, 70CG:30FA, 90Na₂SiO₃:10NaOH</td>
<td>1.062</td>
<td>-0.052</td>
<td>0.323</td>
</tr>
<tr>
<td>7 days, 50°C, 70CG:30FA, 70Na₂SiO₃:30NaOH</td>
<td>1.378</td>
<td>0.049</td>
<td>0.314</td>
</tr>
<tr>
<td>7 days, 50°C, 70CG:30FA, 50Na₂SiO₃:50NaOH</td>
<td>1.381</td>
<td>0.131</td>
<td>0.093</td>
</tr>
<tr>
<td>7 days, 50°C, 70CG:30S, 90Na₂SiO₃:10NaOH</td>
<td>0.773</td>
<td>-0.032</td>
<td>-0.063</td>
</tr>
<tr>
<td>7 days, 50°C, 70CG:30S, 70Na₂SiO₃:30NaOH</td>
<td>1.274</td>
<td>0.007</td>
<td>0.190</td>
</tr>
<tr>
<td>7 days, 50°C, 70CG:30S, 50Na₂SiO₃:50NaOH</td>
<td>1.276</td>
<td>0.023</td>
<td>0.177</td>
</tr>
<tr>
<td>28 days, 21°C, 70CG:30FA, 90Na₂SiO₃:10NaOH</td>
<td>0.675</td>
<td>-0.079</td>
<td>0.112</td>
</tr>
<tr>
<td>28 days, 21°C, 70CG:30FA, 70Na₂SiO₃:30NaOH</td>
<td>0.485</td>
<td>-0.076</td>
<td>-0.103</td>
</tr>
<tr>
<td>28 days, 21°C, 70CG:30FA, 50Na₂SiO₃:50NaOH</td>
<td>0.979</td>
<td>0.079</td>
<td>0.168</td>
</tr>
<tr>
<td>28 days, 21°C, 70CG:30S, 90Na₂SiO₃:10NaOH</td>
<td>1.392</td>
<td>0.136</td>
<td>0.038</td>
</tr>
<tr>
<td>28 days, 21°C, 70CG:30S, 70Na₂SiO₃:30NaOH</td>
<td>1.715</td>
<td>0.091</td>
<td>0.144</td>
</tr>
<tr>
<td>28 days, 21°C, 70CG:30S, 50Na₂SiO₃:50NaOH</td>
<td>1.099</td>
<td>0.081</td>
<td>-0.013</td>
</tr>
<tr>
<td>28 days, 50°C, 70CG:30FA, 90Na₂SiO₃:10NaOH</td>
<td>1.188</td>
<td>0.055</td>
<td>0.123</td>
</tr>
<tr>
<td>28 days, 50°C, 70CG:30FA, 70Na₂SiO₃:30NaOH</td>
<td>1.357</td>
<td>0.180</td>
<td>0.082</td>
</tr>
<tr>
<td>28 days, 50°C, 70CG:30FA, 50Na₂SiO₃:50NaOH</td>
<td>0.714</td>
<td>0.076</td>
<td>-0.046</td>
</tr>
<tr>
<td>28 days, 50°C, 70CG:30S, 90Na₂SiO₃:10NaOH</td>
<td>0.725</td>
<td>-0.130</td>
<td>0.196</td>
</tr>
<tr>
<td>28 days, 50°C, 70CG:30S, 70Na₂SiO₃:30NaOH</td>
<td>1.228</td>
<td>0.031</td>
<td>0.149</td>
</tr>
<tr>
<td>28 days, 50°C, 70CG:30S, 50Na₂SiO₃:50NaOH</td>
<td>0.730</td>
<td>-0.0003</td>
<td>0.126</td>
</tr>
</tbody>
</table>
6.2.2 RG as a Supplementary Filler

RLT tests were done on CG+RG geopolymers with the maximum RG replacement ratio to show the difference in stiffness between CG and CG+RG geopolymers. Figure 6.12 summarises the $M_R$ values of geopolymers with FA as a precursor. At 7 days, although 21°C FA geopolymers have a slow reaction rate, the inclusion of RG particles essentially ensures that the material possessed comparable stiffness to 50°C specimens. With the inclusion of RG, the $M_R$ of FA geopolymers can increase from 20 to 100 MPa at different stress states, indicating that RG stiffened the material mix. In contrast to CG+FA geopolymers, CG+RG+FA geopolymers developed relatively significant strength increase after 28 days of curing. At 28 days, CG+RG geopolymers become more responsive to changes in external pressure compared to 7-days cured specimens as the geopolymeric reactions have mostly manifested, on top of RG providing reinforcement to the material matrix. This occurrence is evident in the 80 MPa difference in $M_R$ for the 50°C 20CG:50RG:30FA specimen. Elevated temperature curing also corresponds with heightened stiffness, as all FA geopolymers cured at 50°C have higher $M_R$ compared to their 21°C counterparts. However, the inclusion of RG minimised the influence of elevated temperature curing. At 7 days, although 21°C FA geopolymers have a slow reaction rate, the inclusion of RG particles essentially ensures that the material possessed comparable stiffness to 50°C specimens.

On the other hand, with S as the precursor, CG and CG+RG geopolymers have a very distinctive difference in $M_R$, as shown in Figure 6.13. Note that at 7 days, CG+RG geopolymers can achieve a range of MR from 200 to 350 MPa, whereas at 28 days, a range of 200 to 400 MPa was recorded. The difference in MR between CG and CG+RG geopolymers is also more evident as CG+RG geopolymers exhibited higher stiffness regardless of curing temperature. Apart from the 7-days 21°C 20CG:50RG:30S specimen which showed lower response, to external stress variations, the $M_R$ of all CG+RG geopolymers increased as the applied axial stress increased. The lower response to external stress corresponds with incomplete geopolymerisation whereas the inverse corresponds to the positive effects of RG on increasing the stiffness of CG geopolymer. However, unlike CG+S geopolymers which gains ductility if cured properly (Kua et al., 2017), CG+RG+S specimens harden with time, regardless of curing conditions. This may be attributed to the replacement of highly compressible CG by RG particles, thus
contributing to a very stiff matrix when the geopolymerisation process cemented CG and RG particles together.

Figure 6.12 Comparison of $M_R$ for CG+FA and CG+RG+FA geopolymers.
Figure 6.13 Comparison of $M_R$ for CG+S and CG+RG+S geopolymers.
After undergoing RLT tests, the UCS of the 100 dia. x 200 height cylindrical specimens were evaluated. The influence of RG on material ductility can be further explained by comparing the stress strain curves of these various CG+RG geopolymers as summarised in Figure 6.14. It can be seen that ductility decreased as the amount of RG in the mix increased. 21°C specimens failed at 1.5% to 11% strain, whereas 50°C specimens failed at 1.5% to 10% strain. In Figure 6.14(a) at 21°C curing temperature for 7 days, FA geopolymers are very ductile, but can only withstand low axial stress. This observation can be explained by the partially reacted aluminosilicates in FA at a low curing temperature. The aluminosilicates have been reconstituted to form a viscous geopolymeric paste but has yet realigned to form strong CSH and NASH compounds due to a slow reaction rate induced by a low temperature environment (Khan et al., 2016; Oh et al., 2010). On the other hand, as RG increased, the geopolymers become brittle but possesses relatively high compressive strengths. The stress-strain curves highlighted the significance of using S as a precursor in room temperature, as early high UCS can be achieved due to rapid geopolymerisation. A combination of CG+RG+S ensures high strength development when RG is at 50%, but the material becomes brittle akin to concrete or even ceramics. On the other hand, in Figure 6.14(b), elevated temperature curing unsurprisingly improved the UCS of the specimens, but for FA geopolymers, material ductility was mostly retained. However, as CG geopolymers consists of cemented granules, this group of materials are still considered brittle relative to malleable material such as metal (Nazari et al., 2014). Therefore, the stress-strain curves of CG geopolymers do not possess any prominent yield points.

Conversely, S geopolymers became stronger but the strain in which the specimens failed were from 1.5% to 4%. 20CG:50RG:30S specimens’ ductility remained constant regardless of curing temperature, albeit gaining higher compressive strength. As it is known from the previous chapter that S geopolymers can achieve high UCS independent of curing temperature, it is interesting to note that elevated curing temperature caused significant decrease in material ductility in CG+RG specimens despite a relatively small increment in UCS. This finding contrasted the previous section in which properly cured CG+S geopolymers were reported to slightly gain ductility after 50°C curing. As CG is a highly compressible material, it can be postulated that a CG+S geopolymer is relatively ductile due to CG. As RG replaces CG in the mix, the geopolymeric material matrix
become dense and stiff due to the hard silica compounds present in RG. Coupled with the rapid setting S geopolymer in elevated temperatures, CG+RG mixes consequently loses ductility.

**Figure 6.14** Influence of RG on stress-strain behaviour of CG geopolymers.
Comparing both Figure 6.14 (a) and (b), S geopolymers cured at 21°C with an RG replacement ratio of 20-35% would be a balanced mix which can be practically used in the field, because albeit not achieving the highest UCS and stiffness in the design mix group, it provides satisfactory UCS while not compromising material ductility. Elevated temperature curing would not be recommended for CG+RG+S geopolymers as it does not significantly contribute to strength gain and may decrease material durability.

As discussed in the previous section, the relationship between the bulk stress exerted on an RLT specimen and the resulting resilience modulus reflects the flexibility of the material. Increasing the bulk stress applied on a stiff material results in proportionate increase in $M_R$ because recoverable strain is not affected by the compression due to bulk stress. On the other hand, increasing bulk stress resulting in near constant $M_R$ may mean the material is very compressible but also elastic, as recoverable strain increases proportionately with external stress. From Figure 6.15, CG+RG+S geopolymers are much stiffer compared to CG+S geopolymers even at 7 days, whereas CG+RG+FA geopolymers show lower stiffness, with 20CG:50RG:30FA cured for 28 days even displaying good elasticity as shown by a negative gradient in Figure 6.15(b) (Kua et al., 2017). Nevertheless, compared to CG geopolymers in terms of predictability, CG+RG geopolymers do not show any improvements because of similar amount of inconsistencies between the the bulk stress-$M_R$ relationship.

Figure 6.16 and Figure 6.17 summarises the results from applying the aforementioned bulk-stress model and 3-parameter model respectively on CG+RG specimens. Once again, the bulk-stress model showed inaccuracy in predicting the $M_R$ of these specimens, whereas the 3-parameter model more correctly represents the measure $M_R$ results. From Figure 6.16 (a), at the early stage, 21°C-cured specimens are more unpredictable compared to 50°C specimens. This may be due to the inconsistent curing rate at 21°C as opposed to accelerated curing at 50°C. However, if specimens are left to cure for 28 days as shown in Figure 6.16(b), the inconsistencies are less apparent. High-temperature curing for long durations further increased result and predictability as seen in Figure 6.17. Using the least square method, the empirically obtained Bulk-Stress Model constants $k_1$ and $k_2$; and the constants $k_1$, $k_2$ and $k_3$ of the 3-Parameter Model for 20CG:50RG:30P mixes were obtained and summarised in Table 4.
Figure 6.15 $M_R$ versus applied bulk stress for (a) 7-days cured and (b) 28-days cured CG+RG geopolymers.
Figure 6.16 Comparison of measured $M_R$ results versus predicted Bulk Stress Model $M_R$ values for CG+RG geopolymers.
Figure 6.17 Comparison of measured $M_R$ results versus predicted 3-Parameter Model $M_R$ values for CG+RG geopolymers.
Table 6.4 Empirical regression constants of CG+RG geopolymers corresponding with
the Bulk-Stress Model and 3-Parameter Model.

<table>
<thead>
<tr>
<th>Material Mix</th>
<th>$k_1$</th>
<th>$k_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CG (Kua et. al., 2017)</td>
<td>1.641 × 10³</td>
<td>0.274</td>
</tr>
<tr>
<td>7 days, 21°C, 70CG:30FA, 70Na₂SiO₃:30NaOH</td>
<td>48.440 × 10³</td>
<td>0.191</td>
</tr>
<tr>
<td>7 days, 21°C, 70CG:30S, 70Na₂SiO₃:30NaOH</td>
<td>36.769 × 10³</td>
<td>0.265</td>
</tr>
<tr>
<td>7 days, 50°C, 70CG:30FA, 70Na₂SiO₃:30NaOH</td>
<td>100.866 × 10³</td>
<td>0.154</td>
</tr>
<tr>
<td>7 days, 50°C, 70CG:30S, 70Na₂SiO₃:30NaOH</td>
<td>8.460 × 10³</td>
<td>0.695</td>
</tr>
<tr>
<td>28 days, 21°C, 70CG:30FA, 70Na₂SiO₃:30NaOH</td>
<td>164.608 × 10³</td>
<td>-0.007</td>
</tr>
<tr>
<td>28 days, 21°C, 70CG:30S, 70Na₂SiO₃:30NaOH</td>
<td>26.648 × 10³</td>
<td>0.379</td>
</tr>
<tr>
<td>28 days, 50°C, 70CG:30FA, 70Na₂SiO₃:30NaOH</td>
<td>61.203 × 10³</td>
<td>0.333</td>
</tr>
<tr>
<td>28 days, 50°C, 70CG:30S, 70Na₂SiO₃:30NaOH</td>
<td>38.789 × 10³</td>
<td>0.427</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material Mix</th>
<th>$k_1$</th>
<th>$k_2$</th>
<th>$k_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 days, 21°C, 70CG:30FA, 70Na₂SiO₃:30NaOH</td>
<td>1.505 × 10³</td>
<td>0.172</td>
<td>-0.005</td>
</tr>
<tr>
<td>7 days, 21°C, 70CG:30S, 70Na₂SiO₃:30NaOH</td>
<td>1.696 × 10³</td>
<td>0.211</td>
<td>-0.014</td>
</tr>
<tr>
<td>7 days, 50°C, 70CG:30FA, 70Na₂SiO₃:30NaOH</td>
<td>2.474 × 10³</td>
<td>0.059</td>
<td>0.090</td>
</tr>
<tr>
<td>7 days, 50°C, 70CG:30S, 70Na₂SiO₃:30NaOH</td>
<td>5.475 × 10³</td>
<td>0.321</td>
<td>0.407</td>
</tr>
<tr>
<td>28 days, 21°C, 70CG:30FA, 70Na₂SiO₃:30NaOH</td>
<td>1.490 × 10³</td>
<td>-0.009</td>
<td>-0.037</td>
</tr>
<tr>
<td>28 days, 21°C, 70CG:30S, 70Na₂SiO₃:30NaOH</td>
<td>2.568 × 10³</td>
<td>0.151</td>
<td>0.253</td>
</tr>
<tr>
<td>28 days, 50°C, 70CG:30FA, 70Na₂SiO₃:30NaOH</td>
<td>4.509 × 10³</td>
<td>0.084</td>
<td>0.293</td>
</tr>
<tr>
<td>28 days, 50°C, 70CG:30S, 70Na₂SiO₃:30NaOH</td>
<td>4.873 × 10³</td>
<td>0.232</td>
<td>0.177</td>
</tr>
</tbody>
</table>

6.4 Summary

The Australian road authority considers any soil stratum with a CBR value more than 2% to be appropriate as a foundation to bear the load of road pavements. Furthermore, a material which possesses a CBR value of 10% is considered a strong subgrade material, thus only the minimum recommended pavement thickness can be adopted for construction. Orthodox soil stabilisation method incorporating Portland
cement and Lime cannot sufficiently strengthen CG to meet the 2% CBR requirement to be considered a subgrade fill. However, if more than 10% of FA or S is added into the CG mix, 4-days soaked CBR values of 2.5% to 4.0% can be achieved. On the other hand, if geopolymerisation is used to stabilise CG into a binded material, high-strength materials can be produced. CG+FA geopolymers have CBR values from 5% to 13%. On the other hand, CG+S geopolymers have CBR values from 19% to 30%. By adding RG into the geopolymer to partially replace CG, the range of achievable CBR for CG+FA geopolymers are 11% to 15%; CG+S geopolymers recorded CBR values of 25% to 35%. The addition of RG increased not only the unit weight of the CG geopolymer, but also improved bearing strength and reduced potential swelling when CG geopolymers are immersed in water.

RLT tests showed that CG geopolymers were sufficiently strong and flexible to withstand repeated traffic loading. With the supplementation of RG, the stiffness of CG geopolymers, particularly that of CG+S mixes, increased significantly. Although for subgrade purposes, an RG replacement ratio of 20% to 35% would be sufficient for strength enhancement for CG geopolymers, as increasing the ratio to 50% decreased material ductility significantly albeit providing high compressive strength. Tentatively, CG+FA geopolymers were relatively ductile when cured in room temperature but produced lower bearing strength. On the other hand, CG+S geopolymers can achieve high strengths but were relatively brittle. The fast setting CG+S geopolymers mean the workability is limited to a short period after alkaline activation. Therefore, while this research found that both CG+FA and CG+S geopolymers can be used as subgrade fills, considerations should be given to either adopt a weaker but workable mix, or a stronger but rapid-setting mix.

Lastly, applying empirically obtained prediction models for granular soils onto CG yields mixed results. While the prediction results for CG geopolymers cannot be considered very precise, a fair amount of data can be estimated depending on the different geopolymeric mix and curing method used, implying some resemblance between CG and granular soils.
CHAPTER 7

ENVIRONMENTAL AND ECONOMIC VIABILITY

7.1 Overview

A common concern once CG is embedded into the soil strata would be the soil or groundwater contamination due to leaching occurrence from CG. Figure 7.1 shows a typical road cross section with the proposed use of CG beneath the pavement layer. The arrows in Figure 7.1 represent the projected flow of rainwater across the pavement structure. In an ideal pavement design, rainwater would become surface runoff, which flows into adjacent drainage systems due to the waterproof asphalt layer. Nevertheless, resulting from material permeability and porosity, a small portion of naturally occurring precipitation would infiltrate the pavement. The downwards percolation of rainfall would gradually carry leachates across the CG fill layer, into the existing soil strata, and subsequently converge with the existing groundwater table. Since stabilized CG is proposed to be a structural subgrade fill material, leachate tests must be done to ensure that there are no toxic compounds present. Materials with toxic metal concentration levels exceeding 100 times the potable water standard would be considered hazardous (EPA, 1999).

Figure 7.1 Pavement cross section displaying proposed use of stabilized CG, depicting projected surface runoff and percolation flow (Kua et al., 2016a).
7.2 Environmental Assessment

Table 7.1 compares detectable heavy metals in CG with benchmarks previously reported for industrial soils, waste materials and industrial fill materials. The level of nickel in CG is high compared to that in soil, while the level of chromium exceeds that of typical backfill materials. It is postulated that the levels of nickel and chromium were affected by the presence of other contaminants presented in the landfill during the course of sampling. Otherwise, by a large margin, other constituents are lower compared to the allowable limits for all three applications. All metals found in CG are considered small compared to those found in a typical waste material.

Table 7.1 Heavy metal concentration in CG compared to relevant benchmarks (Kua et al., 2016a).

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>CG (mg/kg) (Arulrajah et al., 2014b)</th>
<th>Soil (mg/kg) (Rahman et al., 2014)</th>
<th>Waste Material (mg/kg) (EPA, 2009)</th>
<th>Backfill Material (mg/kg) (EPA(AU), 2007)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>&lt;2.72</td>
<td>0.1-40</td>
<td>500</td>
<td>20</td>
</tr>
<tr>
<td>Barium</td>
<td>Not Detected</td>
<td>100-3000</td>
<td>6250</td>
<td>-</td>
</tr>
<tr>
<td>Cadmium</td>
<td>&lt;0.544</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chromium</td>
<td>&lt;6.8</td>
<td>5-1500</td>
<td>500</td>
<td>1</td>
</tr>
<tr>
<td>Copper</td>
<td>24.48</td>
<td>2-60</td>
<td>5000</td>
<td>100</td>
</tr>
<tr>
<td>Lead</td>
<td>&lt;6.8</td>
<td>2-100</td>
<td>1500</td>
<td>-</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.136</td>
<td>10-150</td>
<td>75</td>
<td>1</td>
</tr>
<tr>
<td>Nickel</td>
<td>&lt;6.8</td>
<td>0.01-0.5</td>
<td>3000</td>
<td>60</td>
</tr>
<tr>
<td>Selenium</td>
<td>Not Detected</td>
<td>0.1-5</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>Vanadium</td>
<td>Not Detected</td>
<td>3-500</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zinc</td>
<td>19.04</td>
<td>25-200</td>
<td>35000</td>
<td>200</td>
</tr>
</tbody>
</table>
Table 7.2 shows the leached metal concentrations of CG when the material is tested with acidic and alkaline solutions, which may chemically attack CG differently compared to pH-neutral water. These tests were done to simulate extreme environmental scenarios where CG are exposed to acidic rainfall and alkaline substances leached from road pavement layer. In the acidic leachate extraction test, the concentration of cadmium is double the allowable limit in potable water, while the alkaline leachate extraction test results show that leached arsenic and mercury concentrations exceed the potable water standard prescribed by EPA(USA) (1999).

Table 7.2 Acidic and alkaline leachate test results of CG compared to relevant benchmarks (Kua et al., 2016a).

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Acidic Leachate Extraction (mg/L)</th>
<th>Alkaline Leachate Extraction (mg/L)</th>
<th>Solid inert waste Threshold (mg/L) (Arulrajah et al., 2014b)</th>
<th>Potable Water Standard (mg/L) (EPA, 2009)</th>
<th>Hazardous waste designation (mg/L) (Wartman et al., 2004)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>&lt;0.01</td>
<td>0.12</td>
<td>0.35</td>
<td>0.05</td>
<td>5</td>
</tr>
<tr>
<td>Barium</td>
<td>Not Detected</td>
<td>Not Detected</td>
<td>35</td>
<td>2</td>
<td>100</td>
</tr>
<tr>
<td>Cadmium</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.1</td>
<td>0.005</td>
<td>1</td>
</tr>
<tr>
<td>Chromium</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>2.5</td>
<td>0.1</td>
<td>5</td>
</tr>
<tr>
<td>Lead</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.5</td>
<td>0.015</td>
<td>5</td>
</tr>
<tr>
<td>Mercury</td>
<td>&lt;0.001</td>
<td>&lt;0.005</td>
<td>0.05</td>
<td>0.002</td>
<td>0.2</td>
</tr>
<tr>
<td>Selenium</td>
<td>Not Detected</td>
<td>Not Detected</td>
<td>0.5</td>
<td>0.05</td>
<td>1</td>
</tr>
<tr>
<td>Silver</td>
<td>Not Detected</td>
<td>Not Detected</td>
<td>5</td>
<td>0.05</td>
<td>5</td>
</tr>
</tbody>
</table>

In contrast, concentrations of all leached metals are much below the threshold for solid inert waste prescribed by EPA(AU) (2009), and are far lower compared to the benchmarks to deem a hazardous material based on Wartman et al. (2004). The higher leached arsenic and mercury concentrations relative to potable water quality do not necessarily mean that they will potentially expose negative impacts to the groundwater quality. This is because conventional theoretical analysis, based on advection-diffusion-dispersion theory, of transportation of metals in porous media and impacts of migrated metals to the groundwater quality depends not only on the leached concentrations, but retardative, hydraulic and diffusive properties and initial degree of saturation of the...
pavement/CG subgrade layer, rainfall percolation rate through the pavement/CG subgrade layer, and horizontal groundwater flux in the aquifer (Du et al., 2009; Du and Hayashi, 2006; Du et al., 2005). Also, the geometry of the pavement layer, CG subgrade, and aquifer as well as hydrological conditions are required for conducting the analysis via closed-form solution or numerical method (Du et al., 2009; Du and Hayashi, 2006). Further research is warranted for conducting a site-specific analysis of impacts of leached metals to groundwater quality.

Table 7.3 ASLP test results for CG geopolymers compared to hazardous waste and potable water leachate thresholds.

<table>
<thead>
<tr>
<th>Dissolved Major Anions</th>
<th>70CG0S30FA (mg/L)</th>
<th>70CG30S0FA (mg/L)</th>
<th>70CG15S15FA (mg/L)</th>
<th>Hazardous waste designation (mg/L) (Wartman et al., 2004)</th>
<th>Potable Water Standard (mg/L) (EPA, 1999)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphur</td>
<td>-</td>
<td>123.5</td>
<td>140.5</td>
<td>-</td>
<td>250</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Leachable Major Cations</th>
<th>70CG0S30FA (mg/L)</th>
<th>70CG30S0FA (mg/L)</th>
<th>70CG15S15FA (mg/L)</th>
<th>Hazardous waste designation (mg/L) (Wartman et al., 2004)</th>
<th>Potable Water Standard (mg/L) (EPA, 1999)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>5</td>
<td>5</td>
<td>6.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Magnesium</td>
<td>1.5</td>
<td>&lt;1</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Leachable Metals</th>
<th>70CG0S30FA (mg/L)</th>
<th>70CG30S0FA (mg/L)</th>
<th>70CG15S15FA (mg/L)</th>
<th>Hazardous waste designation (mg/L) (Wartman et al., 2004)</th>
<th>Potable Water Standard (mg/L) (EPA, 1999)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>-</td>
<td>1.2</td>
<td>0.35</td>
<td>-</td>
<td>0.20</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.3</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.35</td>
<td>0.01</td>
</tr>
<tr>
<td>Chromium</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>2.5</td>
<td>0.10</td>
</tr>
<tr>
<td>Copper</td>
<td>0.7</td>
<td>0.15</td>
<td>0.45</td>
<td>100</td>
<td>1.3</td>
</tr>
<tr>
<td>Iron</td>
<td>11.1</td>
<td>1.9</td>
<td>8.9</td>
<td>-</td>
<td>0.30</td>
</tr>
<tr>
<td>Lead</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.5</td>
<td>0.015</td>
</tr>
<tr>
<td>Manganese</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>3.0*</td>
<td>0.05</td>
</tr>
<tr>
<td>Zinc</td>
<td>4.3</td>
<td>2.95</td>
<td>5.25</td>
<td>150</td>
<td>5.0</td>
</tr>
</tbody>
</table>

| Total Cyanide          | 0.012             | 0.011             | <0.004             | 4.0                                                      | 0.20                                     |
To ascertain that use of CG-based geopolymer materials does not pose any environmental concerns to the surrounding environment through leaching of contaminants from the geopolymer materials, a series of chemical tests were conducted. Due to budgetary constraint, tests were conducted for some selected potential contaminants/impurities, which may be present in the ingredients used to make the geopolymer. In addition to selected heavy metals, leaching tests were conducted for Calcium, Magnesium, Cyanide and Sulphur. From each type of blended specimen, three samples were taken and tested. Average of the three measurements for each parameter is reported. Table 7.3 shows the leaching tests’ results along with the EPA Victoria (EPA, 2009) defined upper limits to define a waste material as hazardous. Table 7.3 also show the allowable concentrations of contaminants in the water to be at drinking water standard as per the USA EPA (1999).

From Table 7.3 it is found that among the tested metals, concentrations of Chromium, Lead and Manganese in the leachate were below the detection limit (0.10 mg/L). Among other heavy metals, Arsenic was also found to be below detection level (0.10 mg/L), except for the specimen of “70CG0S30FA”, for which the Arsenic concentration in the leachate was 0.30 mg/L. This concentration is still below the EPA Victoria (EPA, 2009) defined upper limit (0.35 mg/L) for Arsenic to label a waste as hazardous. In all the leachate samples, there were presences of Copper and Zinc, however far below the EPA Victoria (EPA, 2009) defined upper limits for Copper (100 mg/L) and Zinc (150 mg/L) to label a waste as hazardous. Also, some amounts of Aluminium and Iron were present in the leachate samples. However, as both the Aluminium and Iron do not pose any environmental risk, EPA Victoria (EPA, 2009) did not provide any upper limit for these to categorise a waste as hazardous. Consumption of Aluminium do not pose any environmental threat; in reality some amounts of Aluminium may present in drinking water, as often drinking water is processed using aluminium salts. US EPA (EPA, 2017) has set maximum concentrations of Aluminium and Iron in drinking water as 0.20 mg/L and 0.30 mg/L, which are defined as ‘Secondary Maximum Contaminant Levels’. However, these limits are mainly based on compliance with taste, colour and odour, not based on effects on human/animal.

Apart from metals, small concentrations of ‘Total Cyanide’ were present in two specimens, however these concentrations are far below the EPA Victoria (EPA, 2009) defined upper limit (4.0 mg/L) to label a waste as hazardous. Low concentrations of
Calcium and Magnesium were found in all the three specimens. Calcium and Magnesium concentrations cause water to be hard. However, in general hardness has got no health implication, as such EPA Victoria (EPA, 2009) did not assign any value for hardness to define hazardous waste. US EPA (EPA, 1999) also did not assign any limit of hardness for drinking water. However, as hardness causes some other effects in different processes, concentrations of Calcium and Magnesium more than 120 mg/L will cause a water to be hard (Sengupta, 2013), which is more than 15 times higher than the total concentrations of Calcium and Magnesium found in the tested samples. Regarding Sulphur, there are some sulphur concentrations present in the tested samples. However, as Sulphur (and its end-products) do not cause any health/environmental effect (rather some amounts of Sulphur is required by the human body for normal metabolism), EPA Victoria did not assign any limit regarding the maximum concentration of this contaminant to define a waste as hazardous. Only because of aesthetic reasons related to taste and smell, US EPA has defined a maximum secondary limit of Sulphur based components in the drinking water as 250 mg/L, which is almost double the Sulphur concentrations found in the tested samples.

From all the above-mentioned tests, it is clear that concentrations of potential contaminants in the tested samples were far below (some of the heavy metals’ concentrations are even below detection level) the maximum concentrations assigned by the EPA Victoria to define a waste material as hazardous. As such, the tested CG-based geopolymer can be categorised as non-hazardous, hence can be used as pavement subgrade material without any environmental/health risk. Concentrations of only few metals (Aluminium, Arsenic and Zinc) were found to be higher than the US EPA defined maximum allowable primary/secondary limits in drinking water. However, these limits are not enforceable for the proposed reuse scenario, as the people are not expected to drink leachate from the embankment subgrade.

The carbon footprint associated with manufacturing geopolymers have been debatable. Some estimations put the carbon dioxide emission (CO$_2$-e) of geopolymers up to 80% less than the CO$_2$-e produced by manufacturing Portland cement; Other literatures are less optimistic and approximated that the CO$_2$-e by geopolymers to be just 9% less than Portland cement (Turner and Collins, 2013). The large variation in results is caused by the varying mining, transporting, and processing scenarios of raw materials in which
geopolymers are derived from, and whether the energy associated with the manufacturing of the alkaline liquids were considered. Moreover, Turner and Collins (2013) noted that the energy required to cure geopolymers to achieve the necessary strength are usually high and not considered in past studies. In the context of this experiment, most CG geopolymer mixes incorporating FA requires extended curing periods of 50°C to achieve UCSs equivalent to those achieved by S geopolymers cured at 21°C. Thus, CG+S geopolymers would produce minimum CO$_2$-e with maximum strength development.

An upper limit estimation reports the CO$_2$-e per m$^3$ of geopolymer concrete to be 320 kg (Turner and Collins, 2013). The material mix in this study replaces coarse and fine aggregates with CG. As CG is a waste material, the expected CO$_2$-e would be zero, whereas the CO$_2$-e of coarse and fine aggregates are 0.041 and 0.014 kg CO$_2$-e per kg respectively (Turner and Collins, 2013). Interestingly, however, if the life cycle of coffee is considered wholly from farming, cultivating, roasting, packaging, brewing, and disposing, the CO$_2$-e per m$^3$ of CG is postulated to be 4.5 to 13 kg CO$_2$-e per kg (Brommer et al., 2011; Hassard et al., 2014). However, the staggering difference in CO$_2$-e between soil aggregates and CG does not take into account the non-renewable quarry materials compared to coffee, which can be planted and regrown indefinitely. Moreover, the CO$_2$-e generated by the aggregates and CG are mutually exclusive to each other. Therefore, while the consumption of coffee in the food industry may inevitably generate up to 13 kg CO$_2$-e per kg of CG, this can be recycled to reduce the nett CO$_2$-e generated in the construction industry by 0.056 kg CO$_2$-e per kg of aggregate replaced, in addition to reducing the dependency on quarried raw materials.

7.3 Cost Analysis

Construction costs associated with using CG geopolymers were estimated and compared to construction materials in the market. The unit price of the materials, as of 26/04/2017, obtained from their respective manufacturers are shown in Table 7.4. This calculation assumed that CG comes at $0 as it is provided for free by cafés. FA is the cheapest material at $85 per tonne, whereas according to commercial manufacturers in Melbourne, Australia, the current market price of slag is similar to that of Portland cement, and is estimated to be $200 per tonne. NaOH prepared at 8 mol is the costliest at
$7840 per tonne. The market price of aqueous Na$_2$SiO$_3$ is $3296.75 per tonne. Assuming that the dry unit weight obtained from the modified proctor compaction test is accurate, the total price to produce one m$^3$ of CG geopolymer ranges from $1794.79 to $2735.67. CG+S geopolymers are more expensive than CG+FA geopolymers, but produces higher UCS values and can cure at ambient temperatures to develop sufficient compressive strength.

Table 7.4 Cost estimation of producing CG Geopolymers.

<table>
<thead>
<tr>
<th>CG:S:FA</th>
<th>Na$_2$SiO$_3$:NaOH</th>
<th>L/P</th>
<th>Dry Unit Weight (kN/m$^3$)</th>
<th>Mass (tonnes) per m$^3$</th>
<th>Price per m$^3$</th>
<th>Total Price per m$^3$</th>
<th>Price of a 76 mm x230 mm x110 mm (height x length x width) brick</th>
</tr>
</thead>
<tbody>
<tr>
<td>70:30:0</td>
<td>90:10</td>
<td>2.0</td>
<td>8.61</td>
<td>S:FA:Na$_2$SiO$_3$:NaOH</td>
<td>$22.38$</td>
<td>$0.00$</td>
<td>$412.86$</td>
</tr>
<tr>
<td>70:30:0</td>
<td>70:30</td>
<td>1.8</td>
<td>8.74</td>
<td>S:FA:Na$_2$SiO$_3$:NaOH</td>
<td>$22.72$</td>
<td>$0.00$</td>
<td>$1131.55$</td>
</tr>
<tr>
<td>70:30:0</td>
<td>50:50</td>
<td>1.8</td>
<td>8.85</td>
<td>S:FA:Na$_2$SiO$_3$:NaOH</td>
<td>$23.00$</td>
<td>$0.00$</td>
<td>$1909.65$</td>
</tr>
<tr>
<td>70:15:15</td>
<td>90:10</td>
<td>2.0</td>
<td>8.48</td>
<td>S:FA:Na$_2$SiO$_3$:NaOH</td>
<td>$11.02$</td>
<td>$25.93$</td>
<td>$406.63$</td>
</tr>
<tr>
<td>70:15:15</td>
<td>70:30</td>
<td>1.8</td>
<td>8.53</td>
<td>S:FA:Na$_2$SiO$_3$:NaOH</td>
<td>$11.09$</td>
<td>$26.09$</td>
<td>$1104.36$</td>
</tr>
<tr>
<td>70:0:30</td>
<td>90:10</td>
<td>1.9</td>
<td>8.01</td>
<td>S:FA:Na$_2$SiO$_3$:NaOH</td>
<td>$11.16$</td>
<td>$48.99$</td>
<td>$364.88$</td>
</tr>
<tr>
<td>70:0:30</td>
<td>70:30</td>
<td>1.8</td>
<td>8.26</td>
<td>S:FA:Na$_2$SiO$_3$:NaOH</td>
<td>$11.09$</td>
<td>$50.52$</td>
<td>$1069.40$</td>
</tr>
<tr>
<td>70:0:30</td>
<td>50:50</td>
<td>1.8</td>
<td>8.28</td>
<td>S:FA:Na$_2$SiO$_3$:NaOH</td>
<td>$11.16$</td>
<td>$50.64$</td>
<td>$1786.66$</td>
</tr>
</tbody>
</table>

FA = $85/t; S = $200/t; NaOH (8 mol) = $7849/t; Na$_2$SiO$_3$ = $3296.57/t (Melbourne, VIC 2017).

As the cost of pavements is usually calculated in a unit price per m$^2$, comparing the price of CG geopolymers with other construction may provide more insight to the economic
viability of this material. Relatively, the cost of one m$^3$ of Portland cement concrete is approximately $200 to $230 in Melbourne, Australia. On the other hand, if the CG geopolymers are produced in standard masonry units measuring 76 mm x230 mm x110 mm, the cost would be $3.45 to $5.26 per brick. Currently in Australia the price of bricks fall between $1 and $2. Also for comparison, a manufacturer in Sydney, Australia is offering unpainted “recycled bricks” at $2252 per 1000 brick units. From these comparisons, the price of CG geopolymers are not adequately competitive with the price of conventional concrete which is much cheaper. Tentatively, the price of producing CG geopolymer masonry units is approximately triple the price of clay bricks and double the price of recycled bricks marketed in Australia.

Table 7.5 Cost estimation of producing CG Geopolymers supplemented with RG.

<table>
<thead>
<tr>
<th>CG:RG:S:FA</th>
<th>Na$_2$SiO$_3$:NaOH</th>
<th>L/P</th>
<th>Dry Unit Weight (kN/m$^3$)</th>
<th>Mass (tonnes) per m$^3$</th>
<th>Price per m$^3$</th>
<th>Total Price per m$^3$</th>
<th>Price of a 76 mm x230 mm x110 mm (height x length x width) brick</th>
</tr>
</thead>
<tbody>
<tr>
<td>50:20:30:0</td>
<td>70:30</td>
<td>1.2</td>
<td>10.52</td>
<td>0.32</td>
<td>$27.29</td>
<td>$1,822.78</td>
<td>$3.50</td>
</tr>
<tr>
<td>35:35:30:0</td>
<td>70:30</td>
<td>1.0</td>
<td>12.11</td>
<td>0.37</td>
<td>$31.45</td>
<td>$2,465.10</td>
<td>$4.74</td>
</tr>
<tr>
<td>20:50:30:0</td>
<td>70:30</td>
<td>1.2</td>
<td>14.23</td>
<td>0.43</td>
<td>$36.91</td>
<td>$2,988.66</td>
<td>$5.18</td>
</tr>
<tr>
<td>50:20:0:30</td>
<td>70:30</td>
<td>1.2</td>
<td>10.13</td>
<td>0.00</td>
<td>$27.29</td>
<td>$1,822.78</td>
<td>$3.50</td>
</tr>
<tr>
<td>35:35:0:30</td>
<td>70:30</td>
<td>1.0</td>
<td>11.28</td>
<td>0.00</td>
<td>$31.45</td>
<td>$2,465.10</td>
<td>$4.74</td>
</tr>
<tr>
<td>20:50:0:30</td>
<td>70:30</td>
<td>1.2</td>
<td>13.41</td>
<td>0.00</td>
<td>$36.91</td>
<td>$2,988.66</td>
<td>$5.18</td>
</tr>
</tbody>
</table>

FA = $85/t; S = $200/t; NaOH (8 mol) = $7849/t; Na$_2$SiO$_3$ = $3296.57/t (Melbourne, VIC 2017).
Table 7.5 summarises the cost estimation of CG+RG geopolymers. Assuming that RG can be obtained free of charge similar to CG, the price for CG+RG geopolymers are mostly lower compared to CG geopolymers. This is due to the lower optimum L/P ratios required to efficiently activate the CG+RG geopolymers. While CG geopolymers required L/P to be between 1.8 to 2.0, CG+RG geopolymers reduced this ratio by almost half to between 1.0 to 1.2. From Table 7.5, the unit weight of CG+RG are much higher, due to the inclusion of RG, meaning the amount of FA and S required to form a 30% precursor ratio increased. However, while the cost associated with the precursor materials increased, the amount of alkaline liquid, which corresponds with the highest material prices, was significantly reduced. When the ratio of CG:RG:P was fixed at 35:35:30, the unit price of the geopolymers were the lowest due to the lowest L/P ratio of 1.0. Tentatively, CG+RG geopolymers range between $3.23 to $ 4.74, and outperform CG geopolymers by the high strength (10MPa) of CG+RG geopolymers compared to CG geopolymers (1 MPa).

Apart from material price, the cost of procuring and transporting the recycled waste should also be taken into consideration. As there are no exact data on mass-collecting and transporting CG, a guideline used by the Victorian government in Australia was used as a reference (Sustainability-Victoria, 2015). If the proximity of the construction site is 45km to 85km from the recycled source, the cost of transporting the recycled material may be competitive with that of transporting quarried material from a source more than 15km from the site. This implies that CG geopolymers should be used in urban settings as the concentration of cafés tend to be higher where the population density is high. Tentatively, as CG geopolymers are generally lighter than naturally occurring geomaterials with dry unit weights of up to 16 kN/m$^3$ (Terzaghi et al., 1996), the transportation costs associated with this material may be well lower. However, the dry unit weight of CG+RG geopolymers may cause the hauling cost to increase significantly.
7.4 Summary

CG geopolymers were reported to have sufficient strength to be used as a road construction material. The environmental analysis done on this green material shows that while being composed of various industrial wastes and chemicals, embedding CG geopolymers in the ground will not cause adverse environmental impacts to surrounding soils and groundwater. The Australian Standard Leaching Procedure tests done on CG+FA and CG+S geopolymers show that the concentration level of heavy metals in these substances are well below the threshold for hazardous leachates.

On the other hand, while the production of CG produces a significant amount of CO\textsubscript{2}-e, utilizing CG in the construction industry may reduce the nett CO\textsubscript{2}-e produced by decreasing demand for quarried raw construction materials. From the cost analysis done on CG geopolymers, it was found that CG geopolymers CG+S geopolymers are more expensive than CG+FA geopolymers, but produces higher UCS values and can cure at ambient temperatures to develop sufficient compressive strength.

As it is more feasible to use recycled material within the proximity of the source, CG geopolymers may be reused around urban settings where cafés can be easily found. CG geopolymers were found to be more expensive compared to conventional construction material, hence are recommended to be used in small scale construction projects, such as low-volume laneways, bicycle paths, or even pedestrian footpaths in parks. While the cost of CG geopolymers is undeniably higher than available material in the market, CO\textsubscript{2}-e and cost analyses do not consider the factor in which this geopolymer may free up increasing scarce landfill spaces by reusing various wastes from different streams for construction. In the near future, as recycling technology becomes more viable and accessible, the economic value of CG geopolymers may increase to match those of contemporary construction materials.

Introducing RG to partially replace CG in the geopolymer mix results in enhanced compressive strength, material stiffness, and swelling when exposed to inundation. Assuming that CG and RG can be obtained free of charge, CG+RG geopolymers are cheaper due to the lower amount of alkaline liquid needed to produce a strong geopolymer, thus further highlighting the benefits of supplementing CG geopolymers with RG.
CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

This research used spent coffee ground (CG), a waste product from the beverage industry as a parent material to produce a green recycled construction material. CG was collected daily from cafés in Melbourne, Australia and experimented upon with a suite of geotechnical and structural engineering tests. Due to the physical resemblance of CG soils, CG was evaluated as a road subgrade fill material, by employing various orthodox and innovative soil stabilisation methods to strengthen CG into a structurally sound material. Soil stabilisation was done using three groups of additives: 1) industrial purpose Portland cement (PC) and Lime; 2) the industrial wastes Fly Ash (FA) and Slag (S); and 3) the agricultural wastes Rice Husk Ash (RHA) and Bagasse Ash (BA). Additionally, recycled glass (RG) was used to strengthen CG with the supplementation of shear strength by increasing inter-particle friction in the material mix.

Compaction Characteristics

CG by itself is a lightweight material. At an optimum moisture content (OMC) of 130%, CG can be compacted to a maximum dry density (MDD) of 4.4 kN/m$^3$. The high OMC indicates that CG has high water absorption capacities, whereas the low MDD relative to naturally occurring soils point to the possibility of creating a lightweight construction material. By adding 3% to 5% of soil stabilisers and compacting the mixture under modified Proctor effort, the MDD of CG experienced changes up to 0.1 kN/m$^3$, which in ASTM’s definition is insignificant. Thereafter, adding more than 10% of stabilisers into CG increased the MDD of CG proportionately to the specific gravity of the additives added. At a 30% stabiliser replacement ratio, which is the common stabiliser content used throughout the research, the MDD of CG was 8.5 kN/m$^3$ on average. This value is almost double of the MDD of fresh CG. On the other hand, the introduction of 20% to 50% of RG into the CG-Stabiliser mix further increased the MDD of CG to 10 - 14.5kN/m$^3$. 
The OMC of CG also decreased as the ratio of soil stabiliser increased. At 30% replacement ratio, the OMC was found to be 70%. On the other hand, if water is substituted with alkaline solutions for geopolymerisation, the optimum liquid content (OLC) at 30% stabiliser ratio is 55% to 60%. Adding RG into CG further decreases the OLC to 25% on average. However, for CG geopolymers, it was found that the mixes do not typically achieve maximum strength at OLC. Mixes usually develop maximum strength when the administered alkaline liquid is 6% to 10% more than the OLC, and beyond that a saturation point can be observed.

**Material Strength**

The orthodox geotechnical stabilisation method employing 3-5% of PC and Lime does not suit the highly compressible and organic CG. By introducing more than 10% of the industrial wastes FA and S to produce a CG mixture, the requirement of CBR ≥ 2% for subgrade materials could be met. However, unconfined compressive strength (UCS) tests done on these compacted CG+FA and CG+S mixtures showed that there was no significant gain in strength, due to the pozzolanic characteristics of FA and S which do not manifest cementitious properties with pH neutral liquids.

On the other hand, using an alternative cementing process employing geopolymers, CG was found to be successfully encapsulated to form a strong cemented material. Under optimum curing conditions, CG+FA geopolymers achieved UCSs of 800-1200 kPa whereas CG+S geopolymers achieved UCSs of 1000-1200 kPa in 7 days. With the supplementation of RG, CG geopolymers can achieve high strengths between 1 to 11 MPa. Comparatively, the UCS of compacted fresh CG was 35 kPa. Furthermore, CG geopolymers also gain improved bearing strength.

Adding more than 10% of FA or S resulted in 4-days soaked California Bearing Ratio (CBR) values of 2.5% to 4.0%. CG+FA geopolymers recorded 4-days soaked CBR values from 5% to 13%. On the other hand, CG+S geopolymers resulted in CBR values from 19% to 30%. RG further enhanced the bearing strength of CG+FA geopolymers to 11 - 15%; CG+RG+S geopolymers recorded CBR values of 25% to 35%. According to the Australian road authority’s requirements, all CG geopolymers meet the minimum subgrade material strength of CBR>2%. Decisively, geopolymerisation is an effective way to increase the strength of CG. However, a study to assess the effects of
biodegradation on long term material strength is recommended for future study, as this research only covers the effects of geopolymerisation on influencing strength development in stabilised CG.

S is found to be the more effective precursor for this geopolymer compared to FA. On the other hand, mix designs with FA can achieve high UCS as well, but requires longer curing time. Regardless of the curing temperature of 21°C or 50°C, CG+S geopolymers can achieve high strengths that satisfy benchmarks provided by road authorities concerning the minimum UCS of subgrade materials. On the other hand, the UCS of CG+FA geopolymers develops more effectively at an elevated curing temperature of 50°C, hence should be used in hot tropical climates or during warm seasons. This study confirmed that CG+FA geopolymers have a slower rate of UCS development compared to CG+S at 7 days, but given a curing duration of 28 days and 50°C, can achieve UCS values of 1.2 MPa. It is possible to synthesise a material utilizing CG+RHA and CG+BA. However, these materials require the supplementation of S and long curing time in elevated curing temperatures to maintain a steady state of strength development. At the optimum curing condition, these geopolymers derived from agricultural wastes can develop UCS values of 2 MPa after 90 days. However, RHA and BA were found to be unreliable precursors that resulted in mixes that require an impractically high curing duration to reach satisfactory compressive strengths.

Manipulating the L/P ratio in various CG geopolymer mixes revealed that interestingly, some mixes do not adhere to the trend where maximum UCS can be achieved at OLC due to geopolymeric reactions being the main provider of mechanical strength in the material matrix. Furthermore, the selection of precursors must be carefully made under different situations. While a mix of S and FA results in a steady and high strength development, increasing the curing temperature does not necessarily lead to a drastically higher increase of UCS due to the simultaneous reaction of both S and FA products which hinder overall cementation.

The design mix with 70CG:30S + 70Na₂SiO₃:30NaOH and L/S =1.8 is recommended for subgrades, because it produces high strength with a relatively low L content. This mix design also has the potential to achieve high early strength due to the alkaline activation of S, and no heat treatment is required for this formula to achieve the required strength after 7 days of curing to meet performance benchmarks in terms of UCS.
Stiffness and Deformation Pattern

Untreated CG has an $M_R$ range of 4.8 -8.2 MPa. This study finds that geopolymerization improves the resilient modulus and UCS of CG significantly. 21°C-cured CG geopolymers have an $M_R$ range of 48 -150 MPa, whereas 50°C-cured CG geopolymers have a smaller $M_R$ range of 56 -123 MPa. The inclusion of RG to replace 50% of CG increased the $M_R$ range to 200 -300 MPa. Repeated load Triaxial tests done on CG geopolymers indicated that in elevated curing temperature, these materials retain a certain amount of ductility and compressibility while developing high shear strengths after geopolymeric stabilisation. However, this effect is nullified when RG is introduced into the material mix, creating a relatively stiff and heavily cemented material with high compressive strength.

The Bulk Stress Model and 3-Parameter Model were used to gauge their suitability on predicting the $M_R$ of CG geopolymers. Provided that the confining pressure and axial stress are known in the field, the 3-Parameter Model can more accurately predict the $M_R$ of these materials compared to the Bulk Stress Model. Comparing the predicted results with laboratory results showed reasonable accuracy. Nonetheless, the regression constants for each material mixes were different, indicating that different material mixes, curing duration, and temperature all influences the factors required to predict the resilient moduli. Therefore, should CG mixes other than those tested in this research be applied in roadworks in the future, a case by case assessment should be made to evaluate the $M_R$ of a design mix based on the material composition, expected curing time, and surrounding temperature.

Environmental and Economic Viability

Comparison of the leachate obtained from CG with various safety benchmarks for soils, waste materials, and backfill materials deems CG to be safe for use as a fill material. From the leachate tests done on CG+FA and CG+S geopolymers, it was found that the level of hazardous chemical compounds and heavy metals in these materials are well below the maximum benchmark set by the Environmental Protection Agencies in Australia and the USA. Hence, stabilised CG can be safely utilised as a subgrade fill material as it would not contaminate adjacent soils or groundwater sources.
In-depth literature review showed that the production and consumption of coffee generates a large amount of carbon dioxide emission. Nevertheless, with the geopolymerisation of CG into a recycled construction material, the carbon emissions produced in the construction industry can be reduced as there would be lower demand for virgin quarry materials. Moreover, the utilisation of CG, FA, S, and RG would free up increasingly scarce landfill space. The cost analyses done on CG geopolymers found these materials to be expensive relative to existing construction materials. Regardless, the notion of creating a durable green material has been met, by drawing various industrial and agricultural wastes to create a strong yet lightweight cemented material, utilising a relatively low-carbon-emission process. With the current emphasis and rapid development in sustainable technology, future costs of recycling CG may decrease with the advent of newer machines and cheaper manufacturing and recycling processes.

Conclusively, by using geopolymerisation, a material with high compressive strength can be synthesised from CG, a waste material from the beverage industry. This research found that CG geopolymers meet the strength requirements to be considered as a construction material. On the other hand, this recycled CG poses no adverse effects to the environment. CG geopolymers are recommended to be used as a road pavement fill as they can be considered high-strength subgrade materials.

**Recommendation for Future Studies**

While this research has been done in earnest to assess the viability of using CG as a construction material, future studies can be conducted to further justify the usage of CG as a recycled product. Firstly, a comprehensive harvesting method should be designed to efficiently collect and stabilise large volumes of CG before construction. While the strength and flexural durability of CG geopolymers have been tested in the laboratory, a large-scale implementation of stabilised CG in road construction may generate more data on the responses of stabilised CG towards live traffic and weathering conditions. Last but not least, while in this study CG has been stabilised to provide sufficient compressive strength, future research may focus on the long-term settlement pattern of CG pavements, and the bio-degradability of stabilised CG, to further validate the use of recycled CG on the field.
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