Development and Application of Sustainable Binders Comprising of Fly Ash and Ground Glass Fibers in Portland Cement and Geopolymer Concrete

Omar Alsanusi Amer

Clemson University, oamer@g.clemson.edu

Follow this and additional works at: https://tigerprints.clemson.edu/all_dissertations

Part of the Civil Engineering Commons

Recommended Citation

This Dissertation is brought to you for free and open access by the Dissertations at TigerPrints. It has been accepted for inclusion in All Dissertations by an authorized administrator of TigerPrints. For more information, please contact kokeefe@clemson.edu.
DEVELOPMENT AND APPLICATION OF SUSTAINABLE BINDERS COMPRISING OF FLY ASH AND GROUND GLASS FIBERS IN PORTLAND CEMENT AND GEOPOLYMER CONCRETE

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Civil Engineering

by
Omar Alsanusi Amer
December 2020

Accepted by:
Dr. Prasad Rangaraju, Committee Chair
Dr. Amir Poursaeed
Dr. Bradley Putman
Dr. Laura Redmond
ABSTRACT

Since cement production is responsible for a significant share of anthropogenic CO₂ emissions, the sustainability of concrete construction has become one of the most targeted research and construction industry goals. Many suggestions have been in use to encourage sustainability of concrete construction; one such approach is to partially replace cement by industrial byproducts. The most known industrial byproduct used in concrete construction worldwide has been fly ash, which is a byproduct of burning coal for power generation.

Fly ash use in concrete has various benefits. It reduces the water demand, reduces plastic shrinkage, reduces permeability, and thus improving the durability of concrete against the ingress of chemicals such as sulfates and chlorides, increases the ultimate strength, and by replacing cement, the alkalinity of pore solution would decrease to a level at which alkali-silica reaction (ASR)-induced cracks could be less likely. However, the use of fly ash does have some setbacks. For example, it reduces the early-age strength development, and, with some types of fly ashes, higher cement replacement ratios are needed to achieve better performance in concrete durability problems, which affects the setting time and early-age strength. Moreover, the volume of the available fly ash is dwindling as power companies move towards more sustainable fuels for generating power. Lastly, a significant amount of fly ash that does not meet ASTM C618 specifications for use in Portland cement concrete (i.e., Off-spec fly ashes) has been stored in facilities known as ash ponds. These ash ponds have been problematic to the environment, causing soil and groundwater contamination in locations where they are not adequately secured. There have also been incidents where hurricanes or tornadoes have caused ash pond spills, and the leached hazardous materials polluted water streams and rivers.
Therefore, optimizing the use of current fly ash resources and/or search for alternatives to fly ash is essential. One of the substitutes that has not been considerably examined for beneficial uses is the fiberglass waste from the production of glass fibers used in composite materials. This material's performance is superior as a pozzolan, compared to fly ash, in portland cement concrete (PCC), and as an effective precursor for geopolymer concrete (GC) when it is finely ground.

Therefore, the objective of this work, in its first stage, is to investigate the use of ground glass fibers (GGF) in binary and ternary blends with fly ash (in-spec and off-spec); so both materials could be used as either SCMs in PCC or as precursors in GC. In the second stage, to promote the use of these two industrial wastes, one application where selected blends of FA+GGF can be utilized was investigated. This application was the Full Depth Reclamation (FDR) of asphalt pavements, where a considerable amount of cement is used in pavement rehabilitation projects.

The first stage of this study revealed that the ternary blend of GGF with the in-spec fly ashes in PCC had significantly improved both fresh and hardened properties of mortar and concrete. The GGF-containing mixtures' superior performance was confirmed as they had higher early compressive strength, even at a high replacement ratio of 40% in both mortar and concrete. The early-age strength development was enhanced, and the drying shrinkage was reduced for the ternary blended concrete when compared with the performance of binary fly ash blended concrete. The ultimate compressive and tensile strengths were much improved compared to the pure cement concrete. The ternary blend significantly helped in mitigating ASR and resisting sulfate attack and chloride ion penetration.
For the off-spec fly ash, both fresh properties represented in the flow of mortar and slump of concrete and the hardened properties represented in the strength activity index (SAI) and compressive strength of concrete are all improved in the ternary GGF+FA blended mixtures. The combination of high Loss on Ignition (LOI) fly ash and GGF improved ASR mitigation performance even at a low dosage of GGF. Additionally, the combined blend of GGF and high LOI fly ash required less air-entraining agent (AEA) to achieve the same air content in concrete than the binary fly ash mixture. This reduction in air content would help increase the resistance to freezing and thawing cycles, and at the same time, it did not significantly affect the compressive strength since smaller amounts of AEA was added.

Similar improvements were obtained for the geopolymer based on the combined blend of GGF and FA. The inclusion of GGF in fly ash mixtures negated the need for sodium silicate (SS) solution in the activator, which is needed for fly ash-based geopolymerization. Good compressive strength was observed for GGF+FA blended geopolymer mortar using medium temperature for heat curing (60 °C or below). Eliminating the need for SS solution and the use of a moderate temperature of curing are substantial to achieve better sustainability of geopolymer.

From the FDR studies, the results proved the effectiveness of using GGF with fly ash to replace cement either partially when used as a pozzolan in cement-based stabilization or fully when used as precursors for geopolymer-based stabilization. Additionally, the tested stabilized base materials have passed the durability testing of wetting and drying and freezing and thawing.

Finally, this study helps reduce the environmental burdens of the ash that has long stored in ash ponds and promotes its use in concrete to reduce the use of cement
and the associated carbon emissions. The use of GGF and fly ash is an excellent option to alleviate the declining supplies of fly ash and enhance the durability performance of fly ash-containing concrete mixtures.
DEDICATION

Dedicated to the one who would have been the happiest for my achievement had he been alive, to my father. He is gone, but his inspiration and belief in me have made this journey possible. He passed away a year and a half ago while I was preparing to defend my proposal. May Allah grant him paradise.
ACKNOWLEDGMENTS

First and foremost, all praise is due to Allah, the most beneficent, and the most merciful.

I want to thank my esteemed advisor, Prof. Prasad Rangaraju, for his patient guidance, enthusiastic encouragement, and useful comments on this work. It was your hand that stood us up after each stumbling along the way. I would also like to thank all the committee members: Dr. Amir Poursaeae, Dr. Brad Putman, and Dr. Laura Redmond for serving on the committee and providing helpful suggestions and criticisms.

My sincere gratitude, thanks and appreciations to my compassionate mother for her prayers and support the whole time. I must also sincerely thank and appreciate my loving wife, Huda, for always unconditionally being by my side throughout this journey. I would have never achieved this goal if it was not for her love, encouragement, and support. Thanks to my adorable kids, Adam and Ayoub; their presence in my life has taught me a lot. Thanks to all my brothers and sisters for all the support and encouragement.

There is no way to express how much it meant to me to be a member of the SMaRT team at Clemson University. My deepest thanks and appreciation must go to the research team: Hassan Rashidian, Haitham Hussein, Abdul Basit Peerzada, Harish Konduru, weiqi Wang, Haripriya Nekkanti. I would have never made it this far without their help, guidance and support. I have learned a lot from them, especially Hassan, Haitham and Abdul.

I would like to thank the Glenn Department of Civil Engineering for the funding and assistantships provided throughout my study at Clemson. Also, I would like to profoundly thank and appreciate the Ministry of Education in Libya for the scholarship and the opportunity to study abroad. My thanks extend to Duke Energy Corporation for
funding part of this study. I acknowledge Argos Cement, Lehigh Hanson Inc., PPG Industries, Vulcan Materials Company, and King Asphalt for providing the materials used in this study.

Finally, I would like to thank Danny Metz for maintaining good working equipment at the lab, and Kim Ivey, Dr. John Sanders, Dr. Colin McMillen, and Megan Smart, for all their help in conducting some experimental testing for this work. Thanks to all the administrative staff at the Glenn Department of Civil Engineering.
TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter 1 INTRODUCTION</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td>Background</td>
<td>24</td>
</tr>
<tr>
<td>Practical Applications</td>
<td>31</td>
</tr>
<tr>
<td>Scope and Significance of the Study</td>
<td>32</td>
</tr>
<tr>
<td>Research Aim and Proposed Solution</td>
<td>34</td>
</tr>
<tr>
<td>Research Experimental Methods</td>
<td>35</td>
</tr>
<tr>
<td>Contributions to Knowledge</td>
<td>36</td>
</tr>
<tr>
<td>Organization of the Dissertation Chapters</td>
<td>36</td>
</tr>
<tr>
<td>References</td>
<td>38</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 2 LITERATURE REVIEW</th>
<th>42</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly Ash, Properties and Use in Construction</td>
<td>42</td>
</tr>
<tr>
<td>Fly Ash: Overview</td>
<td>43</td>
</tr>
<tr>
<td>Classification of Fly Ash</td>
<td>44</td>
</tr>
<tr>
<td>Hydraulic and Pozzolanic Activity</td>
<td>45</td>
</tr>
<tr>
<td>Effect of Fly Ash on Concrete Properties</td>
<td>46</td>
</tr>
<tr>
<td>Effect of High LOI Fly Ash on Concrete Properties</td>
<td>47</td>
</tr>
<tr>
<td>Use of Fly Ash in Construction</td>
<td>49</td>
</tr>
<tr>
<td>Fly Ash-Based Geopolymer</td>
<td>51</td>
</tr>
<tr>
<td>Binary and Ternary Blends of Fly Ash and Other SCMs as Pozzolan in Portland</td>
<td>55</td>
</tr>
<tr>
<td>Class C Fly Ash (CFA)</td>
<td>55</td>
</tr>
<tr>
<td>Class F Fly Ash (FFA)</td>
<td>58</td>
</tr>
<tr>
<td>Off-Spec Fly Ash (OSFA)</td>
<td>60</td>
</tr>
<tr>
<td>Ground Glass Fibers</td>
<td>61</td>
</tr>
<tr>
<td>Binary and Ternary Blends of Fly Ash and Other SCMs as Geopolymer Precursors</td>
<td>63</td>
</tr>
<tr>
<td>Class C Fly Ash (CFA)</td>
<td>63</td>
</tr>
<tr>
<td>Class F Fly Ash (FFA)</td>
<td>65</td>
</tr>
<tr>
<td>Off-Spec Fly Ash (OSFA)</td>
<td>66</td>
</tr>
<tr>
<td>Full Depth Reclamation</td>
<td>66</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>181</td>
</tr>
<tr>
<td>---------------------------------------------------------------------------------------</td>
<td>-----</td>
</tr>
<tr>
<td>Strength Activity Index (SAI) Results</td>
<td>181</td>
</tr>
<tr>
<td>Compressive Strength of Concrete</td>
<td>182</td>
</tr>
<tr>
<td>Rapid Chloride Permeability Test (RCPT) Results</td>
<td>185</td>
</tr>
<tr>
<td>Rapid Migration Test (RMT) Results</td>
<td>187</td>
</tr>
<tr>
<td>Water Absorption and Sorptivity</td>
<td>189</td>
</tr>
<tr>
<td>Conclusions</td>
<td>192</td>
</tr>
<tr>
<td>References</td>
<td>193</td>
</tr>
</tbody>
</table>

Chapter 7 EXPERIMENTAL INVESTIGATION ON THE EFFECT OF USING A BLEND OF OFF-SPEC FLY ASH AND GROUND GLASS FIBERS ON THE MECHANICAL PROPERTIES AND DURABILITY OF CONCRETE .......... 196

| Introduction                                                                           | 197 |
| Experimental Program                                                                   | 200 |
| Materials                                                                             | 200 |
| Mixture Proportion                                                                     | 204 |
| Test Methods                                                                           | 206 |
| Isothermal Calorimetry                                                                 | 206 |
| Thermo Gravimetric Analysis (TGA)                                                      | 206 |
| Strength Activity Index (SAI)                                                          | 207 |
| Setting Time                                                                          | 207 |
| Flow Behavior                                                                         | 208 |
| Drying Shrinkage                                                                      | 208 |
| Resistance to Alkali-Silica Reaction (ASR)                                             | 208 |
| Foam Index Test                                                                        | 210 |
| Results and Discussion                                                                 | 211 |
| Hydration Kinetics                                                                     | 211 |
| Pozzolanic Activity by TGA                                                             | 212 |
| Strength Activity Index (SAI)                                                          | 215 |
| The Compressive Strength of Geopolymer Mortar                                         | 217 |
| Setting Time                                                                          | 218 |
| Flow Behavior                                                                         | 219 |
| Foam Index Test                                                                        | 219 |
| Drying Shrinkage of Cement Mortar                                                     | 220 |
| Fresh Properties and Compressive Strength of Concrete Mixtures                        | 222 |
| ASR Test Results                                                                       | 224 |
| Resistance to Chloride Penetration                                                     | 227 |
| Conclusions                                                                           | 228 |
| References                                                                            | 229 |
Chapter 8 EVALUATION OF GEOPOLYMER MORTAR BASED ON A BLEND OF PONDED FLY ASH AND GROUND GLASS FIBERS ACTIVATED BY A SODIUM SILICATE-FREE ACTIVATOR .......................................................... 233

Abstract ........................................................................................................................................ 233
Introduction ..................................................................................................................................... 234
Experimental Program .................................................................................................................. 237
Materials ......................................................................................................................................... 237
Ground Glass Fibers (GGF) ............................................................................................................ 237
Fine Aggregate (Siliceous Sand) .................................................................................................... 238
Non-Reactive Coarse Aggregate .................................................................................................... 239
Reactive Coarse Aggregate ........................................................................................................... 239
Alkaline Activator .......................................................................................................................... 239
Mixture Design and Proportions ............................................................................................... 239
  a- The first set of geopolymer mortar mixtures (using sodium silicate-free activator) ............. 239
  b- The second set of geopolymer mortar mixtures (with the use of SS) .................................. 240
  c- Geopolymer concrete mixture proportion (no SS) ................................................................. 240
Test methods .................................................................................................................................... 241
Results and Discussion .................................................................................................................. 242
Ponded Ash Characterization ........................................................................................................ 242
Water Demand, and Workability .................................................................................................. 245
Isothermal Calorimetry Results ................................................................................................... 246
Setting Time of Geopolymer paste .............................................................................................. 247
Compressive Strength of the First Set of Geopolymer Mortar ..................................................... 248
Compressive Strength of the Second Set of Geopolymer Mortar .............................................. 249
Thermogravimetric Analysis (TGA) ............................................................................................ 252
SEM/EDX Results ........................................................................................................................ 253
XRD Results of Geopolymer Pastes ............................................................................................ 255
Dissolution of Geopolymer Paste in HCl ....................................................................................... 255
Extent of Dissolution ..................................................................................................................... 256
Slump and Compressive Strength of Geopolymer Concrete Mixtures ....................................... 257
Alkali-Silica Reaction .................................................................................................................... 257
Conclusions ..................................................................................................................................... 258
References ....................................................................................................................................... 259

Chapter 9 EVALUATION OF COAL ASH AS A SUPPLEMENTARY CEMENTITIOUS MATERIAL FOR APPLICATION IN FULL-DEPTH RECLAMATION OF ASPHALT PAVEMENTS .................................................................................................................. 262

Introduction ..................................................................................................................................... 262
Experimental Work ....................................................................................................................... 265
Materials ......................................................................................................................................... 265
Test Methods .................................................................................................................................... 267
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix Proportion</td>
<td>268</td>
</tr>
<tr>
<td>Materials Preparation</td>
<td>268</td>
</tr>
<tr>
<td>Mixing Procedures</td>
<td>269</td>
</tr>
<tr>
<td>Optimum Moisture Content (OMC%)</td>
<td>269</td>
</tr>
<tr>
<td>Preparation and Curing of the UCS Test Samples</td>
<td>270</td>
</tr>
<tr>
<td>UCS Test Procedure</td>
<td>270</td>
</tr>
<tr>
<td>Durability of CMRB</td>
<td>270</td>
</tr>
<tr>
<td>Shrinkage of CMRB</td>
<td>271</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>273</td>
</tr>
<tr>
<td>Results of Phase I</td>
<td>273</td>
</tr>
<tr>
<td>Results of Phase II</td>
<td>278</td>
</tr>
<tr>
<td>Results of Phase III</td>
<td>279</td>
</tr>
<tr>
<td>Conclusions</td>
<td>283</td>
</tr>
<tr>
<td>Recommendations</td>
<td>284</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td>285</td>
</tr>
<tr>
<td>References</td>
<td>286</td>
</tr>
</tbody>
</table>

Chapter 10 LABORATORY INVESTIGATION OF SUSTAINABLE CEMENT ALTERNATIVES FOR USE IN FULL DEPTH RECLAMATION OF ASPHALT PAVEMENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>287</td>
</tr>
<tr>
<td>Introduction</td>
<td>288</td>
</tr>
<tr>
<td>Experimental Program</td>
<td>292</td>
</tr>
<tr>
<td>Materials</td>
<td>292</td>
</tr>
<tr>
<td>Bound Materials</td>
<td>294</td>
</tr>
<tr>
<td>Tested Properties and Test Methods</td>
<td>295</td>
</tr>
<tr>
<td>Mixture Proportion</td>
<td>297</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>303</td>
</tr>
<tr>
<td>Moisture–Density Relationships</td>
<td>305</td>
</tr>
<tr>
<td>Change of Moisture Content (%MC) VS UCS</td>
<td>305</td>
</tr>
<tr>
<td>Unconfined Compressive Strength (UCS)</td>
<td>308</td>
</tr>
<tr>
<td>Flexural Strength</td>
<td>310</td>
</tr>
<tr>
<td>Drying Shrinkage</td>
<td>311</td>
</tr>
<tr>
<td>Wetting/Drying Durability Test (W/D Test)</td>
<td>312</td>
</tr>
<tr>
<td>Freeze/Thaw Durability Test (F/Z Test)</td>
<td>314</td>
</tr>
<tr>
<td>Tube Suction Test</td>
<td>315</td>
</tr>
<tr>
<td>Compressive Strength from Portions Broken in Flexure</td>
<td>316</td>
</tr>
<tr>
<td>Conclusions</td>
<td>317</td>
</tr>
<tr>
<td>References</td>
<td>319</td>
</tr>
</tbody>
</table>

Chapter 11 CONCLUSIONS AND RECOMMENDATIONS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conclusions</td>
<td>323</td>
</tr>
<tr>
<td>Recommendations</td>
<td>327</td>
</tr>
<tr>
<td>-----------------</td>
<td>-----</td>
</tr>
<tr>
<td>Chapter 12 APPENDICES</td>
<td>329</td>
</tr>
<tr>
<td>Appendix A</td>
<td>330</td>
</tr>
<tr>
<td>Summary Report of the Toxicity Characteristic Leaching Procedure (TCLP) Test Results for the Cement Modified Recycled Bases (CMRB) Incorporating Off-Spec Fly Ashes</td>
<td>330</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 1-1 Chemical and physical requirements for fly ash to suit concrete usage. Copied from ASTM C618-19.</td>
<td>28</td>
</tr>
<tr>
<td>Table 2-1 A) The general effect of each type of known SCM on concrete properties; B) Comparison between CFA and FFA in terms of the effect of using both on concrete properties (from (11)).</td>
<td>47</td>
</tr>
<tr>
<td>Table 3-1 Chemical composition and physical properties of all the materials.</td>
<td>78</td>
</tr>
<tr>
<td>Table 3-2 Average particles diameter by mass for the tested fly ashes.</td>
<td>81</td>
</tr>
<tr>
<td>Table 3-3 Chemical composition for the selected FAs.</td>
<td>82</td>
</tr>
<tr>
<td>Table 3-4 Estimated phase composition by whole pattern fitting.</td>
<td>84</td>
</tr>
<tr>
<td>Table 4-1. Chemical composition and physical properties for the materials.</td>
<td>114</td>
</tr>
<tr>
<td>Table 4-2. Mixture proportions and test methods.</td>
<td>115</td>
</tr>
<tr>
<td>Table 4-3. Fresh and hardened mortar test results.</td>
<td>124</td>
</tr>
<tr>
<td>Table 4-4 Results of setting time.</td>
<td>125</td>
</tr>
<tr>
<td>Table 5-1 Chemical composition and physical properties for the materials.</td>
<td>142</td>
</tr>
<tr>
<td>Table 5-2 Cementitious materials proportion for all the mixtures.</td>
<td>144</td>
</tr>
<tr>
<td>Table 5-3 Strength activity index test results.</td>
<td>151</td>
</tr>
<tr>
<td>Table 5-4 Ultrasonic pulse velocity measurements of concrete cylinders.</td>
<td>153</td>
</tr>
<tr>
<td>Table 5-5 The results of sorptivity and correlation with RCPT results, the diagonal cells in the tables are showing cumulative correlations ($R^2$ Value) for: (a) initial absorption (b) secondary absorption.</td>
<td>161</td>
</tr>
<tr>
<td>Table 6-1 Chemical composition and physical properties for the materials.</td>
<td>175</td>
</tr>
<tr>
<td>Table 6-2 Relative proportions in the binder.</td>
<td>176</td>
</tr>
<tr>
<td>Table 6-3 Strength activity index for all mixtures.</td>
<td>182</td>
</tr>
<tr>
<td>Table 6-4 Comparison between the tested RCPT and RMT samples for the depth of chloride penetration.</td>
<td>189</td>
</tr>
</tbody>
</table>
Table 7-1. Chemical composition and physical properties for the materials.................. 204
Table 7-2. Mixture proportions and test methods. .......................................................... 205
Table 7-3 geopolymer mixtures proportions. ................................................................. 206
Table 7-4 Fresh and hardened mortar test results........................................................... 216
Table 7-5 Compressive Strength of RFA+GGF-based Geopolymer................................. 217
Table 7-6 Setting Times of RFA+GGF Binary and Ternary Mixtures............................... 218
Table 7-7 Fresh Properties of Cement Concrete Mixtures........................................... 223
Table 7-8 Test Results for RCPT and RMT ................................................................. 227
Table 8-1 Labels, mixture proportions and test methods. ............................................. 241
Table 8-2 Physical properties and chemical composition of CSFA and GGF................. 243
Table 8-3 The flow results of the tested geopolymer mortar......................................... 246
Table 8-4 Setting time results. ...................................................................................... 248
Table 8-5 7-day compressive strength results for the second set of mixtures. ............... 250
Table 8-6 EDX analysis results...................................................................................... 254
Table 8-7 Results of dissolution of geopolymer paste in HCl. ........................................ 256
Table 8-8 Results of testing the extent of dissolution of precursors............................... 256
Table 8-9 Results of compressive strength and splitting tensile strength of geopolymer concrete............................................................................................................. 257
Table 9-1 Chemical composition of the cement............................................................. 266
Table 9-2 Average particles diameter by mass for the tested fly ashes.......................... 273
Table 9-3 Chemical composition for the selected FAs.................................................. 275
Table 9-4 SAI%, and setting time tests results. ............................................................. 279
Table 9-5 UCS results for all mixtures, psi (MPa) (1 psi = 0.0069 MPa)............................ 280
Table 10-1 Chemical composition and physical properties of the materials used in this study. ...................................................................................................................... 294
Table 10-2 Mixtures proportion and test methods. ......................................................... 304
Table 10-3 Change of UCS relative to change of MC above or below the OMC.................307
Table 10-4 the Final dielectric values from the tube suction test results ...................... 316
Table 10-5 Results of UCS taken from broken prism samples........................................ 317
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1-1</td>
<td>Change in primary energy sources shows a decline in coal-based energy production (copied from [16]).</td>
</tr>
<tr>
<td>Figure 1-2</td>
<td>Comparison between Life Cycle Assessment (LCA) of geopolymer mortar production [44].</td>
</tr>
<tr>
<td>Figure 2-1</td>
<td>X-Ray Diffractogram for FFA (above) and CFA (below). Copied from (9).</td>
</tr>
<tr>
<td>Figure 2-2</td>
<td>Correlation between CaO content and the sum of the oxides for 30 different ashes in the US (11).</td>
</tr>
<tr>
<td>Figure 2-3</td>
<td>Effect of fly ash LOI on concrete water demand (15).</td>
</tr>
<tr>
<td>Figure 2-4</td>
<td>Illustration for how unburned carbon affect the air-entraining agents compared to cement (11).</td>
</tr>
<tr>
<td>Figure 2-5</td>
<td>The geopolymerization process.</td>
</tr>
<tr>
<td>Figure 2-6</td>
<td>OPC consumption in FDR projects in SC.</td>
</tr>
<tr>
<td>Figure 3-1</td>
<td>Flowchart for all the experimental work in this dissertation.</td>
</tr>
<tr>
<td>Figure 3-2</td>
<td>Fly ash portion of each collected ash.</td>
</tr>
<tr>
<td>Figure 3-3</td>
<td>Particle size distribution of all four FAs using laser diffraction.</td>
</tr>
<tr>
<td>Figure 3-4</td>
<td>SEM images for A, B, C, and D FAs.</td>
</tr>
<tr>
<td>Figure 3-5</td>
<td>XRD results of a) A, b) B, c) C, d) D fly ashes.</td>
</tr>
<tr>
<td>Figure 3-6</td>
<td>Rapid migration test setup (copied from NT build 492).</td>
</tr>
<tr>
<td>Figure 4-1</td>
<td>SEM image for a) CFA, b) GGF.</td>
</tr>
<tr>
<td>Figure 4-2</td>
<td>a) Heat flow; and b) heat release curves (w/c = 0.40) @ 23 °C.</td>
</tr>
<tr>
<td>Figure 4-3</td>
<td>Results of TGA test: a) at 7 days; b) at 28 days; and c) the ratio of CH of test mixtures relative to the control.</td>
</tr>
<tr>
<td>Figure 4-4</td>
<td>Drying Shrinkage Results: a) for all mixtures; b) shrinkage values as compared to control at 28 and 98 days.</td>
</tr>
<tr>
<td>Figure 4-5</td>
<td>ASR AMBT Results.</td>
</tr>
</tbody>
</table>
Figure 4-6 a) ASR MCPT results, showing the expansion values at 56 days; b) Correlation between AMBT and MCPT test results .................................................. 131

Figure 4-7. Sulfate attack test results ........................................................................ 132

Figure 5-1 Results of pozzolanic activity by TGA ......................................................... 150

Figure 5-2 a) Compressive strength of concrete mixtures; b) comparison of the binary CFA and GGF mixtures ........................................................................ 152

Figure 5-3 Splitting tensile strength test results .......................................................... 154

Figure 5-4 Miniature concrete prisms ASR expansion results ........................................... 156

Figure 5-5 Relative DME for the concrete prisms tested in MCPT. ................................. 158

Figure 5-6 RCPT test Results for CFA+GGF Binary and Ternary Mixtures ....................... 159

Figure 5-7 Results of surface resistivity of concrete mixtures and correlation with RCPT results ........................................................................................................ 160

Figure 6-6-1 Resistance to chloride penetration after a 10-year exposure to a tidal zone (From [6]) .................................................................................................. 171

Figure 6-2 Concrete sample under sorptivity testing ...................................................... 179

Figure 6-3 The RCPT test setup ..................................................................................... 180

Figure 6-4 Rapid migration test setup: (a) plastic cylinders were modified to serve as the rubber sleeve prescribed in NT Build 492; (b) Measurement of chloride penetration after the test; (c) The cathode and anode connections; (d) The plastic reservoir and the support of the cylinders at an angle of 32 degrees; (e) Silicon was used to seal the sides of the sample from top and bottom ........................................... 181

Figure 6-5 Compressive strength of all concrete mixtures ............................................. 184

Figure 6-6 The compressive strength of the binary concrete mixtures ................................ 185

Figure 6-7 RCPT results ............................................................................................. 185

Figure 6-8 Results of surface resistivity and correlation with RCPT results ..................... 187

Figure 6-9 RMT results ............................................................................................... 188

Figure 6-10 Sorptivity test results ................................................................................. 191

Figure 6-11 Water absorption test results ..................................................................... 191
Figure 7-1 SEM image for (a), (b), and (c) RFA at different magnification levels, b) GGF
Figure 7-2 XRD Analysis for a) GGF b) RFA
Figure 7-3 Particle size distribution of RFA in both original state and sieved state, and GGF
Figure 7-4 a) Heat flow; and b) Heat release curves (w/c = 0.40) @ 23 °C.
Figure 7-5 Results of TGA test: a) at 7 days; b) at 28 days; and c) the ratio of CH of test mixtures relative to the control.
Figure 7-6 Compressive strength of mortar for the binary and ternary RFA and GGF mixtures.
Figure 7-7 Foam index test results.
Figure 7-8. Drying shrinkage results: a) for all mixtures; b) shrinkage values as compared to control at 60 days.
Figure 7-9 Compressive strength of concrete mixtures.
Figure 7-10 ASR AMBT Results
Figure 7-11. ASR MCPT results, showing the expansion values at 56 days for a) RFA binary mixtures, b) GGF binary mixtures, c) RFA+GGF ternary mixtures, and d) Correlation between MCPT and AMBT test results.
Figure 8-1 Chemical composition of GGF compared to cement and some other cementitious materials.
Figure 8-2. SEM image for a) CSFA, b) GGF.
Figure 8-3 Particle size distribution for the ponded fly ash and GGF.
Figure 8-4 XRD results for the ponded fly ash.
Figure 8-5 Isothermal calorimetry test result on geopolymer paste.
Figure 8-6 Compressive strength of geopolymer mortar.
Figure 8-7 The effect of variable alkali modulus on the compressive strength of geopolymer mortar.
Figure 8-8 TGA results for geopolymer pastes.
Figure 8-9 SEM Images of the geopolymer pastes.
Figure 8-10 XRD test results for the geopolymer pastes. ................................................................. 255
Figure 8-11 Alkali-Silica Reaction test results. ............................................................................ 258
Figure 9-1 OPC consumption in FDR projects in SC. ...................................................................... 265
Figure 9-2 Particle size distribution of all four FAs using laser diffraction. .............................. 274
Figure 9-3 XRD results of a) A b) B c) C d) D fly ashes. .............................................................. 276
Figure 9-4 SEM images for A, B, C, and D FAs. ................................................................................. 278
Figure 9-5 Comparison between UCS of control mixtures and 20% FA mixtures. ...................... 281
Figure 9-6 Comparison between UCS of control mixtures and 40% FA mixtures. ................. 281
Figure 9-7 Drying Shrinkage Results ............................................................................................ 283
Figure 10-1 SEM image for the ponded fly ash, (a) after sieving, (b) in the original state. ......................................................................................................................... 294
Figure 10-2 Particle size distribution of base soil + RAP ............................................................... 295
Figure 10-3 The mixer (right) and the OMC testing (left). ............................................................... 296
Figure 10-4 Elastic modulus test setup. ......................................................................................... 297
Figure 10-5 Wetting and drying durability test a) wire brushing, b) CMRB samples, c) samples in oven. .......................................................................................................................... 300
Figure 10-6 F/T samples under testing. .......................................................................................... 301
Figure 10-7 Tube suction test setup. ............................................................................................. 303
Figure 10-8 Natural resonance frequency measurements. ........................................................... 303
Figure 10-9 Experimental program layout. .................................................................................... 304
Figure 10-10 Moisture-density relationship. The dotted lines are the range of OMC for all tested mixtures. ................................................................................................................................ 305
Figure 10-11 Change of moisture content vs UCS ........................................................................ 307
Figure 10-12 Unconfined compressive strength (UCS) for all mixtures in an ascendant order for the binder ratio (6, 9, and 12%). ...................................................................................... 309
Figure 10-13 Flexural strength, Fr, psi, and correlation between Fr and UCS and resonance frequency in both flexural and torsional modes ........................................................................ 311
Figure 10-14 Drying shrinkage results................................................................. 312

Figure 10-15 W/D durability test results............................................................. 313

Figure 10-16 F/T test results.................................................................................. 314

Figure 10-17 F/T specimens: the left picture was taken at the beginning of the test, and
the right picture was for (6% G&F) specimens after 11 cycles of F/T. .................. 315

Figure 10-18 Correlation between dielectric values and W/D and F/T test results........ 316
Chapter 1

INTRODUCTION

Background

The massive infrastructure development in the construction industry has resulted in the extensive use of ordinary Portland cement (OPC). The production of OPC in the US has increased from 1.52 billion metric tons in 1998 to 4.1 billion metric tons in 2018 [1], increasing by 170% in twenty years. The manufacturing process of OPC is energy-intensive not only because of the high energy involved in the extraction of raw materials but also the energy required in heating them to high temperatures during the production of OPC. Additionally, OPC manufacturing causes significant environmental degradation as each 1 ton of cement requires 2.8 tons of raw materials [2] and generates about 1 ton of CO₂ emissions. As a result, this process is responsible for about 7% of anthropogenic CO₂ emissions [3]. Therefore, sustainability has become one of the main objectives of the concrete industry. Sustainability can be achieved by reducing OPC consumption or making the OPC manufacturing process more efficient.

One of the well-known methods of reducing cement consumption is to partially replace it with supplementary cementitious materials (SCMs). According to ASTM C125-19 [4], SCMs are “an inorganic material that contributes to the properties of a cementitious mixture through hydraulic or pozzolanic activity or both.” Between 25% and 30% reduction of CO₂ emissions can be achieved by substituting OPC with SCMs [5]. Various types of materials have been used as SCMs, including natural materials as well as industrial byproducts. Examples of natural materials are calcined clay, shale, metakaolin, volcanic ash, rice husk ash, etc. While the industrial byproducts include slag, fly ash, silica
fume, glass powders, etc. Among all SCMs, fly ash is the most widely used material in the construction industry since its first use in the 1930s [5].

Fly ash is a byproduct of coal-burning thermal power plants. Fly ash represents about 80% of the ash produced at power plants and is collected by baghouses and electrostatic precipitators. While the remaining 20% of the ash generated is called bottom ash, and it is accumulated at the bottom of the boilers. In 2018, there was a 2.6% increase in coal-based generated energy, and it is still the largest source of electricity worldwide [6]. Total ash generation from burning coal can range between 25 and 60 percent by weight of the burnt coal, with annual fly ash generation ranging between 600 and 800 million tons globally [7]. In the US, 50 million tons of fly ash is projected to be produced annually and will remain steady for the next 15 years [5].

There are two methods to dispose of all the ash produced. The first method is the dry collection of fly ash, which can be either commercially used or disposed in off-site landfills. ASTM C618-19 [8] classifies the fly ash that can be used in concrete into two categories; class C fly ash (CFA) and class F fly ash (FFA) according to their chemical composition and physical attributes. The second method of disposal is called wet disposal [9]. In this method, both fly and bottom ashes are mixed with water to form a slurry, which facilitates pumping it out into storage facilities called ash ponds.

The ash ponds have harmed the environment on several occasions. Dan River coal ash spill is one example [10], where millions of gallons of coal ash sludge spilled into the river through a broken pipe. The river provides drinking water to communities in NC and VA. Additionally, some evidence shows that unlined pond ashes have polluted shallow groundwater with traces of harmful elements [11]. In 2018, Hurricane Florence floodwater threatened to spill toxic waste from an ash storage pond into the Cape Fear River in
Wilmington, NC [12]. All these concerns have necessitated the need for effective waste management to improve environmental sustainability.

Efforts to improve the environmental sustainability of coal for energy production have resulted in the reclamation of fly ash in the construction sector [7]. Historically, the utilization of fly ash, both CFA and FFA, in concrete resulted from a necessity of managing the coal combustion residues from being landfilled and offering environmental sustainability. However, it was soon realized that fly ash significantly enhances fresh and hardened concrete properties. Fly ash has been found to increase the workability of the fresh mortar and concrete mixtures, reduce drying shrinkage and permeability, increase the ultimate compressive strength, and provide adequate mitigation against various durability problems such as alkali-silica reaction (ASR), sulfate attack, and chloride penetration when used in sufficient quantities. Generally, CFA is considered to be not as effective as FFA in addressing durability problems in concrete such as ASR and sulfate resistance, unless when used at higher dosage levels [13]. However, at high dosages of fly ash, especially for CFA, early-age strength, and setting time are negatively affected [14], [15]. Thus, there is a need to improve class C fly ash performance at higher levels of OPC replacement.

The reclamation of fly ash in the construction industry represents a widely adopted approach to managing coal waste. Although fly ash is widely used as a cement replacement material at present, the reality is that coal, from which fly ash is produced, is a finite resource that will one day need to be replaced with other energy resources. Growing environmental concerns have already forced power producers to switch to alternative fuels such as natural gas, as shown in Figure 1-1, and the concrete industry will soon need to
find alternative supplementary cementitious materials (SCMs) or find ways to maximize and optimize the use of existing fly ash resources.

Among the existing fly ash resources that have not been fully utilized in beneficial applications are the Off-Spec Fly Ashes (OSFA). Specific requirements need to be met for fly ash to be suitable for use as an SCM with OPC in structural-concrete applications. ASTM C618-19 [8] specifies the conditions required for this purpose, and all requirements are shown in Table 1-1. However, a large amount of the coal ash produced from burning coal at power plants does not meet at least one of these requirements, such as loss of ignition (LOI). Environmental regulations that have been imposed on power plants have led to the production of very low-quality ashes [5]. Consequently, most of the ashes that have been disposed of in the storage ponds awaiting future environmentally-sound applications are the OSFA.
The high LOI in fly ash affects the water demand of concrete. An increase in LOI by 4% would require about 5% more water to account for the slump reduction in concrete [17], which in turn would negatively affect the strength and increase the porosity and permeability of concrete. In coal-based power plants, the boilers are run at reduced power during seasons of lower demand for energy to save on cost. However, once energy demand increases, the boilers are operated at full power generation capacity. However, it takes long time to raise the performance of the boilers to full power and power plants always inject oil into the furnace to accelerate the process [16]. During this boosting process, the fly ash
is produced with higher LOI. Also, high-rank types of coal, such as anthracite, are difficult to combust and thus result in higher LOI content [16], [18].

One possible way of enhancing the performance of fly ash is to blend it with high-quality material. The idea of using ternary blends (two additional SCMs blended with cement) in concrete is well known at both the research and industry levels, where the deficiency caused by the first material is alleviated by using a second material. Therefore, researchers have investigated the use of other SCMs along with fly ash, such as slag [19], [20], rice husk ash [21], glass powder [22], meta-kaolin [20], [23]–[25], silica fume [26]–[28], and FFA+CFA [20], [29], [30]. The better performance of some of the ternary blends in various mortar and concrete mixtures has been well proven.

Despite the improvement in properties of ternary-blended concrete, there are some implications of using each material. For example, silica fume is known to cause an increase in water requirements and plastic shrinkage [27]. Furthermore, silica fume is costly compared to other SCMs, and it costs even more than OPC [27]. Meta-kaolin can negatively influence the water-demand and hence workability, while the use of slag can cause significant concerns in cold-weather conditions [31], [32]. The alkali level of glass powder from soda-lime glass is relatively high and is a concern that could affect ASR performance [22]. Therefore, there is a need for other alternatives to be investigated, especially those substitutes that have not been considerably examined for beneficial uses. One of these materials is the fiberglass waste from the production of glass fibers for use in composite materials.

In the glass fiber industry, the glass composition is carefully monitored, and the quality of the glass filament is thoroughly inspected for defects. During the production, a significant quantity of glass fiber that does not meet the specification requirements (lack
of adequate physical attributes, not relating to chemical composition) is discarded as off-spec glass fiber. As a result, the off-spec glass fiber is removed from the production line as industrial waste and sometimes pulverized to reduce the volume and reduce transportation costs [33]. Since glass fibers are difficult to recycle [33], all the off-spec glass fibers are landfilled. Although the use of recycled glass generated from soda-lime glass in concrete is well documented, there have been only a few publications that investigated the use of ground glass fibers (GGF) as an SCM [34]–[36]. In places where GGF is abundant, it could be an excellent alternative to fly ash.

Another possible way of alleviating the cement industry's environmental impacts, which has vastly developed in the past few decades, is the use of geopolymer binders. These binders are produced by activating an alumino-silicate material by an alkali solution. It has been well established that the mechanical properties of geopolymers are competing with those of Portland cement concrete (PCC). Even better performance has been observed for geopolymer concrete (GC) over PCC in terms of acid resistance, fire resistance, and ASR [2], [37]. Most of the work done on fly ash-based geopolymer has used FFA [2] and, on a smaller scale, CFA, whereas minimal studies have dealt with OSFA [38]. The GGF has superior performance as a geopolymer precursor [37], [39], and thus combining its use with fly ash should improve the fly ash-based geopolymer performance.

As power companies are moving towards alternative fuel sources, the availability of high-quality fly ash is limited [5]. Many US states have studied other fly ash alternatives to be used in the concrete industry [40]. At the same time, the production of glass fibers is growing [41], and hence the glass fiber waste generated. Therefore, the combined use of both materials would result in several benefits. First, it would overcome the short supply of fly ash. Second, it would provide a beneficial use for the waste glass fibers and ponded
ash, thus reducing the environmental burden. Third, it would help reduce OPC consumption by replacing cement with these pozzolans at a higher replacement level. Additionally, the combined use of this blend is expected to enhance the performance of mortar and concrete mixtures in both PCC and GC systems.

**Practical Applications**

In the concrete research industry, significant effort is directed towards the characterization of natural and industrial byproducts and their performance in OPC and geopolymer concrete. Moreover, many research studies focus on one or two concrete properties and study how they could be affected by particular parameters in the concrete mixture proportions. However, a limited number of studies deal with finding real applications where all these designed mixtures and materials could be utilized, which is equally important. Quoting an essential phrase from the 2009 book by Provis and Vandeventer [42] that says: "*a material that is well characterized but not used in the real world is in effect useless,*" emphasizes this view. Therefore, besides finding ways how fly ash performance in OPC and geopolymer concrete can be improved, another objective of this work is to examine real-world applications where these mixtures can be a part of.

Finding real avenues for GGF and ponded ash, where they can realistically be applied, not only facilitate their use in such channels but would also help in consuming large amounts of these industrial byproducts and save the environment from the implications of landfilling otherwise. Thus, one vital application was selected to be explored using the suggested combinations. The selected application was the full depth reclamation (FDR) of asphalt pavements, which is a rapid means to rehabilitate existing pavements by mixing the pulverized old asphalt layer and the base materials beneath with OPC and stabilizing the whole blended materials with water.
**Scope and Significance of the Study**

The use of fly ash as a cement replacement material has faced numerous limitations, especially the complexity of chemical and physical properties that impact durability [43]. It should be noted that the performance of fly ash depends on multiple factors, such as the physical and chemical properties of the fly ash and its dosage level in concrete as a cement replacement material. According to ASTM C618-19, fly ash is identified as Class C or Class F fly ashes characterized by high calcium and low calcium, respectively. However, it has been established that some of the fly ashes do not meet the ASTM C618 requirements and are called the off-spec fly ashes. Such materials are mostly stored in the ash ponds as they wait for beneficial uses. Studies have demonstrated that Class F fly ash performs better in both the GC and the PCC than Class C fly ash over the long term. Besides, class F fly ash has been noted to perform better regarding mitigation of most of the durability challenges related to PCC, such as sulfate attack, resistance to chloride ion penetration, and alkali-silica reaction.

The use of fly ash in geopolymer concrete requires the use of a concentrated alkaline solution and heat curing to facilitate its quality, especially the strength. Mostly, the alkaline solution is made by combining sodium silicate and sodium hydroxide [43]. However, these procedures have been noted to affect the carbon footprint of geopolymer, which has been considered by many researchers and builders as a sustainable alternative to the PCC. It has been established that the use of sodium silicate as an alkaline solution is the most contributing factor towards the total carbon footprint of the geopolymer concrete, as shown in Figure 1-2 [44]. In this regard, it has been suggested that eliminating the use of the sodium silicate alkaline solution while still maintaining good quality performance by the material is one of the ways that would significantly reduce the geopolymer concrete carbon footprint.
As previously mentioned, it is incredibly imperative to find beneficial uses of the off-spec fly ash materials to avoid environmental pollution. Considering the volume of ash available, large-volume applications that can beneficially employ ash as a construction material consistently need to be developed. One such application that is both sustainable and can potentially add value to the application is to use ash in combination with OPC in the stabilization of pavement bases as well as in full-depth reclamation of asphalt pavements. While ponded ash consists of a mixture of bottom ash and fly ash, the ash that is most influential in reacting with portland cement is the fly ash. Therefore, any consideration of using a ponded ash with portland cement for application in base stabilization should involve determining the fly ash content of the mixture. The relative
proportions of the bottom ash and the fly ash will likely dictate the volumes of ponded ash that can be blended with the base materials and portland cement for stabilization.

Depending on the fly ash's chemical composition and physical characteristics, blending ash with portland cement can significantly enhance the blended material's strength and durability through pozzolanic reactions. This synergy can not only improve the performance of the application in which it is used, but large volumes of ash can be consumed, while simultaneously alleviating the demand for the portland cement.

**Research Aim and Proposed Solution**

This study seeks to propose ways in which fly ash use can be boosted to, partially or entirely, replace OPC in concrete without affecting its mechanical and durability properties. To enhance the performance of fly ash, both class C and class F, as well as off-spec fly ashes, in this study blending the fly ash with other materials that have a superior performance in both the geopolymer concrete (GC) and the Portland cement concrete (PCC) has been considered. Also, to ensure the highest possible sustainability levels, the material used to strengthen the performance of fly ash should be an industrial waste material that has not been thoroughly investigated for beneficial applications, but it shows high potential as a SCM. Therefore, this study suggests using ground glass fibers (GGF) that has been noted to perform effectively as cement replacement in PCC and as a precursor in GC. The significance of GGF and its performance in the PCC, as well as in the GC, was researched and discussed by Rashidian Dezfooli (2017) in his Ph.D. dissertation [45], who confirmed its significance in enhancing the quality of concrete [46].

Although this work deals with the aforementioned types of fly ash (in-spec and off-spec), in this research, more focus would be cast on the off-spec fly ashes and how their performance can be improved in both PCC and GC. In addition to the first suggestion
mentioned above, which is blending the OSFA with GGF, this study aims only to utilize the finer particles of the off-spec ashes collected for the study. It has been proven that, regardless of the fly ash type, the fly ash particles with a size above 45 microns are considered inert and do not participate in the pozzolanic activity [47], so they act only like a filler. On the other hand, particle sizes below 10 microns and between 10 microns and 45 microns contribute to the early and later concrete strength, respectively [47]. Another reason why the finest particles perform better is that the amount of unburnt carbon, represented by the loss on ignition (LOI) value, a property that huge amounts of fly ashes have failed to meet, is mostly in the coarser particles. Therefore, eliminating the coarser particles along with blending with GGF would reduce the high LOI of the OSFAs and enhance its performance in PCC and GC.

**Research Experimental Methods**

Various procedures will be used to assess the performance of the blends of GGF and fly ashes in both PCC and GC. The combinations of all the classes of fly ashes (Class C, Class F, and off-spec fly ashes) will be tested in both the binary and the ternary mixtures in replacing cement in PCC. Secondly, the same blends tested will be activated using a lower carbon footprint alkaline solution in GC to ensure the best sustainable utilization. The alkaline solution preferred for use in this investigation will be based only on sodium hydroxide. Once the GC is mixed, only ambient to moderate heat of curing (up to 60 °C) will be applied. Once the blends have been developed and the procedures complete, their qualities will be investigated in both the GC and the PCC based on the properties that they depict. The materials will be examined for their fresh properties, such as the setting time and workability, mechanical properties, such as compressive and tensile strength, as well as durability properties, such as ASR mitigation, sulfate attack, chloride penetration, and
freezing and thawing. Additionally, the materials will be considered for their real application properties for base soil stabilization in full depth reclamation (FDR). Results of the mechanical properties of the full depth reclaimed bases will be correlated with basic features of the binding mediums and try to come up with non-destructive methods, such as ultrasonic pulse velocity or resonance frequency measures, for evaluation.

**Contributions to Knowledge**

By implementing the planned scope of work, the following output to knowledge is anticipated:

1- Optimization of the current resources of fly ash that are on a threat of diminishing and thus maximizing the use of fly ash in construction.

2- Finding ways to facilitate the use of pond ash that has been stored for a long time in storage ponds in concrete.

3- Achieving a better performance of fly ash-based geopolymer without the need for sodium silicate, a significant contributor to geopolymer’s total carbon footprint.

4- Promoting alternatives to cement in full depth reclamation of asphalt pavements, ranging from partial to complete replacement.

**Organization of the Dissertation Chapters**

This dissertation is organized as follows:

- Chapter 1: Introduction:

This chapter identifies the research problem, significance, proposed solution, and methods.

- Chapter 2: Literature Review:
This chapter introduces the topic of fly ash and how it is being utilized in construction industry. Also, it summarizes the advantages and disadvantages of using fly ash in concrete. Then, it presents a literature review about other SCM that were used along with fly ash in ternary blends in both PCC and GC. In addition, an introduction to the selected applications, full-depth reclamation, is provided.

- **Chapter 3: Experimental Work:**
This chapter provides the whole set of experiments, materials, and methods used throughout the different chapters. Also, it included the results of the four selected off-spec fly ash characterization.

- **Chapter 4 to Chapter 10:**
Manuscripts for research papers that are either submitted, in review or being prepared to be submitted for publication. Chapters 4 and 5 investigated the use of class C fly ash and GGF in both hydraulic cement mortar and concrete, respectively. Chapter 6 is a study about the resistance of concrete containing blends of CFA, FFA, GGF to chloride ingress. Chapter 7 is assigned to show the work of high LOI fly ash in which one of the OSFA was selected to be blended with GGF as SCM in cement mortar and concrete. While chapter 8 includes the research work of geopolymer mortar and concrete based on one of the selected blend of ponded ash and GGF. Chapter 9 is where all the OSFAs were investigated to be used as a partial replacement for cement in cement modified recycled base (CMRB). Chapter 10 is also about FDR, but it investigated a wider range of options to replace cement either partially in cementitious material based stabilization or entirely in geopolymer-based stabilization.

**Chapter 11: Conclusions and Recommendations:**
A summary of the essential findings and the recommendations from this study are provided in this chapter.

References


Chapter 2

LITERATURE REVIEW

Fly Ash, Properties and Use in Construction

The acceleration of global economic development is due, in large part, to increased consumption of fossil fuels, including coal. Current research indicates that coal is coming closer to exceeding oil as the world’s largest energy source (1). Although coal is typically viewed as a reliable and secure energy resource, use of this fossil fuel for energy generation results in substantial production of waste, including fly ash (1). Total ash generation from burning coal can range between 25 and 60% by mass of the burnt coal, with annual fly ash generation ranging between 600 and 800 million tons globally (2). Efforts to improve the environmental sustainability of coal for energy production have resulted in the reclamation of fly ash in the construction sector (2). More specifically, fly ash is extensively utilized to produce cement, concrete, and structural fill (2).

The reclamation of fly ash in the construction industry represents a novel approach to managing coal waste. Although fly ash is widely used as a cement replacement material at present, the reality is that coal from which fly ash is produced is a finite resource that will one day need to be replaced with renewable energy resources. Growing environmental concerns have already forced power producers to switch to alternative fuels such as natural gas, and the concrete industry will soon need to find alternative SCMs or find ways to maximize and optimize the use of existing fly ash resources.

The following subsections provide a review of critical topics, including an overview of fly ash to describe the material and a review of how fly ash is currently being utilized in the construction industry. Through a review of these topics, it will be possible to provide
a more comprehensive understanding of fly ash and its importance for the construction industry.

**Fly Ash: Overview**

Coal is the most available and extensively used fossil energy supplier in the world (3). The increased combustion of coal across the globe has increased fly ash production. Worldwide, the amount of fly ash has increased so significantly that this material is recognized as the fifth largest raw material resource (4).

Fly ash is a heterogeneous powder described as having a “glassy and amorphous structure” resulting from the inorganic and incombustible materials present in coal (4). This byproduct is typically light or dark grey, depending on the amount of unburnt carbon present in the material (2). Although these essential characteristics of fly ash are common, research does indicate that the chemical and physical properties of fly ash vary much based on the features of the coal and the combustion technique utilized (2). Despite variations in the product, the following physical properties have been identified for fly ash utilized in various industries: specific gravity, 2.10 – 2.81; particle size distribution, 0.001 – 0.075 mm; bulk density, 1.12 – 1.28 g/cm³; and specific surface area, 1.0 – 9.44 m²/g (2).

Micromorphology studies of fly ash have shown that particles in fly ash are typically spherical in nature and consist of solid irregular-shaped debris as well as porous carbon particles (5,6). The irregular shapes of fly ash particles result from the softening of inorganic materials found in coal (5). Most of these materials do not combust at high temperatures; instead, they only soften (5). Chemically, coal fly ash is one of the most sophisticated materials that has been characterized. Studies to evaluate the chemical composition of fly ash have demonstrated that this compound contains 316 individual
minerals as well as 188 different mineral groups (5). The typical observed crystalline minerals in fly ash are shown in Figure 2-1.

Chemical Composition of all Fly ashes contains silicon, aluminum, iron, titanium, and calcium oxides (2). Besides, all types of fly ash can contain heavy metals and metalloids, including arsenic, cobalt, and lead (7). Under acidic conditions, these elements can leach into the environment resulting in considerable damage (7). Bulk fly ash deposits placed in landfills are particularly susceptible to environmental leaching and have caused significant destruction of land and soil resources (7,8).

Classification of Fly Ash

According to ASTM C618 (10), fly ash is classified into two main types, identified as Class F and Class C. Class C fly ash (CFA) is produced as a result of burning lignite or sub-bituminous coal. Class F fly ash (FFA), in contrast, is produced as a result of burning bituminous or anthracite coal (2,6). In the US, CFA is available more in the region to the
west of the Mississippi river, while FFA is available more in the region to the east of the Mississippi river.

Fly ash is classified mainly by its bulk chemical composition. ASTM C618 used the sum of the oxides, which is the sum of \((\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)\) content, as the principal classifier. However, this method has been criticized for being not specific and not based on calcium oxide (CaO) content (11). However, there is a good correlation between the sum of the oxide and CaO content, and, thus, classification based on either is acceptable (11). The CaO content that differentiates between CFA and FFA based on Figure 2-2 is \((18\% \pm 4\%)\). It is worth mentioning that the Canadian Specification classifies fly ash based on its CaO content: Type F < 8% CaO, Type CI 8-20% CaO, and Type CH >20% CaO (CSA A3000) (11).

![Figure 2-2 Correlation between CaO content and the sum of the oxides for 30 different ashes in the US (11).](image)

**Hydraulic and Pozzolanic Activity**

Hydraulic activity is a property whose material sets and hardens by the chemical reaction with water. Cement is described as hydraulic because it hardens when mixed with
water. Also, some types of SCM have hydraulic activity, such as slag or class C fly ash. The main products in this hydraulic reaction of cement are the calcium silicate hydrate (C-S-H) and calcium hydroxide (CH: portlandite). C-S-H is the skeleton of concrete as it provides the strength of concrete, whereas CH not only does it not contribute much toward the strength of concrete but is also involved in many deteriorating reactions damaging the concrete and affecting durability. Pozzolanic reactivity is the reaction between pozzolan (SCM) and the undesirable CH to produce more C-S-H gels, which add to the strength, and thus, the durability of concrete (11).

**Effect of Fly Ash on Concrete Properties**

Compared to control concrete mixture, the use of fly ash in concrete has the following effects (9):

- improved workability,
- lower heat of hydration,
- lower concrete cost,
- improved resistance to sulfate attack,
- improved resistance to alkali-silica reactions (ASR),
- higher long-term strength,
- opportunity for higher strength concrete,
- similar freeze-thaw durability,
- lower shrinkage characteristics, and
- lower porosity and decreased permeability.

However, fly ash use in concrete does have some downsides, including the slower early strength gain, prolonged setting time, the need for high dosage levels to mitigate
durability problems such as ASR or sulfate attack especially with CFA, and the effect of unburnt carbon content (LOI) in fly ash on the air content of concrete (11).

A comparison between the two types of fly ash and other SCMs (slag and silica fume) for the effect of using each SCM on concrete properties is shown in Table 2-1 below.

Table 2-1 A) The general effect of each type of known SCM on concrete properties; B) Comparison between CFA and FFA in terms of the effect of using both on concrete properties (from (11)).

<table>
<thead>
<tr>
<th>Property</th>
<th>Class C Ash</th>
<th>Class F Ash</th>
<th>Slag Cement</th>
<th>Silica Fume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Set Time</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>–</td>
</tr>
<tr>
<td>Strength Gain (early)</td>
<td>+</td>
<td>–</td>
<td>–</td>
<td>+</td>
</tr>
<tr>
<td>Strength Gain (late)</td>
<td>o</td>
<td>+</td>
<td>+</td>
<td>&lt; &gt;</td>
</tr>
<tr>
<td>Setting Time</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>–</td>
</tr>
<tr>
<td>Heat of Hydration</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>+</td>
</tr>
<tr>
<td>Plastic Shrinkage Cracking</td>
<td>&lt; &gt;</td>
<td>&lt; &gt;</td>
<td>&lt; &gt;</td>
<td>+</td>
</tr>
<tr>
<td>Permeability</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>ASR Mitigation</td>
<td>&lt; &gt; or o</td>
<td>+</td>
<td>&lt; &gt; or +</td>
<td>–</td>
</tr>
<tr>
<td>Sulfate Attack Mitigation</td>
<td>o</td>
<td>+</td>
<td>&lt; &gt; or +</td>
<td>+</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Property</th>
<th>Class C Replacement</th>
<th>Class F Replacement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Set</td>
<td>Delayed</td>
<td>Delayed</td>
</tr>
<tr>
<td>Rate of Strength Gain</td>
<td>Same or higher</td>
<td>Slower</td>
</tr>
<tr>
<td>Heat of Hydration</td>
<td>Lower</td>
<td>Significantly lower</td>
</tr>
<tr>
<td>Early Strength (3-7 days)</td>
<td>Higher</td>
<td>Lower</td>
</tr>
<tr>
<td>Late Strength (28-56 days)</td>
<td>Same or higher</td>
<td>Same or higher</td>
</tr>
<tr>
<td>ASR Mitigation?</td>
<td>Only at high replacement</td>
<td>Significant mitigation above pessimism replacement levels</td>
</tr>
</tbody>
</table>

+ indicates increase, – indicates decrease, 0 indicates no change, and < > indicates the effect varies depending upon the characteristics of the SCM or the replacement level.

**Effect of High LOI Fly Ash on Concrete Properties**

In coal-based power plants, the boilers are run at reduced power during seasons of lower demand for energy to save on cost. But once demand increases, they are required to be placed back to full power operation. However, it takes a long time to raise the boilers' performance to full power and power plants always inject oil into the furnace to accelerate the process (12). During this boosting process, the fly ash is produced with a higher LOI. Also, high-rank types of coal, such as anthracite, are challenging to combust and result in
higher LOI content (12,13). Additionally, environmental regulations have caused the coal not to be fully burnt to control the emissions of NOx (14).

The ASTM C618-19 specification places a limit on LOI of 6% for fly ash to be suitable for use in concrete. A value of LOI up to 12% is allowed, as per the footnote mentioned in ASTM C618-19 under table 2, when satisfactory laboratory results are obtained using such fly ashes. As such, power plants that are not functional at full load year-round have ash ponds full of high LOI ashes awaiting proper disposal or beneficial usage. The high LOI affects the water demand for concrete. As shown in Figure 2-3, an increase by 4% in LOI would require about 5% more water to account for the slump reduction of concrete (15), which would affect the strength of concrete, pore sizes, and permeability.

![Figure 2-3 Effect of fly ash LOI on concrete water demand (15).](image)

The high-LOI fly ash is known to absorb the air-entraining agents (AEA) that are meant for providing resistance to freeze-thaw cycles, which negatively impacts the air content in high-LOI FA-including concrete (11,13). The mechanism of how the AEA
stabilizes the air bubbles in cement pastes is that the polymers of AEA have two ends with one being hydrophilic and the other hydrophobic, as shown in Figure 2-4. The hydrophilic ends stick to cement particles while the other ends stabilize the air bubbles around the cement particles. But when the carbon grains are present, and with their adsorptive nature, there are not enough AEA to stabilize the air bubbles (11).

Therefore, when using a high-LOI fly ash in concrete, higher AEA dosages are required to provide the designed air content of the concrete mixture. However, high dosages of AEA affect concrete strength. For each 1% of AEA (usually measured as a ratio of cement mass), there is a 5% reduction in concrete strength (16).

Figure 2-4 Illustration for how unburned carbon affects the air-entraining agents compared to cement (11).

**Use of Fly Ash in Construction**

Even though bulk coal ash, when placed in landfills, has the potential to cause widespread environmental harm, efforts have been made to increase fly ash recycling to acquire both economic and ecological benefits. Current global utilization rates of recycled
fly ash remain steady at 67 percent (5). These numbers vary based on location. In the US, 50 percent of fly ash is recycled, while in the EU this number is closer to 90 percent (5). Fly ash has been noted to have an excess of uses including soil improvement and wastewater treatment applications (2). Further, fly ash has been extensively used in the ceramics industry as well as in the manufacture of fireproof products (2).

Even though fly ash has been extensively used in various applications, the most prominent fly ash use has been in the construction industry. More specifically, fly ash is used as a direct raw material or an additive to make construction products, including cement (5). The inclusion of fly ash as an additive to cement improves the workability of the material and reduces bleeding that occurs when concrete is freshly mixed and poured (5). When added to cement, fly ash has also been shown to improve the long-term durability properties of concrete (5). Hardened concrete fly ash has been consistently shown to have increased strength and lower permeability (5). Consequently, fly ash has been integrated into concrete production used for pavement, walls, and parking lots; in some instances, as much as 80 weight percent of concrete is fly ash (5).

While cement production is the most common use of fly ash in the construction industry, research also shows that this material can be mixed with sand and lime to produce solid brick and ceramic tile (2). Blocks made from fly ash have been shown to have a higher crushing strength when compared with their clay counterparts (2). Additionally, bricks made from fly ash provide notable cost savings, with data indicating that these materials cost, on average, 30 percent less to produce than clay bricks (2). Further, these materials are lighter in weight and have lower water absorption (2). Terracotta tiles made from fly ash have also demonstrated improved physical and
mechanical properties making them a superior choice for use in the construction industry (2).

Additional applications of fly ash in the construction industry involve the use of the material in building dams and embankments as well as road construction layers (5). Although large amounts of fly ash, when placed in landfills, can significantly harm soil, when the material is recycled for use in construction, the applications typically have considerable environmental benefits (5). Fly ash can be used as a soil stabilizer and filling material on construction sites (2). This material is often cheaper than soil, making it a sustainable solution for use in this industry (2). Additionally, when used as a soil stabilizer, fly ash provides essential benefits such as increased bearing capacity and decreased displacement (2). These benefits enable fly ash to be utilized in highway construction as well as for building dams (2).

**Fly Ash-Based Geopolymer**

**Brief Introduction to Geopolymer**

Cement is the most commonly used binder to produce concretes. However, cement manufacturing requires very high temperatures of around 1400°C that creates high energy dispersion and emissions. Each ton of cement produced releases about 600-800 kg of carbon dioxide, accelerating global warming, among other environmental drawbacks (17). Therefore, there is a need to replace Portland cement with another greener alternative that does not have numerous environmental implications. However, there is a challenge to obtain materials that have the same desirable mechanical properties and durability to substitute cement (18). One of the novel replacements includes the aluminosilicate inorganic polymers that are called alkali-activated binders (or geopolymers).
By many researchers, geopolymers are considered the best alternative for OPC-based binders due to its lower energy consumption, lesser emissions, lower materials cost, and competitive compressive strength (19,20). Studies have demonstrated that geopolymer has numerous superior mechanical properties, including the excellent ability to resist acid, negligible shrinkage, high compressive strength, and thermal stability. However, studies are still being conducted to suggest how geopolymer's performance can be improved to facilitate its application and possible replacement of cement.

The conventional type of geopolymer (called two-part geopolymers) is made by adding a concentrated alkaline solution to a solid aluminosilicate source. The alkaline solution can be alkaline hydroxide, carbonate, silicate, or sulfate. However, from the literature, the most alkaline solution used with geopolymer has been a combination of sodium hydroxide and sodium silicate. While the aluminosilicate sources can be either natural such as clay, volcanic ash, rice husk ash, or based on industrial byproducts, such as fly ash, slag, red mud, glass powder etc. (21) the two-part geopolymer has been widely researched and used in different applications such as the precast industry where the mixing procedures are more controlled (22). Nevertheless, the hazardous alkaline solution is one of the major obstacles in front of geopolymers' practicality (20).

Geopolymerization Mechanism

The first published work that scientifically explained the reaction mechanism in geopolymer was the work of Glukhovsky in 1959 (23). The four main steps in Glukhovsky theory were: destruction, coagulation, condensation, and crystallization (23). The first step involves the breakdown of the silica and alumina bonds because of the activator solution's high alkalinity. The broken down species form a gelatinous structure, and as more Si and Al are released, the structure is condensed and finally crystallized (23). The
silica and alumina network is what provides the strength to geopolymer, unlike the C-S-H gel in OPC concrete that could be present in little quantities in geopolymer products (24).

Many publications have investigated the reaction mechanisms of conventional geopolymer, one of which is the work of Duxson et al., 2007 (25). As it can be seen in Figure 2-5 taken from the previous source (25), the geopolymerization process starts off with the dissolution of silica and alumina in the precursor after the addition of alkaline solution until equilibrium occurs. After that, the gelation stage starts forming a simple structural form that keeps reorganizing and connecting. As the process continues, a 3D
aluminosilicate network forms and then the structure starts to densify and finally polymerize.

One of the factors that affect geopolymerization is the release rate of Si and Al species. The release rate is crucial because it affects the type of network formed and thus the strength. The Si-rich gel helps most in the strength of geopolymer than the Al-rich gel. Therefore, Si to al (or SiO2 to Al2O3) ratio is an important parameter in the geopolymer process and the resulted compressive strength [7]. Because of the stable crystal nature of Silica in fly ash making it difficult to be released, the soluble Si is usually supplied in the system by the sodium silicate (SS) solution. However, The GGF has a significant content of amorphous silica that can quickly be released into the system without the need for SS solution [7]. Furthermore, GGF can also provide other elements that are not present in SS solution and are essential for geopolymerization process, mainly Al and Ca.

The presence of Ca in the geopolymer system affects its properties at both the fresh and hardened state. The calcium oxide (CaO) accelerates the setting time of the geopolymer [10], [11]. Additionally, the CaO reacts with the geopolymer products to form calcium silicate hydrate (C-H-S)-like gel, which is calcium aluminosilicate hydrate (C-A-S-H) [12], [13]. This product densifies the geopolymer structure and contributes to the Mechanical properties of geopolymer concrete. Since the ponded ash usually has low calcium content, blending it with GGF would make the CaO available in the system, and it will most likely enhance the produced geopolymer properties.

The physical properties of precursors also play an important role in geopolymer. It is been established that the fineness of precursor affects the compressive strength of geopolymer [14], [15]. This is mostly attributed to the increase of the source material's specific surface area and the resulting small size pores in the produced geopolymer. The
GGF is significantly fine when compared to fly ash. Therefore, if blended with fly ash, the total blend's fineness will increase, and this should positively reflect on the strength of the geopolymer. Moreover, the GGF particles are much stronger than the fly ash particles, which means that even the unreacted GGF particles in the system will boost the strength, acting as micro reinforcement to the geopolymer system.

**Binary and Ternary Blends of Fly Ash and Other SCMs as Pozzolan in Portland Cement Concrete**

**Class C Fly Ash (CFA)**

Class C fly ash (CFA) has been extensively used as supplementary cementitious material in the construction industry. Too many investigations have been carried out to study the effectiveness of using CFA as a SCM in concrete. The main topics that have always been of interest to researchers are setting time and early-age strength, drying shrinkage, alkali-silica reaction (ASR), and sulfate attack.

Shrinkage affects the performance and durability of concrete and therefore decreases the life of concrete structures. For normal concrete, drying shrinkage is responsible for the most considerable portion of the total shrinkage (26). Factors such as the fineness of the cementitious materials, water-to-cementitious materials ratio, and concrete physical properties, such as porosity, affect drying shrinkage (27). Vimonsatit et al. (27) found out that drying shrinkage increased with fly ash fineness. Incorporating GGF with the fly ash, suggested in this work, could increase the fineness of the total particles that replaces OPC, and thus it was considered essential to investigate drying shrinkage of the GGF and CFA binary and ternary blends.

Limited previous studies tested drying shrinkage for ternary mixtures made of CFA and another SCM in OPC mortar. Zhu et al. (28) investigated the drying shrinkage
behavior for a ternary blend of slag and CFA and concluded that slag's inclusion slightly increased the drying shrinkage.

Another property that is investigated here is alkali-silica reaction (ASR). ASR is a reaction between the alkali ions in the pore solution, namely K\(^+\) and Na\(^+\), and hydroxyl (OH\(^-\)), and the amorphous or crypto-crystalline silica from siliceous minerals present in reactive types of aggregates, which produces an expansive product called ASR gel. As the reaction continues and the reaction products absorb moisture, expansion increases, and eventually, cracks develop, leading to a possible failure of the concrete elements. The use of supplementary cementitious materials (SCMs) has been shown to be effective in mitigating ASR-related damages.

Previous researches have shown that class F (low-calcium) fly ash, silica fume, and meta-kaolin are by far the most effective SCMs to mitigate ASR (29). Also, Rashidian-Dezfouli and Rangaraju (30) showed that ground glass fibers (GGF) had excellent potential for use as a pozzolan to mitigate ASR. However, CFA, as well as slag, are not as useful, except at higher dosages of cement replacement (40% or more) (29,31–33)

Since the CFA's binary blends are relatively not effective in mitigating ASR, a ternary blend could be a good alternative. Hanson (34) suggested the use of ternary blends over binary blends to mitigate ASR at lower levels of cement replacement. The author explored the possibility of using blends of CFA, FFA, ground granulated blast furnace slag (GGBFS), and Metakaolin in binary and ternary mixtures with cement to reduce the ASR expansion. He suggested blending 30% of CFA with other SCMs to improve the ASR mitigation performance in concrete. Hence, in this study, it was decided to investigate a total replacement of cement of 40% with binary blends of CFA and GGF so an optimum combination can be concluded.
Afshinnia and Rangaraju (35) studied the effect of using binary and ternary blends of soda-lime glass powder (GLP) with other SCM, including CFA, on the ASR behavior. Pozzolanic reactivity was tested by strength activity index (SAI) and thermogravimetric analysis (TGA), then the combined effect of using both materials on ASR mitigation was studied. They concluded that the ternary mixtures outperformed the binary mixtures in SAI. However, neither of the tested CFA and GLP blends met the ASR expansion limit of ASTM up to the 30% tested total replacement, which resulted from the high reactivity of GLP leading to higher degree of ASR reaction. In the current investigation, the use of GGF, which was proven to suppress ASR, along with CFA spectacularly should enhance the overall ASR mitigation performance.

Moser et al. (36) tested the performance of the CFA’s binary and ternary blends and two types of metakaolin (MK) in ASR. The study showed a better reduction of ASR expansion for MK mixtures than CFA mixtures. Further, CFA and MK’s ternary blends resulted in a higher reduction of ASR expansion than the binary blends. However, nothing of all tested blends were capable of suppressing ASR expansion to the accepted ASTM limits because the lowest expansion for the ternary mixtures, which resulted from the mix of 8%MK and 25% CFA, was 0.129%. it has been evidenced that the CFA dosage required to mitigate ASR is high (40% or more), and that could have been why the dosages used in the mentioned study were not enough to lessens the ASR expansion.

McKeen et al. (37) conducted a study to determine the amount of additives needed to mitigate ASR in New Mexico. Among the suggested methods, they investigated the use of ternary blends of CFA and FFA, but they concluded that FFA’s use was not adequate to enhance the performance of CFA in mitigating ASR.
The last property explored here was resistance to sulfate attack. This attack can be externally by the chemical reaction between calcium hydroxide (CH) -produced from cement hydration- with external sources of sodium and magnesium sulfate, or internally by the topochemical reaction between gypsum and mono-sulfate. Both reactions produce expansive products placing high internal pressure on concrete that could lead to a complete failure. The use of SCMs is one of the mitigation measures for sulfate attack because they consume CH and convert it into a C-S-H gel, which, in turn, reduces the permeability of concrete.

Kandasamy and Shehata (38) investigated the use of slag and CFA to improve sulfate resistance performance. They tested up to 40% in binary mixtures and up to 60% in both materials’ ternary mixtures. The length change of mortar bars subjected to a sodium sulfate solution was monitored for two years. They concluded that adding slag improved the sulfate resistance performance at a level of 20% or higher with CFA up to total replacement of 60%. However, there were no studies of the effect of such high replacement level on the mortar and concrete’s mechanical properties.

**Class F Fly Ash (FFA)**

The small amount of lime present in FFA results in a lower early strength when partially replaces OPC. However, the amount of amorphous silica in FFA is abundant and its reaction with CH from OPC hydration increases the ultimate strength since it produces more C-S-H gel (39). Usually smaller dosages of FFA than CFA are needed to mitigate concrete durability problems such as ASR, or sulfate attack. The following sections review some of the studies involved the use of FFA as an SCM in binary and ternary blends.

A study by Hooton et al., 1994 (40) of isothermal calorimetry of binary blend of class F fly ash and cement indicated that the tested FFA's pozzolanic reaction started after
a few days of mixing, during which the FFA acted as an inert filler. This was evident by the heat released from the FFA-containing mixtures, which was less by about 60% of the heat released by the control mixture (40).

Medina et al. (41) studied the synergetic interaction between class F fly ash (FFA) and rice husk ash (RHA) when used to replace 0%, 15%, and 30% of cement. They assessed the pozzolanicity of these systems and several mechanical properties were investigated. Also, they studied the effect of introducing this blend on the rheology, calorimetry, and microstructure of the product. They concluded better pozzolanic reactivity for FFA in the mixtures contained RHA. In terms of strength, they noticed a decline in strength at 90 days of 2% and 19% for the 15% and 30% replacement ratio mixtures, respectively. They attributed this drop to a change in the pores structure.

Ferraris et al., 2001 (42) investigated the effect of binary blends of cement with fly ash and silica fume on cement paste rheology, and the results were confirmed by testing concrete. They used three types of fly ashes with different particle sizes ranging from coarse to ultrafine particles (18 µm to 3 µm). The ultrafine fly ash improved the workability and the rheology of cement paste and concrete without adding any superplasticizers or water to maintain the workability (42).

Investigating concrete containing fly ash and silica fume individually and combined, Bouzoubaa et al., 2004 (43) revealed that the ternary blended concrete resulted in better performance in water demand, plastic shrinkage, and had a lower permeability than the control and the binary blended concrete. They came up with an optimal blend of 20% fly ash and 4% silica fume. In their study, three types of fly ash were investigated, including two FFA and one CFA. The use of silica fume enhanced the early age
characteristics of concrete while the fly ash, especially FFA, improved the later age properties.

In the current study, not much attention was cast on FFA because it mostly has acceptable performance in aspects where CFA most likely fail to fulfill. The FFA was only tested in the chloride penetration study (See chapter 6).

**Off-Spec Fly Ash (OSFA)**

High unburned carbon content (LOI) and a high concentration of sulfate content are the main properties of the off-spec fly ash (44). Kozhukhova et al. (44) suggested using ternary cementitious mixtures containing two off-spec fly ashes that were spray dry absorber fly ash and harvested ash along with cement to produce roller-compacted concrete. The first fly ash is known for its high sulfate concentration, which would lead to a higher chance of impacting concrete durability by sulfate attack, whereas the second fly ash is highly pozzolanic. Therefore, their work's objective was to develop green and durable concrete mixtures that had good strength and resistance to sulfate attack using the off-spec fly ash.

They test a total replacement of 50% of cement by combining the two mentioned fly ashes. The produced concrete was tested for chloride ion penetration and sulfate attack as well as compressive strength. As they described them, the results were promising, and that would promote the beneficial use of the off-spec fly ash in a full-scale application.

A few other studies (45–48) have dealt with off-spec fly ashes and sought to find beneficial uses for them. Most of them were investigating the use of OSFAs for soil stabilization and embankment. The high LOI is the most off-spec aspect in fly ash that most previous studies have investigated beneficial uses for (48–51).
**Ground Glass Fibers**

The first use of GGF as a SCM was in 2004 by the work of Hemmings, in which he named the ground glass fibers as VCAS pozzolan that stands for vitreous Calcium-Aluminate-Silicate. The DOE sponsored a full-scale study aimed at recycling 100% of the waste glass fibers into a valuable material (52). By doing so, they reported that the glass fiber industry can provide about 500,000 tons per year to be processed into value-added material. About 10% to 20% of the produced glass fibers are landfilled at a very high cost and negatively impacting the environment. The DOE study converted the glass fibers into very fine powdered material (about 4-micron average particle size) to be used as pozzolan to partially replace OPC in concrete. The VCAS pozzolan is white, very consistent in its chemical composition, and low on iron and alkali which can be promoted to successfully work as pozzolan (52).

It has been found that the VCAS improved the fresh and hardened properties of OPC concrete. The inclusion of 20% OPC replacement by VCAS was found to improve the flowability of the mix by more than 130%, strength activity index of 123% at 7 days, and was capable of suppressing sulfate attach and ASR damages significantly (52). The report estimated the environmental benefits of recycling glass fibers waste and stated that for each ton of recycled glass fibers, about 5 BTU (British Thermal Unit) energy could be saved annually.

Neithalath et al. (53) proved the significant pozzolanic reactivity of GGF even at an early age (7 days). The hydration degree of GGF containing cement pastes was studied in the work of Kamali and Gharemaninezhad (54). The content of Ca(OH)2 was evaluated using thermogravimetric analysis (TGA) and X-ray diffraction (XRD). Other properties, such as chemical shrinkage, setting time and microstructure characteristics were also explored. The addition of GGF enhanced the hydration of cement paste and pozzolanic
reaction and refinement in the pores was detected for the GGF-containing mixtures. The study also used a class F fly ash to compare results with GGF and the GGF performed better in all tested properties. On the contrary, the pozzolanic reactivity of GGF was described as limited in the work of Tashima et al. (55), but it does have hydraulic activity (or cementing properties). However, the compressive strength of mixtures containing up to 30% OPC replacement by GGF experienced no change compared with the control mixture containing pure OPC. Porosity and capillary pores were improved compared to OPC mixtures, too (55).

Hossain et al. (56) sought to investigate the concrete properties that included GGF as pozzolans compared with concrete containing silica fume. They explored the effect of both pozzolans on the workability of fresh concrete, shrinkage behavior, and chloride penetration resistance. The concrete slump was lower than the control in the SF containing mixtures while it was increased in GGF-containing mixtures. GGF mixtures provided higher Chloride penetration resistance than SF’s. The plastic and drying shrinkage behavior of both pozzolans containing concrete was higher than the control, with GGF mixtures having less shrinkage than SF mixtures at the same replacement ratio.

Most of the previous studies have focused on the use of GGF as an OPC replacement in terms of pozzolanic and hydration reactions. However, only a few explored the effect of introducing GGF as SCM on concrete durability (53,56). Recently, a full study was performed by Rashidian Dezfooli and Rangaraju (24) for the effect of using GGF on the durability aspects of concrete, such as ASR, sulfate attack, and chloride penetration test. The following sections will summarize the findings of this work.

Rashidian-Dezfooli and Rangaraju (30) investigated the feasibility of using GGF as a pozzolan in OPC concrete. The pozzolanic activity, fresh and hardened concrete
properties and potential for use as an SCM to mitigate ASR, sulfate attack, and chloride penetration. They concluded that the use of GGF up to 30% replacement did not affect concrete's mechanical properties. Also, the performance of mixtures containing GGF in mitigating ASR and sulfate attack was excellent at both 20% and 30%.

**Binary and Ternary Blends of Fly Ash and Other SCMs as Geopolymer Precursors**

Generally, for fly ash to perform well in producing geopolymer with excellent compressive strength, highly concentrated alkaline solutions are required (57). Other factors affecting the compressive strength of geopolymer, in general, are the water to binder ratio, sand to binder ratio, the activator modulus, which is the ratio of SiO$_2$/Na$_2$O in the activator and curing conditions (24,58). The following sections review some of the work done about geopolymer based on CFA, FFA, and OSFA.

**Class C Fly Ash (CFA)**

Studies have shown that the high calcium content, lower silica and alumina content, and the lack of glass content in CFA reduce the rate of geopolymerization and thus reduce the compressive strength (25,59–62). Nevertheless, CFA-based geopolymer with high strength levels has been produced in many research works (58,63,64), as will be reviewed in the following sections.

Guo et al. (63) have investigated the use of CFA to produce geopolymer mortar. Different parameters were explored in their study, including the effect of curing period and temperature, alkaline solution concentration, and proportion (the activator modulus viz., the molar ratio of SiO$_2$/Na$_2$O). They used a combination of NaOH and Na$_2$SiO$_3$ solutions to activate the CFA. The conclusion they made was CFA could produce high
strength geopolymer concrete, and the optimal design condition that rendered the maximum strength was 1.5 activator modulus, Na₂O to binder of 10%, and curing for 75°C for 8 hours followed by 23°C up to the test date.

Li et al. (64) investigated the effect of curing conditions on the mechanical properties and strength development of geopolymer based on high calcium precursors. They used CFA, slag, and FFA with two additions to account for its low calcium content, which were calcium hydroxide and slag. Steam and oven curing was used at periods of 6 hours and 24 hours at 60°C and standard curing at 23°C and 95% humidity. CFA-based geopolymer strength development was high at an early age up to 7 days, then slowed down afterward. Oven curing resulted in a higher strength than steam curing. The addition of slag and calcium hydroxide did improve the strength of FFA-based geopolymer mortars.

Li et al. (58) examined the flowability and early compressive strength of geopolymer paste and mortar based on CFA. The alkaline solution used in this study was a combination of NaOH and NaSiO₃ solution. The activator modulus ratio SiO₂/Na₂O was 1.3, while the Na₂O to binder ratio was fixed at 10%. The water to binder ratio ranged from 0.3 to 0.35, while the sand to binder ratio was 2.75. Samples were ambient cured for the first 24 hours; then they were heated up to 70°C for another 24 hours. After that, the samples were let to cool down for 1 hour before testing the compressive strength. A strength of 85 MPa (12,300 psi) was achieved at that age, which is very high. XRD pattern on the hardened mortar and pastes showed a highly amorphous structure confirming gel formation. The authors explained the possible ways of how calcium from fly ash present in the geopolymer. They stated that it may precipitate as Ca(OH)₂, fixed in the geopolymeric gel, or react with dissolved silicate to form C-S-H gel.
**Class F Fly Ash (FFA)**

Class F fly ash (FFA) has been used in many studies as a precursor for geopolymers due to its chemical composition and preferred physical properties (65–68).

Palomo et al. (69) investigated geopolymer production based on FFA activated by different alkaline solutions. The alkaline activators they used were 12N NaOH solution and a combination of NaOH and Na$_2$SiO$_3$ with SiO$_2$/Na$_2$O = 1.23. The resulting compressive strengths were between 35-40 MPa for the first activator and about 90 MPa for the second activator.

Fernandez-Jiménez and Palomo (70) investigated the effect of activator on FFA-based geopolymer composition and microstructure. The fly ash was activated with NaOH, Na$_2$CO$_3$, and Na$_2$SiO$_3$ (water glass) solutions for activation. The solution to binder ratio was 0.35, with the first two activators and 0.4 with the last one. The Na$_2$O to fly ash ratios ranged from 6.5% to 14.9%. The fly ash geopolymer samples were cured at 85°C for 20 hours. The samples were tested for compressive strength and flexural strength, and the microstructural characteristics were studied. The results indicated For NaOH activated systems, the highest compressive strength achieved was 70.4 MPa (10,210 psi), while it was 36 MPa (5,220 psi) for the Na$_2$CO$_3$ group. The NaOH+Na$_2$SiO$_3$ group had a stronger strength at 91.6 MPa (13,290 psi). The microstructure study revealed that the gel formed when NaOH was used as activator had the following characteristic: Si/Al = 1.6 – 1.8 and Na/Al = 0.46 – 0.68 ratio, while they increased remarkably to Si/Al= 2.7 and Na/Al = 1.5 ratios in the combined activator. The use of Na$_2$CO$_3$ acidified the system resulting in a lesser mechanical strength.
**Off-Spec Fly Ash (OSFA)**

Most of the studies related to fly ash-based geopolymer have dealt with standard fly ash (class F or class C).

**Full Depth Reclamation**

Full Depth Reclamation (FDR) is a rapid means to rehabilitate existing pavements by mixing the pulverized asphalt and base materials with ordinary portland cement (OPC). Compacting the resulting blend at optimum moisture content provides a stable base upon which a new layer of asphalt pavement can be constructed. This technique has been implemented since the 1980s, and many transportation agencies have extensively performed it. The advantages that have aided the rapid rise of FDR are (71–74):

- Cost-effective method;
- Uses 100% recycled materials, reducing the impact on the environment.
- Ability to rehabilitate severely distressed roads.
- Thoroughly carried out in situ with minimal traffic interruption.
- Provides a high resistance for cracks, decreasing the reflected cracks on the pavement layer; and
- The new stable base boosts the structural performance of the new pavement.

Cement is the most frequently used stabilizer in the FDR process. Also, Class C fly ash, hydrated lime, asphalt emulsion, and foamed asphalt, have been used in FDR (71). Class C fly ash is not abundantly available in the state of SC. The use of lime and asphalt-based stabilizers results in lower initial strength and more susceptibility to moisture than cement-based stabilization (74). Besides, the use of cement is suitable for a broader range of soil types than any other stabilizer (74).
Over the last decade, the South Carolina Department of Transportation (SCDOT) has successfully used OPC in pavement rehabilitation projects using FDR. As a result of this on-going success, SCDOT is progressively ramping up the use of FDR in its pavement rehabilitation operations. The pavement condition of over 50% of state-maintained roadways is rated as poor and very poor (75), which mandates a definite increase in FDR applications. The average percent increase of the total OPC used in FDR projects in SC for the past five years from 2014 to 2018 was 30% compared to 2013 construction season, as shown in Figure 2-6 [Jesse Thompson, a pavement engineer at SCDOT, personal communication, March 2019]. However, with increasing demand for OPC in other construction sectors, such as structural applications, OPC’s availability for highway applications has become uncertain.

One option that can alleviate the need for cement is to partially replace it with quality supplementary cementitious materials (SCMs) such as Class F fly ash, a by-product of burning coal in power plants. Large volumes of fly ash (FA) and bottom ash (BA) are stored in temporary storage facilities, known as ash ponds. In the US, about 130 million tons of coal ash were produced in 2014, of which only 46 million tons had beneficial uses (76).
Therefore, this study investigated the feasibility of using fly ashes from selected ash ponds in the Carolinas as SCMs to partially replace OPC in FDR projects. Thus far, SCDOT has not employed any SCMs in the FDR operations and has been interested in considering options that can supplement the limited OPC quantities available in the state. The use of the ponded ash or part of it as a cement replacement would alleviate the environmental impacts in two ways; firstly, by reducing the OPC consumption, and secondly by reducing the amount of ash that has long been stored in the ash ponds.

Although many studies have investigated different SCMs for utilization as a partial or full replacement of OPC in FDR, a few have studied the geopolymer-based full depth base stabilization (77–79). Adhikari et al. (78) class F fly ash-based geopolymer to stabilize a blend of soil and reclaimed asphalt pavement (RAP). A combination of NaOH and Na$_2$SiO$_3$ solution was used as the activator. Reference mixtures of 5% and 10% OPC-based stabilization were used. The fly ash, soil, and RAP were all mixed dry then the alkali solution was added and thoroughly mixed. Samples were heat cured for 48 hours at 60 °C, then they were demolded 24 hours after removal from oven and tested for unconfined
compressive strength (UCS). They concluded that geopolymer use to stabilize the base materials is effective, and good strength and durability could be achieved.

Although the use of geopolymer for base soil and RAP stabilization was successful in some studies, none of them studied the practicality of using such technology in the field. For example, the use of heat curing for 24 or 48 hours is impractical. Also, it is difficult to handle the corrosive liquid used for activating the geopolymer. Therefore, this study aims to investigate the performance of geopolymer stabilized bases in practical ways as possible. Ambient cured geopolymer stabilized samples will be studies, and the wet mixing of geopolymer pastes with the base materials will be used.

**Concluding Remarks on Literature**

Based on the reviewed literature, CFA has mostly been investigated for its ASR mitigation, sulfate attack resistance, setting time, and drying shrinkage. None of the reviewed studies came up with blending CFA with ground glass fibers (GGF) as suggested in the current study. The previous SCM that showed some beneficial synergy were silica fume and metakaolin.

Class F fly ash (FFA) does not have several problems associated with its use in concrete. The focus should be centered on the off-spec fly ash and study how optimized their performance would be when blended with GGF. A few work have dealt with OSFA (44–47) and most of them were in the past decade. Therefore, this topic is a trending research topic that is worth to be further investigated.

For the selected FDR application, several studies investigated the use of different SCMs to partially replace cement in FDR. However, none has explored the use of GGF along with off-spec fly ash or slag to enhance the FDR properties. Furthermore, the use of geopolymer to stabilized the base materials has not been thoroughly investigated.
Therefore, it was decided to investigate the use of geopolymer-based stabilization of the whole blend of base materials and RAP and compare its performance with that based on OPC.

References


23. Li C, Sun H, Li L. A review: The comparison between alkali-activated slag (Si+Ca) and metakaolin (Si+Al) cements. Cement and Concrete Research. 2010 Sep;40(9):1341–9.


Chapter 3

EXPERIMENTAL PROGRAM

For achieving the previously mentioned objectives of this study, a whole plan for the experimental program was developed. The flowchart shown in Figure 3-1 represents the planned experimental program for this dissertation.

Figure 3-1 Flowchart for all the experimental work in this dissertation.
This chapter will include all the materials used in this study and the test methods for each section. Although the materials and test methods are mentioned again in their respective chapter, it is good to have them all listed here for quick referencing.

**Materials**

**Cement**

Two types of ordinary portland cements (OPC) meeting ASTM C150 [1] were used in this study: A Type I/II OPC (Na₂Oₐq = 0.38%) that was obtained from Argos cement company, SC, and a Type I high alkali portland cement (Na₂Oₐq = 1.00%) that was provided by Lehigh Hanson, Inc.. The Type I/II OPC was used for most of the tests, while the high alkali cement was used only in tests related to ASR, i.e., the miniature concrete prism test (MCPT) as per AASHTO T380 [2]. The chemical compositions and physical properties of portland cement are presented in Table 3-1.

**Ground Glass Fibers (GGF)**

The Ground Glass Fiber (GGF) used in this study was prepared by milling the off-spec glass fibers to a fine white powder with an average particle size of 4 microns. The GGF was provided by PPG Industries Inc. in NC in the ground form. The GGF was characterized for its chemical compositions and physical properties and all are presented in Table 3-1.

**Class C Fly Ash (CFA)**

A high-calcium fly ash (CaO = 24.2%) with a specific gravity of 2.77 was used and the chemical composition is given in Table 3-1.

**Class F Fly Ash**

In this study, a class F fly ash (ASTM C618) was used as a SCM and a source material for geopolymer studies. The material had a specific gravity of 2.25 and average
particle size of 28 microns. The chemical compositions and physical properties of the fly ash are presented in Table 3-1.

**Slag**

Ground granulated blast furnace slag grade 100 was used only in the FDR study (chapter 10). The purpose of using slag was to offer better ambient cured geopolymer properties when blended with GGF. The specific gravity of this slag was 2.92 and its chemical compositions are given in Table 3-1.

Table 3-1 Chemical composition and physical properties of all the materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific Gravity</th>
<th>Blaine's Fineness, cm²/g</th>
<th>LOI</th>
<th>Chemical Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SiO₂</td>
</tr>
<tr>
<td>OPC</td>
<td>3.15</td>
<td>1475</td>
<td>2.6%</td>
<td>19.93</td>
</tr>
<tr>
<td>High alkali cement</td>
<td>3.15</td>
<td>--</td>
<td>--</td>
<td>19.00</td>
</tr>
<tr>
<td>CFA</td>
<td>2.50</td>
<td>4688</td>
<td>1.6%</td>
<td>37.60</td>
</tr>
<tr>
<td>FFA</td>
<td>2.25</td>
<td>3485</td>
<td>0.46</td>
<td>50.70</td>
</tr>
<tr>
<td>GGF</td>
<td>2.60</td>
<td>7012</td>
<td>1.0%</td>
<td>47.72</td>
</tr>
<tr>
<td>Slag</td>
<td>2.92</td>
<td>5950</td>
<td>--</td>
<td>38.17</td>
</tr>
</tbody>
</table>

**Fine Aggregate (Siliceous Sand)**

A non-reactive siliceous natural river sand from Glasscock Co. in Sumter, SC with an oven-dry specific gravity of 2.63, an absorption ratio of 0.35% and a fineness modulus of 2.6 was used in this study.

**Reactive Coarse Aggregate**

Highly reactive rhyolitic aggregate, Las Placitas gravel from New Mexico (NM) was used for testing ASR. The specific gravity and percent absorption of this aggregate were 2.6 and 1%, respectively. This aggregate was either pulverized to be used as a fine aggregate graded as per ASTM C1260 [3] and ASTM C1567 [4], or crushed to be used as a coarse aggregate graded as per AASHTO T380 [2].
**Chemicals**

**Sodium Hydroxide**

Sodium hydroxide pellets with 99% minimum assay were acquired from Fisher Chemicals. These pellets were used to prepare the alkali solution that is used in ASR testing or in geopolymer as the activator. They were also used to increase the alkali level of concrete mixes for MCPT test method as required by (AASHTO T380).

**Sodium Sulfate**

An ASC (American Society of Chemicals) grade sodium sulfate acquired from AMERSCO Inc. was used in this study. Sodium sulfate powder were used to prepare the 5% concentrated solution for the sulfate attack test as per ASTM C1012-18 [5].

**Sodium Silicate Solution**

Sodium silicate solution was obtained from the CQ Concept company and had the following chemical ratios: 60% water content, 9% Na₂O and 31% SiO₃. This sodium silicate solution was used.

**Off-Spec Ashes:**

Four different ashes from four different Duke Energy Power Plants were used in this study. Throughout this work, they are referred to by: A, B, C, and D FAs. The sources of A, B, C, and D ashes were Marshall, Cliffside, Roxboro, and Riverbend, power station respectively. In some of the chapters, the fly ash is referred to by the initial of its source (such as CSFA in chapter 8 and RFA in chapter 6). All these power plants are in NC.

These ashes were sampled in their original form, i.e. as they had been stored in storage ponds. Only the fly ash (FA) portion, i.e. passing No. 200 (75-µm) U.S.A. standard sieve, was considered in evaluating the use of these ashes as SCM.
Figure 3-2 shows a photograph of each fly ash portion from each source of ash. The color of Riverbend fly ash (D FA) is light gray while Marshall fly ash (A FA) is dark gray and Cliffside fly ash (B FA) is in between. Roxboro fly ash’s (C FA) color is black. All ashes were brought in a 55-gallon drum directly from each power plant. Marshall ash was the driest among the other fly ashes that were highly wet especially Roxboro ash. Marshall and Riverbend ashes were mostly powdered while the other two ashes had some lumps that could easily be crushed and manually finely milled.

**Characterization of the Off-Spec Fly Ashes**

Full characterization was carried out to all the four ashes and the results are summarized below.

**Physical Properties of FAs:**

The specific gravity ranged from 2.19 to 2.26 for the four FAs. The moisture content for A FA was very low (0.3%) because it was collected directly from the power plant,
whereas the moisture contents of the other ashes were high and ranged from 20% to 28% because they were collected from the ponds where they had been stored.

Based on laser diffraction test results Figure 3·3, the FA portion of the bulk ash produced at the four investigated Duke Energy power plants was large (ranged from 70% to 86%), based on particles size of 75 micron, indicating the possible utilization of large amount of the ponded ashes in future pavement rehabilitation projects. Among the tested FAs, D FA had the finest particles, according to the average particle diameter by mass (D$_{50}$) shown in Table 3-2, followed by B and A FAs. Whereas the size of C FA particles was much larger. This suggested better pozzolanic reactivity for D FA and similar performance for B and A FAs. These findings were supported by SEM images as will be shown.

Table 3-2 Average particles diameter by mass for the tested fly ashes.

<table>
<thead>
<tr>
<th>FA Source</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>D$_{50}$ (micron)</td>
<td>27.39</td>
<td>24.85</td>
<td>44.32</td>
<td>22.60</td>
</tr>
</tbody>
</table>

Figure 3-3 Particle size distribution of all four FAs using laser diffraction.
**Chemical Composition of FAs:**

The Chemical composition based on the XRF results are listed in Table 3-3. As shown, the sum of the oxides (SiO$_2$ + Al$_2$O$_3$ + Fe$_2$O$_3$) indicates that the minimum requirement of ASTM C618 for both classes of FAs (C, F) was met. However, when examining the LOI values presented in the same table, only A, B, and D FAs met the requirement of the footnote of class F FA that permits the use of FAs with LOI values up to 12% when acceptable performance or laboratory test results are available. Calcium Oxide percentage, on the other hand, was small for all FAs, which indicated low self-cementing properties. This suggested the incapability of using a high percentage of cement replacement with any of the tested FAs. The alkali content (Na$_2$O$_{eq}$) was small (less than 2%) in all FAs. Additionally, as per ASTM C618 [6], the maximum percentage of Sulfur trioxide (SO$_3$) for both class C and class F FAs is 5%, which was met by all the tested FAs.

To assess the crystalline phases of FAs, XRD was performed and results are shown in Figure 3-5 and Table 3-4. Once all crystalline phases were identified, the amount of amorphous was estimated. The amorphous structure accelerates the pozzolanic reactivity. The amorphous percentage was good for A and B FAs (averaged 64% and 53%, respectively); whereas D FA was 45%. C FA, however, had the highest amorphous at 69%, but its LOI was also the highest at 20.54%.

Table 3-3 Chemical composition for the selected FAs.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Unit</th>
<th>A FA</th>
<th>B FA</th>
<th>C FA</th>
<th>D FA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$ (A)</td>
<td>%</td>
<td>27.98</td>
<td>25.33</td>
<td>24.93</td>
<td>27.45</td>
</tr>
<tr>
<td>CaO</td>
<td>%</td>
<td>1.51</td>
<td>4.94</td>
<td>3.51</td>
<td>0.91</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>%</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>Fe$_2$O$_3$ (F)</td>
<td>%</td>
<td>8.17</td>
<td>8.12</td>
<td>13.86</td>
<td>6.71</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>%</td>
<td>2.34</td>
<td>2.33</td>
<td>1.87</td>
<td>2.11</td>
</tr>
<tr>
<td>MgO</td>
<td>%</td>
<td>1.12</td>
<td>1.21</td>
<td>1.36</td>
<td>0.98</td>
</tr>
</tbody>
</table>
Examining the SEM images shown in Figure 3-4, most of the particles are uniformly spherical. Some of the spheres show pores on the surface; these pores increase the surface area leading to a better chemical reactivity. Unburned carbon fragments (shown as dark irregularly shaped particles) are present in all ashes (specifically C ash), which supports the high LOI% value shown in Table 3-3.
Figure 3-4 SEM images for A, B, C, and D FAs.

Table 3-4 Estimated phase composition by whole pattern fitting.

<table>
<thead>
<tr>
<th>Phase</th>
<th>A FA, %</th>
<th>B FA, %</th>
<th>C FA, %</th>
<th>D FA, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz (Si O$_2$)</td>
<td>13.42±0.71</td>
<td>13.44±0.59</td>
<td>8.78±0.69</td>
<td>28.16±1.40</td>
</tr>
<tr>
<td>Mullite (Al$_6$Si$<em>2$O$</em>{13}$)</td>
<td>20.04±1.17</td>
<td>21.38±1.10</td>
<td>18.80±1.44</td>
<td>16.81±1.03</td>
</tr>
<tr>
<td>Hematite (Fe$_2$O$_3$)</td>
<td>2.64±0.32</td>
<td>2.64±0.34</td>
<td>3.61±0.38</td>
<td>1.81±0.31</td>
</tr>
<tr>
<td>Graphite</td>
<td>–</td>
<td>9.54±1.64</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Muscovite (KAl$_2$(Si$<em>3$AlO$</em>{10}$)(OH)$_2$)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>4.14±0.76</td>
</tr>
<tr>
<td>Kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>3.24±1.06</td>
</tr>
<tr>
<td>Amorphous</td>
<td>63.90±5.19</td>
<td>53.00±3.63</td>
<td>68.81±6.67</td>
<td>45.83±5.09</td>
</tr>
</tbody>
</table>
Reclaimed Asphalt Pavement (RAP) and Base Soil:

A blend of base soil and RAP was brought from a SCDOT pavement rehabilitation project that was being performed by King Asphalt Inc. at (1409 to 1523 N Old Pendleton Rd, Easley, SC 29642). The samples were taken from different spots along the road right after the passing of the reclamer machine. In order to separate RAP and base soil, a No. 4 (4.75 mm) standard sieve was used.

Characterization of RAP and Base Soil

The sieve analysis indicated that the test sample consisted of approximately 35% coarser than No. 4 sieve (gravel size RAP particles), around 60% between No. 4 and No. 200 sieves (sand size particles), and about 5% finer than No. 200 sieve (silt and clay particles).
The classification of base soil according to AASHTO M145 [7] is A-1-b. The usual constituents of this type of soil are stone fragments, gravel and sand with non-plastic or marginally plastic fines. This type of soil is excellent for subgrade materials. According to PCA guidelines, the minimum requirement for gradation of the bulk pulverized materials for the portion passing No. 4 sieve was 55%, which was in compliance with the tested bulk materials. Therefore, when the base materials were mixed for casting the cement modified recycled base (CMRB) samples, the RAP ratio was chosen to be 35% of the tested blend of RAP and base soil as it was in the original blend.

**Test Methods**

*Fly Ash Characterization:*

**Particle Size Distribution Using Laser Diffraction**

Particles of any material, if irradiated by laser beam, scatter light. The scattered light corresponds to the size and shape of the particle by which it is hit. Based on this principle, the particles’ size distribution can be determined.

**X-ray Fluorescence (XRF)**

To assess the bulk oxide contents, XRF was performed for all materials. The basic principle of XRF is that if fly ash is excited by high energy X-ray, it gives off secondary X-rays (or Fluorescence). Each oxide has a unique fluorescence by which it can be identified.

**Mineralogy Using X-ray Diffraction (XRD)**

XRD is a speedy technique for identifying the crystalline phase of a material in a qualitative and quantitative way. When X-Rays hit the sample, they diffract at different angles. The intensity at which the X-Ray diffracts is distinctive for each phase. Relating
the diffracted intensities to the diffraction angles creates a pattern that can be plotted and interpreted.

**Scanning Electron Microscope (SEM)**

By using SEM images, valuable information about each ash sample's surface topography and composition can be obtained. The surface topography is detected by secondary signals from scattered electrons when applying an electron beam on the sample. The intensity that electrons are scattered back with depends on the atomic number of the element at the hitting point. As a result, the lighter the color in the reflected image, the higher the atomic number. Based on this, usually bright white, gray, and dark colors correspond to the elements of iron, silica and alumina, and carbon, respectively.

**Loss on Ignition (LOI)**

LOI value is a representation of the amount of unburned carbon in fly ash. The test was carried out by heating a sample of fly ash to a high temperature and measuring the weight loss. Small LOI values is an indicator of well-burnt ash. Modern power plants that are equipped with proper incineration systems result in low LOI ashes.

The reason why unburned carbon content was investigated was that it significantly affects fly ash’s suitability to be used as cement replacement. High LOI ashes require higher water to binder ratio to get acceptable workability, thus reducing strength and increasing porosity.

**Pozzolanic Activity Testing:**

**Thermo-Gravimetric Analysis (TGA)**

TGA is a commonly used experiment to determine the degree of hydration of cement and fly ash. The basic principle of the TGA test is to first, gradually heat a sample
taken from the hardened paste of cement and fly ash to about 800°C and monitor the weight loss caused by evaporation and chemical decomposition.

The purpose of this test was to determine the extent of fly ash’s pozzolanic reactivity with cement by measuring the content of Calcium Hydroxide (CH). CH along with C-S-H gel are ones of the main products of cement hydration. C-S-H gel gives the strength of the hardened cement paste, while CH does not add much to strength. When using fly ash as a SCM, the silica in fly ash reacts with the CH resulting in more C-S-H gel and ultimately more strength. It is known that CH decomposes into calcium oxide and water at a temperature from 420°C to 520°C. Therefore, the original CH percentage that was in the matrix can be estimated by measuring the percentage of weight loss caused by the decomposition of CH. Once the CH% is determined, whether fly ash has pozzolanic reactivity can be verified.

The prepared samples underwent TGA testing by using an AutoTGA 2950 V5.4A instrument. The samples were heated from room temperature to 800°C at a rate of 30°C/minute for the first 300°C, then the rate dropped to 20°C/minute for the rest of the test. The derivative of the weight loss versus temperature curves were plotted on a graph using a free TA Universal Analysis software.

**Strength-Activity Index (SAI) Test (ASTM C311)**

To further investigate the pozzolanic activity, strength activity index (SAI) test was performed. The pozzolanic activity was measured by testing the compressive strength of 2” mortar cubes at 7 and 28 days. Two mixtures were prepared according to ASTM C311 [8]: the first mixture was the control using cement only, and the second was the test mixture using 20% replacement with fly ash. According to ASTM C618 [6], a minimum of 75% SAI is required for test samples in order to consider fly ash as an effective pozzolan.
In this study, all four off-spec fly ashes were tested for SAI. Standard sand was prepared in the lab from natural river sand according to the requirements of ASTM C778 [9]. In terms of mixing water content, two sets of test mixtures were prepared. The first set used the water amount required to yield the same flow as the control mix as per ASTM C311, while the second set used the same water to binder ratio for all test mixtures. Six 2” mortar cubes were cast for each test mixture, three of which were tested for compressive strength after 7 days of curing, and the rest were tested after 28 days of curing.

Test Methods for Fresh Properties of Mortar and Concrete

Setting Time Using Vicat Needle Apparatus (ASTM C191)

The purpose of this test is to assess the effect of substituting fly ash for a portion of cement on the length of time cement paste sets. The setting time was measured according to ASTM C191 [10] using Humboldt Vicat consistency apparatus with the hard rubber conical mold (2.5 in. top diameter, 3 in. bottom diameter, and 1.5 in. height). Practically, the setting time of cement/fly ash paste is prolonged because more calcium ions are absorbed during hydration since surface area is higher.

Fly ash to cement replacement ratios that were tested in this study were 20% and 40%. Per ASTM C191, a total amount of 650 grams of binder is to be mixed. The amount of water used to test setting time is equal to what yields a normal-consistency mixture. Normal Consistency was tested according to ASTM C187 [11].

Flow Behavior (ASTM C1437)

The flowability of each test mixture was measured and compared to control mixture. Also, from the results of the mixtures that were used to cast the mortar cubes for the strength activity indices, the water requirement was determined for each test mixture.
The flow was measured in accordance to ASTM C1437 [12], and the water requirement was determined according to ASTM C311 [8].

**Hydration Kinetics**

For the purpose of evaluating the heat evolution in the blends of GGF and FA and compare it to that of GGF and FA individually, and to the OPC control mixture, isothermal calorimetry was conducted. The cement, water and SCMs were preconditioned to 23°C and hand mixed in a plastic vial (150 mL) and placed in the calorimeter. For the analysis, Calmetrix iCal HPC 4000 isothermal calorimeter was used. The instrument was calibrated by using a standard Portland cement sample of known heat evolution. All the measurements were carried out at 23°C. The procedures of both ASTM C1679-17 [13] and ASTM C1702-17 [14] were followed to conduct this test.

**Slump Test of Concrete**

To evaluate the slump of the concrete mixtures, the standard ASTM C143 [15] test method was used. In this method, the freshly mixed concrete is poured into the slump cone in three layers equal in volume and compacted by rodding each layer 28 times. After that, the surface is leveled, and the mold is vertically lifted so the concrete is allowed to freely slump. The vertical distance between the original and new position of the center of the top surface of the concrete is measured and reported as the slump of the concrete.

**Unit Weight of Concrete**

The standard ASTM C138 / C138M [16] test method was used to assess the unit weight of cement concrete. In this method, a freshly mixed concrete is placed in a metal container with a known volume in three equal layers and tamped 25 times after each layer with tamping rod. After tamping the last layer, the top of the container is leveled. Measurements are recorded for the mass of the fresh concrete filling the container. Once
the mass is determined, and using the volume of the measure, the unit weight of fresh concrete can be calculated.

**Air Content of Concrete**

The standard ASTM C231-17 [17] test method was used to measure the air content of freshly mixed concrete by the pressure meter method. In this method, the pressure meter bowl of known measure is filled in a manner similar to that of measuring the unit weight. Once the measure is filled and the top is leveled and closed with the pressure meter lid, water is added in the pressure meter through one of the two petcocks until complete fill is ensured when the water come out of the other petcock. The petcocks are closed, and the initial pressure is applied. Then, the air is released into the meter by pressing down on the valve on the top of the meter with tapping the meter while doing this to ensure all air is removed. Then the reading for the air content is taken from the meter.

**Test Methods for Hardened Mortar and Concrete**

**Compressive Strength of Concrete Cylinders**

The standard ASTM C39-20 [18] test method was used to evaluate the compressive strength of concrete cylinders. The concrete cylinders with dimensions of 4in. diameter and 8in. length were prepared according to ASTM C192-19 [19] practice. The specimens were cured in a moist room until they were tested.

**Split Tensile Strength of Concrete Cylinders**

The standard ASTM C496 [20] test method was used to evaluate the splitting tensile strength of concrete cylinders. The concrete cylinders with dimensions of 3in. diameter and 6in. length were prepared according to ASTM C C192-19 practice. At the test age, the cured specimens were placed in the compression testing machine and load was applied along the length of specimen with the aid of a steel prism to distribute a uniform
load until the specimen is split. The maximum failure load is then used to calculate the splitting tensile strength using the formula listed in the standard.

**Drying Shrinkage (ASTM C596)**

Mortar bars were prepared and cured for all the test mixtures according to ASTM C596 [21], in order to evaluate the drying shrinkage behavior and assess the effectiveness of blends of GGF and fly ash in reducing it. The mixtures, which had 750 g of cement and 1500 g of sand, were designed to achieve similar flow (110 ± 5 %) values as per ASTM C596, which resulted in different water-to-binder (w/b) ratios for different blends. Length change measurements of mortar bars were monitored until no further shrinkage occurred. during the test period, the mortar bars were kept at 23 °C and 50% relative humidity.

**Accelerated Mortar Bar Test (AMBT) (ASTM C1260 & ASTM C1567)**

Accelerated mortar bar tests (AMBT) (ASTM C1260 [3] and C1567 [4]) were conducted to evaluate the effectiveness of the tested blends of GGF and CFA to suppress ASR-induced expansion. In this investigation, a rhyolitic gravel from Las Placitas gravel pit was employed as the reactive aggregate. In each test, four mortar bars (1 in. × 1 in. × 11.25 in.) were cast with an embedded stainless-steel gage stud at each end of the mortar bar. After demolding, the specimens were kept in water at an 80 °C for 24 hours, then they were placed in 1 N NaOH solution at 80 °C as per the specification. Length change of the mortar bars was measured at periodic intervals over a test duration of 28 days. The specification requires a mortar bar expansion of less than 0.10 % at 14 days of exposure in 1N NaOH solution for the tested SCM dosage to be considered as an effective ASR mitigation.
Thermo Gravimetric Analysis (TGA) After ASR Test

At the end of the 28-day expansion measurements for the mortar bars, samples were cut from the center of the mortar bars that were subject to AMBT test. The samples were ground using mortar and pestle to pass standard sieve No. 80. The calcium hydroxide (CH) content in the samples was estimated by measuring the weight loss that occurred between 400 °C and 500 °C, at which the decomposition of CH \((\text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O})\) occurs, and between 600 °C to 800 °C, at which calcium carbonate \((\text{CaCO}_3)\) decomposes [22]. TGA test was performed using a TA instrument Q5000 in a platinum crucible up to 1000°C on powdered sample with hydration stopped using solvent exchange methods. For each specimen, approximately 50 mg of sample was loaded in the crucible and analyzed at a temperature ramp of 10°C/min with nitrogen gas purge of 30 mL/min.

Miniature Concrete Prism Test (MCPT) (AASHTO T380)

To confirm the results obtained by the AMBT (ASTM C1260), which was done on mortar samples and exposed to severe settings during the test, the AASHTO T380 [2] Miniature Concrete Prism Test (MCPT) was also conducted in this study. Although there is a well-known and more reliable method to test ASR, which is ASTM C1293 [23], it takes one or two years to test ASR mitigation. The MCPT method is becoming more popular as it offers the advantage of conducting ASR testing and getting results in only 56 to 84 days.

In this test, three 2 in. x 2 in. x 11.25 in. concrete prisms are cast using a high alkali cement \((0.9\pm 0.1\% \text{Na}_2\text{O}_{eq.})\) with additional boosting of alkalis to 1.25% \text{Na}_2\text{O}_{eq.} by mass of cement, with either a reactive fine and non-reactive coarse aggregate or contrariwise, whichever reactive aggregate is being evaluated. Once prisms cast, they are cured for 24 hours in a fog room at 23 °C before demolding the next day. The next 24 hours, the demolded prisms are soaked in water at a 60 °C before placing them in a 60 °C 1N NaOH
solution. Length change measurements are observed periodically up to 56 or 84 days, depending on the level of expansion observed in the prisms. When mitigation measures are to be evaluated, the Portland cement is replaced with SCM and the alkali content of the mix is boosted to 1.25% by mass of Portland cement in the mixture. AASHTO T380 specifies a level of expansion of less than 0.02% at 56 days for the tested proportion to be considered effective in ASR mitigation.

In this study, a non-reactive quartz fine aggregate was used along with a reactive coarse aggregate -graded in accordance to AASHTO T380 [2]- in preparing the samples. After demolding, the samples were conditioned as per the test method and stored in a sealed plastic container. The plastic container was placed in a water bath adjusted to a temperature of 60 °C for the remainder of the test duration. In this study, the test was conducted for 84 days, regardless of the expansion level at 56 days so that a full behavior can be observed.

**Sulfate Attack Resistance (ASTM C1012)**

The expansion of 1in. × 1in. × 11.25 in. mortar bars soaked in a 5% sodium sulfate solution was determined according to the ASTM C1012 [5]. The test specimens were immersed in the soak solution after the mortar reached a compressive strength of 3000 psi, as measured by testing 2in. x 2in. x 2in. mortar cubes, which were prepared along with the mortar bars. The bars and the cubes were cured in a lime-saturated water until the desired compressive strength was reached. Then, initial and subsequent length change measurements were taken at times as specified by ASTM C1012 [5]. The purpose of doing this test is to check how well the blend of GGF and FA resist sulfate attack compared to the 100% cement control mixture.
Rapid Chloride-Ion Permeability

The standard ASTM C1202 [24] was employed to assess the permeability of chloride ions through concrete. 4in. diameter by 8in. long concrete cylinders were cast and cured for 28 days. After that, each concrete cylinder was cut by a water-cooled saw into three discs of 2in thickness. Then, the sides of the samples were epoxy coated after they were dried at room temperature. The samples are then preconditioned as per ASTM C1202 by vacuum desiccator for three hours then they were saturated under vacuuming for another hour. At least 18 hours later, the prepared samples were placed in the RCPT cells where the reservoir at one side was filled with a 3% NaCl solution and the other side’s reservoir was filled with a 0.3N NaOH solution. The test was then initiated by applying the 60 V potential for 6 hours and readings for the current and charge were taken every half hour. The total charge (coulombs) passed through the samples are averaged and used to indicate how resistant the concrete is to chloride ingress.

Nord Test Method NT BUILD 492 (Rapid Migration Test)

This test measures the non-steady state migration coefficient ($D_{nsm}$) to assess the chloride permeability in concrete. The samples used for this test are prepared and conditioned in a matter similar to that of the RCPT. The test is standardized in NT Build 492 [25] and it is considered a simple and a quick tool to evaluate the chloride ingress in concrete. The concrete samples are placed in a rubber or plastic sleeve tightly clamped on the sample to prevent leakage of solutions, then the samples are placed in a plastic reservoir in a way that they are inclined 32 degrees to the horizontal line by placing a plastic support at the base of the reservoir. The reservoir is filled with 10% NaCl solution (catholyte) and the upper side of the specimen (the rubber sleeve)
is filled with 300 ml of 0.3 NaOH (anolyte). Both sides are connected to a power supply capable of applying up to 60 V DC voltage. The test is initiated by applying 30 V potential difference and recording the resulted current passing through the sample. Based on the recorded current, the final applied potential and the duration of the test are determined as per the standard [25]. After the test is over, the samples are taken out of the sleeves and cut into two halves. One half is sprayed with 0.1N silver nitrate on the split section. Next, the chloride ingress is measured by a caliper or a roller and average of at least 5 readings is used in the calculations of D_{nsm}. The setup of this test is shown in Figure 3-6.

![Figure 3-6 Rapid migration test setup (copied from NT build 492).](image)

**Sorptivity and Water Absorption**

In that study, water absorption and sorptivity tests were performed. The volume of permeable pores was investigated in accordance with ASTM C642 [26] and the rate of water absorption by capillary suction was measured in accordance with ASTM C1585 [27]. In the water absorption test, broken chunks of concrete that are free of cracks are chosen to be the test samples as long as their volume is larger than 300 cc (about 800 g for normal concrete). The samples are first dried in oven at 110 °C for until they are completely dry,
and then the dry masses are taken. After that, the samples are saturated for at least 48 hours to ensure full saturation of the voids, then the SSD masses are taken. Next, the samples are boiled in water for 5 hours and then cooled at room temperature for at least 14 hours after which the SSD masses for the boiled samples are taken. Lastly, the submerged weights are taken and then the density, voids, and absorption of the concrete samples can be calculated as prescribed in ASTM C642.

For the sorptivity test, Concrete discs with dimensions of 2 in. thickness and 4 in. diameter were cut from a concrete cylinder. Next, they were conditioned by vacuum desiccation for 3 hours followed by vacuum saturation for one hour. After that, the discs were placed in sealed container and put in an environmental chamber at 50 C and 80% RH for 3 days followed by a minimum of 15 days storage at 23 C. The side of the discs were, then, epoxy coated, and the top surface was wrapped by a plastic sheet to prevent moisture loss. After that, the absorption procedure started, where the discs were placed on supports in a pan with water covering from 1 mm to 3 mm from the bottom of the disc (above the supports). Subsequent measurements of the mass of each disc were taken at certain times up to 8 days, as specified in ASTM C1585. The mass of water absorbed throughout the test period is divided by the density of water and the surface area that was exposed to water. The measured values are plotted against the square root of time and two absorption rates are measured: the initial absorption and the secondary absorption, in unit of length per time to the power of half (L/T^{1/2}). The initial absorption is represented by the slope of the straight line that best fits the data collected from the start of the absorption procedure to the end of the first 6 hours. Whereas the secondary absorption rate is the slope of the best fitted straight line representing the rest of the data until the end of the test. The initial rate of absorption is typically considered by the capillary suction of the pores, while the
secondary rate is affected by not only the capillary pores but by other aspects such as filling air voids and larger pores [28].

**Foam Index Test**

To evaluate the effect of fly ash on the AEA performance, the foam index test was conducted. In this test, a known concentration of AEA is added to the slurry of cement and fly ash placed in a plastic bottle in similar amounts of drops. After that, the bottle is shaken for the same period for all mixtures. Once the shaking is stopped, the foam formed on the surface of the paste is observed for whether it covers the whole surface and is able to persist for some time on the surface. If the foam was not stable, the procedure is repeated by adding more drops of AEA solution, until a “stable” foam layer stays for 15 seconds or more. Once a stable foam layer is achieved, the total number of the added AEA solution is recorded.

According to the recommendations set by Harris et al. 2008, [29] the following test criteria were used:

- the bottle shake method was chosen, a 5 cm diameter and 10 cm tall (200 ml) plastic bottle with a screw-on lid was used.
- Volume of tested paste was 100 ml with w/c = 2.0 and SCM/c = 0.2
- Air Entraining Agent (AEA) used was Sika-AEA-14 with concentration between 5 and 10%.
- Each drop was 0.15 ml of AEA.

Test Procedures: 45 second initial shaking, add 5 drops, followed by 10 seconds shaking with 4 shakes per second, followed by 30 second rest period. Observe the formed foam and repeat until stable foam is achieved.
Freeze Thaw Resistance

In this research program durability was evaluated using freeze-thaw tests on the concrete beams. The test was conducted in accordance with ASTM C666, Procedure A. Two beams of 3-inch x 3-inch x 12-inch dimensions were cast for each mix. They were cured in water for 14 days and then placed in freeze thaw machine. The parameters included while taking the readings for freeze thaw tests were length change, weight and frequency measurements.

Tests Methods on Geopolymer Paste, Mortar, and Concrete

Extent of Dissolution of Geopolymer Precursors

In this study, the degree of solubility of the precursors used in geopolymer studies in high alkali media was determined. A sample of 5g of each source material was mixed in 100ml of 5N NaOH solution for 2h at ambient temperature and at heat curing of 60 °C using a magnetic stirrer. The solution was filtered using microfiber filters and then diluted to 1:100 using deionized water. The results were then back calculated for the original concentration of the dissolved elements in the 5N NaOH solution.

Dissolution of Geopolymer Paste in HCl Acid

The HCl solution is known to dissolve the geopolymerization products. Therefore, it was used in some studies to assess the amount of unreacted particles of the precursor [30], [31]. The HCl solution was prepared by mixing 50 ml of 1N HCl solution for each 1000 ml of distilled water. The geopolymer paste at the test age was crushed and ground to pass the standard sieve No. 100 and be retained on the standard sieve No. 200. After that, 2 g of the collected paste powder was placed in a 500 ml of the prepared HCl solution. Next, the solution was mixed for 3h using a magnetic stirrer. Finally, the solution was...
filtered by a 1.5 µm microfiber filter paper using a vacuum pump and the residue was
dried and measured and related to the original 2 g to calculate the unreacted particle ratio.

**Inductively Coupled Plasma (ICP)**

In this test, the sample of the extracted solution obtained by the previously
mentioned test of extent of dissolution was diluted with deionized water at a ratio of 1:100
(i.e., 1 ml of extract solution in 100 ml of deionized water). The diluted solution was then
analyzed using ICP test for Si, Al, and Ca ion concentrations.

**Base Soil Characterization:**

**Specific Gravity of Base Soils**

ASTM D854 [32] method B test procedures were followed in order to calculate SG
of the base soil. The base soil was granular and non-plastic. The calculated SG for the base
soil was found to be 2.70, which is a typical value for soils.

**Particle Size Distribution of Base Soil (ASTM D6913)**

The particle size distribution was analyzed using the sieve analysis procedures in
accordance with ASTM D6913 [33]. A well-graded soil with minimal amounts of clay and
silt requires less cement content to produce a strong and durable recycled base layer.
Whereas clayey soil or gap-graded soil requires more cement content to get the required
strength and durability. After a representative sample was obtained from the base soil,
different particles sizes were separated over the No. 8, No. 16, No. 30, No. 50, No. 100,
and No. 200 standard set of sieves (8-inch diameter sieves).
Water Soluble Sulfate and Chloride Ions Content in Base Soils

The presence of sulfate and chloride in soils affects the strength and causes considerable volume change in terms of swelling. Subsequently, it is imperative to check the concentration of these two chemical compounds.

Sulfate and sulfide minerals chemically react with calcium-based stabilizers such as cement. This reaction results in a compound called ettringite (hydrated calcium trisulfoaluminate $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$) which is known for its swelling properties. Sulfate-induced heaves in pavement are a phenomenon caused by this swelling in the form of excessive pavement roughness.

Chloride ions also have the potential to react with cement compounds and form ettringite. Soils rich of chloride ions are subject to decrease in unconfined compressive strength (UCS) when stabilized by cement compared to soils with low chloride content. They can also delay the formation of cement hydration compounds leading to strength gain interruption.

The Inductively Coupled Plasma (ICP) test method was used to determine sulfate and chloride ions content in base soil. The Agricultural Service Laboratory in Clemson University performed the ICP test. The test was performed on a filtered solution that was prepared by mixing 30 grams of soil, passing a 600 µm sieve, with 250 ml of deionized water for one hour on a magnetic stirrer. A microfiber filter was then used to filter the extraction.

**Test Methods for Stabilized Base Soil and RAP:**

**Optimum Moisture Content for the Cement-treated Base Material (AASHTO T 99).**

The purpose of this test is to determine the moisture content required to result in the maximum density of blended materials. According to SCT-26 [34], this test should be
performed on the blend that has the medium cement content, which is 6% from the total weight of RAP and base soil. The optimum moisture content (OMC) obtained using this proportion should be used for all other binder ratios (i.e. 3% and 9%). The procedures listed in AASHTO T 99 [35] were followed.

Unconfined Compressive Strength for Cement-treated RAP and Base Soil (SC-T-26 and SC-T-142).

SCT-26 [34] requires two specimens for each tested mixture. The specimens were prepared using a 4-inch (100 mm) diameter proctor mold and 5.5 lbs. (2.495 Kg) rammer. Each specimen was made by compacting three equal layers using 25 blows of proctor rammer. Following the compaction of each specimen, it was extruded using a manual sample extruder.

All specimens were covered and cured in a 100% humidity room at 23°C for a period of 28 days before testing. On the night the test was due, specimens were soaked overnight according to SCT-26 [34]. Although SCT-26 requires testing CMRB specimens at 7 days of age, it was decided to test them at 28 days allowing more time for FA-cement interaction and hydration.

Durability Tests for the Stabilized Base Material

Wetting and Drying (W-D) (AASHTO T135)

Durability test using the criteria of wetting and drying cycles was established in the 1930s when soil-cement started to see more developments. In this test, two Specimens were prepared. Following preparation, they should be cured for seven days in a curing room. After that, specimens are subject to what consists of one cycle of wetting and drying, which is submerging the specimens for 5 hours followed by placing them in a 71°C oven for 42 hours. The test should include 12 cycles. At the end of each cycle, wire brushing is
applied to all of the surface area of the specimens twice to remove any loosened materials. The pressure applied by the wire scratch brush should be about 3-lbs. Weight loss is monitored at each cycle and the final weight loss is used to indicate durability. AASHTO T135 – method B [36] was followed here since the maximum size of the used materials was 19 mm (3/4”).

The first specimen (labeled No. 1 specimen) in the durability test is used to monitor volume change after each wetting and drying cycle. Volume of specimens was calculated by taking the average diameter and average height by digital caliper measurements taken at the same points each time. The wire brushing is applied on the second specimen (labelled No. 2 specimen). The 3-lb pressure applied while brushing was achieved by placing a 3-lb object on top of the wire scratch brush. At the end of all cycles, specimens were put in a 110°C oven for 24 hours and the final oven-dry masses were obtained. These masses were corrected for water of hydration retained in specimens which -according to AASHTO T135- is estimated to be 1.5% for A-1 soil.

**Freezing and Thawing of Soil-Cement (ASTM D 560)**

In this test, after compacting and extruding the two samples from a 4-in. diameter standard proctor mold, initial measurements for the mass and volume are taken. Then, all samples are cured for seven days in a standard curing room. Next, the samples are subjected to 12 cycles of freezing and thawing. Each cycle consists of freezing at -23 ± 2° for 24 hours, followed by thawing at the standard moist room for another 24 hours. Measurements of volume and mass are taken after each half cycle. At the end of each cycle, a brushing using wire brush is performed on one of the samples. The weight loss and volume changes are to be calculated at each cycle. Not among the ASTM D560 [37]...
requirements, the UCS values are usually measured after completion of all F-T cycles and compared to the original UCS.

**Shrinkage of CMRB**

There is no standard method for testing shrinkage of soil-cement. It was decided to follow the same standards and testing methods for testing length change of concrete. ASTM C157-17 [38] and ASTM C490-17 [39] were both followed in this test. Some test requirements had to be adjusted to suit the use of CMRB materials instead of concrete for which the standards were designed.
References


Chapter 4
EFFECTIVENESS OF BINARY AND TERNARY BLENDED CEMENTS OF CLASS C FLY ASH AND GROUND GLASS FIBERS IN IMPROVING THE DURABILITY OF PORTLAND CEMENT CONCRETE

Abstract

Class C fly ash (CFA) has been used extensively as supplementary cementitious material (SCM) to partially replace cement in concrete. However, to meet the concrete durability demand, such as to mitigate alkali-silica reaction (ASR) or sulfate attack, higher amounts of CFA are required, which results in a slower strength gain and longer setting time. Studies have shown that ground glass fiber (GGF) is quite an effective SCM if it is finely ground.

This work explores the performance of binary and ternary blends of GGF and CFA with portland cement. Pozzolanicity of the combinations was first assessed by the Thermogravimetric analysis (TGA) and strength activity index (SAI). Then, drying shrinkage, resistance to sulfate attack, and alkali-silica reaction were evaluated. Results showed that GGF could significantly alleviate the shortcomings of CFA, both in terms of strength and durability, even when GGF is introduced in ternary blends at modest levels.

Keywords: Ground Glass Fibers, Class C fly ash, Alkali-Silica Reaction, Isothermal Calorimetry.

Introduction

Fly ash is the most abundant supplementary cementitious material (SCM) in the world [1]. The reclamation of fly ash for use in the construction industry represents a

---

1 Submitted to and being reviewed by the Journal of Sustainable Cement-Based Materials.
widely adopted approach to managing the waste produced from burning coal by power plants. Annual fly ash generation from burning coal can range between 600 and 800 million tons globally [2]. Although fly ash is being widely used as a cement replacement material, the coal from which fly ash is produced is a finite resource that will one day need to be replaced with renewable energy resources. Growing environmental concerns have already forced power plants to switch to alternative fuels such as natural gas, and the concrete industry will soon need to find alternative SCMs or find ways to maximize and optimize the use of existing fly ash resources.

The use of fly ash in concrete significantly enhances the properties of both fresh and hardened concrete. Fly ash has been found to reduce drying shrinkage and permeability, increase the workability and compressive strength, and provide adequate mitigation against various durability problems such as alkali-silica reaction (ASR), sulfate attack, and chloride penetration when used in sufficient quantities. Generally, class C fly ash (CFA) is considered to be not as effective as class F fly ash (FFA) in terms of both ASR or sulfate resistance except at higher dosage levels [3]. However, at high dosages of fly ash, especially for CFA, early-age strength and setting time are negatively affected [4,5].

The idea of using ternary blends (two combined SCMs with cement) in concrete is well known at both the research and industry levels, where the deficiency caused by the first material is alleviated by blending with a second material. Therefore, researchers have investigated the use of other SCMs along with CFA, such as slag [6,7], rice husk ash [8], glass powder [9], meta-kaolin [7,10–12], silica fume [13–16], and FFA [7,17,18]. While the performance of mixtures containing ternary blends of cementitious materials is generally improved over the respective binary mixtures, in some instances the performance of the ternary mixtures has not been optimal.
Hanson [7] suggested the use of ternary blends of cementitious materials over binary blends to mitigate ASR at lower dosage levels of cement replacement. Hanson found that blending 30% of CFA with a 10% to 20% slag was required to improve the ASR mitigation performance in concrete. Afshinnia and Rangaraju [9] studied the effect of using binary and ternary blends of soda-lime glass powder (GLP) with other SCMs, including CFA, on the ASR behavior. They concluded that the ternary mixtures outperformed the binary mixtures in SAI. However, neither of the tested binary and ternary blends involving CFA and GLP met the ASR expansion limit of ASTM C1567 (less than 0.10% at 14 days) up to the total tested replacement of 30%. Moser et al. [10] examined the performance of binary and ternary blends of CFA and metakaolin (MK) in ASR. Their study showed that the ternary mixtures of CFA and MK resulted in a higher reduction of ASR expansion than the binary blends. However, none of the combinations were capable of suppressing ASR expansion to an acceptable level per ASTM C 1567 test. Kandasamy and Shehata [19], in their study, concluded that adding slag improved the sulfate resistance performance at a level of 20% or higher with CFA up to a total replacement of 60%. However, there were no studies on the effect of such a high replacement ratio on the mechanical properties of the mortar and concrete. Zhu et al. [6] investigated the drying shrinkage behavior for a ternary blend of slag and CFA and concluded that the inclusion of slag slightly increased the drying shrinkage.

Despite the improvement in properties of ternary-blended concrete, there are some implications of using each material. For example, silica fume is known to cause an increase in water requirements and plastic shrinkage [14]. Moreover, silica fume is more expensive than other SCMs and OPC itself [14]. Similarly, meta-kaolin can have a negative influence on the water-demand and hence workability, while the use of slag can cause
significant concerns in cold-weather conditions [20,21]. The alkali level of glass powder from soda-lime glass is relatively high and is a concern that could affect the ASR performance [9]. Therefore, there is a need for other alternatives to be investigated, especially those substitutes that have not been considerably examined for beneficial uses yet. One of these materials is ground glass fibers (GGF).

Type E glass is a low-alkali, general-use type of glass fiber, and it forms more than 95% of the produced glass fibers. In the glass fiber industry, the composition of glass is carefully monitored, and the quality of the glass filament is thoroughly inspected for defects. During production, a significant quantity of glass fiber that does not meet the specification requirements (lack of adequate physical attributes, not relating to chemical composition) is discarded as off-spec glass fiber. As a result, the off-spec glass fiber is removed from the production line as industrial waste and sometimes pulverized to reduce the volume and, thus, reduce the cost of transportation [22]. Since glass fibers are difficult to recycle [22], these off-spec glass fibers are landfilled. The glass fiber industry in the US alone could provide 500,000 tons per year of waste glass fibers to be utilized in beneficial applications [23]. Although the use of recycled glass, generated from soda-lime glass in concrete is well documented, there have been only a few publications that investigated the use of type E ground glass fibers (GGF) as an SCM [24–26].

Rashidian-Dezfouli and Rangaraju [24] investigated the feasibility of using GGF as a pozzolan in OPC concrete. Based on their X-ray diffraction studies, GGF was found to be highly amorphous. Their results indicated that the use of GGF up to 30% replacement did not affect the mechanical properties of concrete. Also, the performance of mixtures containing GGF in mitigating ASR and sulfate attack was excellent at both 20% and 30%. The beneficial effects of GGF were attributed to its pozzolanic activity that is proven in
their study up to 30% cement replacement, as well as the dense microstructure created in the cementitious matrix by the fineness of GGF.

As power companies are moving towards alternative fuel sources, the availability of high-quality fly ash is becoming limited. Many states have studied other alternatives to fly ash for use in the concrete industry [27]. At the same time, the production of glass fibers is growing worldwide [28], and so is the glass fiber waste generated. Therefore, the combined use of both materials would benefit the environment in many ways: first, it would overcome the short supply of CFA; second, it would provide a way to make beneficial use of the waste glass fibers and fly ash; third, it would help to reduce the consumption of OPC by replacing cement with these pozzolans at a higher replacement ratio; finally, the combined use of this blend is expected to enhance the performance of mortar and concrete mixtures.

Therefore, the objective of the current study is to investigate the effectiveness of binary and ternary blends of GGF and CFA to enhance the overall performance of cementitious mixtures in terms of compressive strength, drying shrinkage, and resistance to ASR, and sulfate attack. The combination of CFA and GGF could be an effective ternary blend that can address multiple performance aspects of concrete synergistically.

**Experimental Program**

**Materials**

**Cement**

Two types of ordinary portland cements meeting ASTM C150 [29] were used in this study: A Type I/II ordinary portland cement (OPC) (Na$_2$O$_{eq}$ = 0.38%), and a Type I high alkali portland cement (Na$_2$O$_{eq}$ = 0.88%). The Type I/II OPC was used for most of
the tests, while the high alkali cement was used only in tests related to ASR, i.e., the miniature concrete prism test (MCPT) (AASHTO T380). The chemical compositions and physical properties of portland cement are presented in Table 4-1.

**Ground Glass Fibers (GGF)**

The Ground Glass Fiber (GGF) used in this study was prepared by milling the off-spec glass fibers in a ball mill to a fine white powder with an average particle size of 4 microns. The chemical composition and physical properties of GGF are presented in Table 4-1. Morphological characteristics of GGF are shown in a scanning electron microscopy (SEM) image provided in Figure 4-1. The GGF particles are angular and fine, having Blaine’s fineness of 600.25 m²/kg.

**Class C Fly Ash (CFA)**

High-Calcium fly ash (CaO = 24.2%) with a specific gravity of 2.50 was used; and the chemical composition is given in Table 4-1. Also, Figure 4-1 provides an SEM image of CFA showing different sizes of spherical particles.
Figure 4-1 SEM image for a) CFA, b) GGF

**Fine Aggregate (Siliceous Sand)**

A non-reactive siliceous natural river sand from Glasscock Co. in Sumter, SC with an oven-dry specific gravity of 2.63, an absorption ratio of 0.35%, and a fineness modulus of 2.6 was used in this study.

**Reactive Coarse Aggregate**

Highly reactive rhyolitic aggregate, Las Placitas gravel from New Mexico (NM), was used for testing ASR. The specific gravity and percent absorption of this aggregate were 2.6 and 1%, respectively. This aggregate was either pulverized to be used as a fine aggregate graded as per ASTM C1260 [30] and ASTM C1567 [31] or crushed to be used as a coarse aggregate graded as per AASHTO T380 [32].

**Mixture Proportion**

Different combinations of GGF and class C fly ash were used to replace a total of 40% of cement by mass. The mixture proportions of the mortar mixtures followed the requirements for each test method. The mixture proportion and the test methods employed in this study are shown in Table 4-2.

Table 4-1. Chemical composition and physical properties for the materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Physical Properties</th>
<th>Chemical Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Specific Gravity</td>
<td>LOI</td>
</tr>
<tr>
<td>OPC</td>
<td>3.15</td>
<td>2.6%</td>
</tr>
<tr>
<td>CFA</td>
<td>2.50</td>
<td>1.6%</td>
</tr>
<tr>
<td>GGF</td>
<td>2.60</td>
<td>1.0%</td>
</tr>
</tbody>
</table>
Table 4-2. Mixture proportions and test methods.

<table>
<thead>
<tr>
<th>Label</th>
<th>Materials proportion</th>
<th>Control</th>
<th>40G00C</th>
<th>30G10C</th>
<th>20G20C</th>
<th>10G30C</th>
<th>00G40C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>100%</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
<td>60%</td>
<td></td>
</tr>
<tr>
<td>GGF</td>
<td>00%</td>
<td>40%</td>
<td>30%</td>
<td>20%</td>
<td>10%</td>
<td>00%</td>
<td></td>
</tr>
<tr>
<td>CFA</td>
<td>00%</td>
<td>00%</td>
<td>10%</td>
<td>20%</td>
<td>30%</td>
<td>40%</td>
<td></td>
</tr>
<tr>
<td>Blain’s Fineness of blended cementitious materials (based on weighted average), m²/kg</td>
<td>372.3</td>
<td>387.3</td>
<td>406.3</td>
<td>425.4</td>
<td>444.4</td>
<td>463.5</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Test methods performed and the followed standard</th>
<th>Isothermal Calorimetry</th>
<th>Setting Time</th>
<th>TGA</th>
<th>Flow test</th>
<th>Water Demand</th>
<th>SAI</th>
<th>Drying Shrinkage</th>
<th>AMBT</th>
<th>MCPT</th>
<th>Sulfate attack</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM C1679 &amp; ASTM C1702</td>
<td>√</td>
<td>√</td>
<td>×</td>
<td>√</td>
<td>√</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASTM C191</td>
<td>√</td>
<td>√</td>
<td>×</td>
<td>√</td>
<td>√</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASTM C1437</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td></td>
<td>√</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASTM C311</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td></td>
<td>√</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASTM C311</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td></td>
<td>√</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASTM C596</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td></td>
<td>√</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASTM C1260 &amp; ASTM C1567</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td></td>
<td>√</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AASHTO T380</td>
<td>√</td>
<td>√</td>
<td>×</td>
<td>√</td>
<td>×</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASTM C1012</td>
<td>√</td>
<td>√</td>
<td>×</td>
<td>√</td>
<td>√</td>
<td></td>
<td>√</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

√, ×: The corresponding mixture was, or was not, tested for the corresponding test.

**Test Methods**

**Hydration Kinetics**

In this study, Calmetrix iCal HPC 4000 isothermal calorimeter was used to evaluate the heat evolution in 20G20C mixture and compare it with that of 40G00C and 00G40C, and to the OPC control mixture. The instrument was calibrated using a standard Portland cement sample of known heat evolution. The cement, water, and SCMs were preconditioned to 23 °C and hand-mixed in a plastic vial (150 mL), using water to
cementitious materials ratio of 0.40, and placed in the calorimeter for the analysis. All the measurements were carried out at 23 °C.

**Thermo Gravimetric Analysis (TGA)**

In order to investigate the pozzolanic reactivity of the binary and ternary blends of GGF and CFA with OPC, the thermogravimetric analysis (TGA) was conducted on the four mixtures shown in Table 4-2. At age of 7 days and 28 days, the hardened paste samples were crushed and ground using mortar and pestle to a fineness of less than 150µm (No. 100 standard sieve). The calcium hydroxide (CH) content in the samples was estimated by measuring the weight loss that occurred between 400 °C and 500 °C, at which decomposition of CH (Ca(OH)₂ → CaO + H₂O) occurs, and between 600 °C to 800 °C, at which calcium carbonate (CaCO₃) decomposes to CaO and CO₂ [39]. TGA test was performed using a TA instrument, Q5000, in a platinum crucible heated up to 1000 °C. Approximately 50 mg of powdered hardened paste samples, with hydration stopped using solvent exchange methods (i.e. diethyl ether and isopropyl alcohol), was loaded in the crucible and analyzed at a temperature ramp of 10 °C/min with nitrogen gas purge of 30 ml /min.

**Strength Activity Index (SAI)**

In this study, the strength activity index (SAI) values were determined for all the mix proportions according to ASTM C311 [34]. The purpose of this test was to further check the pozzolanic activity of the blend of CFA and GGF and compare it with that of the control and the binary mixtures. The control mixture, as per ASTM C311, consisted of 500 g cement, 1375 g sand, and 242 g water, while the test mixtures, shown in Table 4-2, had the same amount of cement and sand but just enough water to produce a flow equal to that
of control ± 5%. The SAI values were determined at the ages of 7 and 28 days, during which mortar cubes were cured in saturated lime water in a standard moist room.

**Setting Time**

To investigate the effect of the binary and ternary blends of CFA and GGF on the setting time of the cementitious paste, the setting time was measured for mixtures shown in Table 2, using Vicat needle apparatus following ASTM C191 [35].

**Flow Behavior**

The flowability of each mixture was measured and compared with that of the control mixture. In addition, the results of flowability tests that were performed on mortar mixtures during the strength activity index test were used to determine the water requirement of each mixture. The flow was measured following ASTM C1437 [36], and the water requirement was determined according to ASTM C311 [34].

**Drying Shrinkage**

Incorporating GGF with the fly ash in replacing the OPC, as suggested in this work, increases the fineness of the total cementitious materials (the fineness of the blended cementitious materials is increasing by 11.6% with each added 10% of GGF, as shown in Table 4-2), which could affect the drying shrinkage performance [37]. Drying Shrinkage is the largest part of the total shrinkage, and it is the main trigger of cracks in concrete [38]. In order to evaluate the drying shrinkage behaviour of the binary and ternary CFA and GGF mixtures, mortar bars were prepared and cured according to ASTM C596 [39]. The mixtures, which had a total of 750 g of binder and 1500 g of sand, were designed to achieve similar flow of 110 ± 5 % as per ASTM C596. The resulting water-to-binder (w/b) ratios were 0.42, 0.44, 0.41, 0.40, 0.37, and 0.36 for the mixtures; Control, 40G00C, 30G10C, 20G20C, 10G30C, and 00G40C, respectively, as listed in Table 4-3. Length change
measurements of mortar bars were taken over a 14-week period, during which the mortar bars were kept at 23 °C and 50% relative humidity. It is worth mentioning that the ASTM C618 optionally specifies a maximum difference in shrinkage at 28 days of 0.03% from control.

**Resistance to Alkali-Silica Reaction (ASR)**

**Accelerated Mortar Bar Test (AMBT)**

Accelerated mortar bar tests (AMBT) (ASTM C1260 [30] and C1567 [31]) were conducted to evaluate the effectiveness of the tested blends of GGF and CFA to suppress ASR-induced expansion. In this investigation, rhyolitic gravel from Las Placitas gravel pit was employed as the reactive aggregate. The test was performed for all tested mixtures listed in Table 4-2. In each test, four 1 in. × 1 in. × 11.25 in. (25 × 25 × 285-mm) mortar bars were cast with an embedded stainless-steel gage stud at each end of the mortar bar. After demolding, the specimens were kept in water at 80 °C for 24 hours, and then they were placed in 1 N NaOH solution at 80 °C as per the specification. Length change of the mortar bars was measured at periodic intervals over a test duration of 28 days. The specification requires a mortar bar expansion of less than 0.10 % at 14 days of exposure in 1N NaOH solution for the tested SCM dosage to be considered as an effective ASR mitigation.

**Miniature Concrete Prism Test (MCPT)**

AMBT test was conducted on mortar samples. However, to investigate the effectiveness of the binary and ternary blends in mitigating ASR in concrete, AASHTO T380 [32] Miniature Concrete Prism Test (MCPT) was also conducted. Although there is a well-known and more reliable method to test ASR, which is ASTM C1293 [40], it takes two years to check ASR mitigation, whereas in MCPT, it only takes 84 days. Also, studies
have shown a good correlation between both MCPT and ASTM C1293 for a variety of reactive aggregate [41,42].

In this test, three 2 in. x 2 in. x 11.25 in. (50 x 50 x 285-mm) concrete prisms are cast using a high alkali cement (0.9±0.1% Na$_2$O$_{eq}$) with additional boosting of alkalis to 1.25% Na$_2$O$_{eq}$ by mass of cement, with either a reactive fine and non-reactive coarse aggregate or contrariwise, depending on which reactive aggregate is being evaluated. Once prisms are cast, they are cured for 24 hours in a fog room at 23 °C before demolding the next day. For the next 24 hours, the demolded prisms are soaked in water at a 60 °C before placing them in a 60 °C 1N NaOH solution. Length change measurements are observed periodically up to 56 or 84 days, depending on the level of expansion detected in the prisms. When mitigation measures are to be evaluated, the Portland cement is replaced with SCM, and the alkali content of the mix is boosted to 1.25% by mass of Portland cement. AASHTO T380 specifies a level of expansion of less than 0.020% at 56 days for the tested proportion to be considered as effective in ASR mitigation.

In this study, a non-reactive quartz fine aggregate was used along with a reactive coarse aggregate—graded per AASHTO T380 [32]—in preparing the samples. The test was performed on four mixtures, as listed in Table 4-2. After demolding, the samples were conditioned as per the test method and stored in a sealed plastic container. The plastic container was laid in a water bath adjusted to a temperature of 60 °C for the remainder of the test duration. In this study, the test was conducted over 84 days, regardless of the expansion level at 56 days, so that a full behavior can be observed.

**Resistance to Sulfate Attack**

In this investigation, the expansion of 1in. x 1in. x 11.25 in. (25 x 25 x 285-mm) mortar bars soaked in a 5% sodium sulfate solution was determined according to the
ASTM C1012 [43]. The test specimens were immersed in the soak solution after the mortar reached a compressive strength of 3000 psi (20.7 MPa), as measured by testing 2in. (50-mm) mortar cubes, which were prepared along with the mortar bars. The bars and the cubes were cured in lime-saturated water until the desired compressive strength was reached. Then, initial and subsequent length change measurements were taken at times, as specified by ASTM C1012 [43]. It should be noted that this test was only run for the control with pure cement and the ternary mixtures of 20G20C and 10G30C. The purpose of doing this test was to study how well the blend of GGF and CFA would resist sulfate attack as compared with the control mixture with 100% cement content. For CFA, the ASTM C618 [44] places an expansion limit of 0.10% and 0.05% for moderate and high sulfate resistance, respectively.

Results and Discussion

Hydration Kinetics

Figure 4-2 (a) and (b) show the heat flow and heat release of systems with different binder blends viz. control, 40G00C, 20G20C, and 00G40C. The results show that the duration of the induction period is 2.6h for control, 4.1h and 5.4h for 20G20C and 00G40C, respectively. However, there is no significant effect of the binary GGF mixture (40G00C) on the induction period as compared to control. The induction period results indicate that the inclusion of GGF with CFA in the ternary mixture reduced the setting time of the binary CFA mixture. It should also be noted that the second peak (aluminate peak) is substantially enhanced in the mixtures containing CFA, which also corresponds well with the higher Al₂O₃ content of CFA, as shown in Table 4-1. The heat release curve indicates that the control produces the highest amount of heat (300 J/g), followed by 00G40C at 277 J/g, 240 J/g for 20G20C, and 233 J/g of heat for 40G00C. Also, the heat
release curve of CFA-based blend (00G40C) surpassed both CFA/GGF-based (20G20C) and GGF-based (40G00C) blends at 17.4h.

a) 

![Graph a](image)

b) 

![Graph b](image)
Figure 4-2 a) Heat flow; and b) heat release curves (w/c = 0.40) @ 23 °C.

**Pozzolanic Activity by TGA**

The TGA curves at 7 and 28 days and the ratio of CH content in the test mixtures relative to that of the control mixture are shown in Figure 4-3a, 3b, and 3c, respectively. Since there is a dilution effect, as a result of replacing 40% of OPC with the tested SCMs, it can be assumed that pozzolanic activity is proven if the ratio of $\text{CH}_{\text{test}}/\text{CH}_{\text{control}}$, shown in Figure 4-3c, is less than 60%. The results clearly show a reduction in CH content which indicates that it is consumed by the SCM to produce C-S-H gel. As expected, the results at 28 day show lesser CH content than that at 7 days, evidencing the effect of pozzolanic activity. The 40G00C mixture had a higher content of CH than 20G20C and 00G40C at both 7 and 28 days. The inclusion of GGF in the ternary mixture (20G20C) did not affect the CH content much compared to the binary 00G40C mixture, as both had about the same CH content at 28 days. It should be noted that when OPC is replaced by SCM, the amount of water available to react with OPC is higher at the same w/b ratio. Therefore, higher amounts of CH could be produced and react with the replacing SCM. Also, the use of finer SCMs such as GGF can act as nucleating agents for accelerated reaction of OPC. These two phenomena are the likely reasons to explain the higher ratio of $\text{CH}_{\text{test}}/\text{CH}_{\text{control}}$ of 40G00C than 60% OPC by itself at 7 days. The pozzolanic activity is further evaluated by measuring the strength activity index.
(continued)
Figure 4-3: Results of TGA test: a) at 7 days; b) at 28 days; and c) the ratio of CH of test mixtures relative to the control.

**Strength Activity Index (SAI) Results**

The results of the SAI test are shown in Table 4-3. All tested mixtures, at both 7 and 28 days, passed the minimum SAI of 75%, specified by ASTM C618 [44], except 30G10C at 7 days. However, at 28 days, all the ternary mixtures achieved SAI values of 95% or higher, which was significantly better than that of binary mixtures. Both the fineness of the GGF and the amorphous structure most likely helped improve the pozzolanic reaction. Likewise, since the particle size of GGF is smaller than that of fly ash, they provided a better packing of the particles; that should suggest a filling effect which could impact the SAI test results. However, the TGA results showed no increase in CH content of the ternary mixture of 20G20C, compared to the binary blend 00G40C. Therefore, the pozzolanic activity of the GGF and CFA in the ternary mixtures increased the strength, which clearly is reflected in the SAI values.

Table 4-3. Fresh and hardened mortar test results.

<table>
<thead>
<tr>
<th>Tested Property</th>
<th>Control 00G40C</th>
<th>40G00C</th>
<th>30G10C</th>
<th>20G20C</th>
<th>10G30C</th>
<th>00G40C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow, % (at a constant w/b = 0.485)</td>
<td>112</td>
<td>112</td>
<td>113</td>
<td>114</td>
<td>114</td>
<td>115</td>
</tr>
<tr>
<td>Water requirements, % (to achieve same flow as control)</td>
<td>100.0</td>
<td>101.2</td>
<td>99.2</td>
<td>97.8</td>
<td>95.0</td>
<td>92.1</td>
</tr>
<tr>
<td>7-Day Compressive strength, psi (MPa)</td>
<td>6350 (43.8)</td>
<td>4790 (33.0)</td>
<td>4660 (32.1)</td>
<td>4940 (34.0)</td>
<td>5260 (36.3)</td>
<td>4590 (31.6)</td>
</tr>
<tr>
<td>7-Day SAI (%)</td>
<td>100</td>
<td>75.4</td>
<td>73.4</td>
<td>77.8</td>
<td>82.8</td>
<td>72.3</td>
</tr>
<tr>
<td>28-Day Compressive strength, psi (MPa)</td>
<td>7920 (54.6)</td>
<td>6640 (45.8)</td>
<td>7540 (52.0)</td>
<td>7800 (53.8)</td>
<td>7810 (53.8)</td>
<td>6930 (47.8)</td>
</tr>
<tr>
<td>28-Day SAI (%)</td>
<td>100</td>
<td>83.8</td>
<td>95.2</td>
<td>98.5</td>
<td>98.6</td>
<td>87.5</td>
</tr>
</tbody>
</table>

**Setting Time Results**

The results of setting time of the four tested mixtures are shown in Table 4-4. As it can clearly be observed, the CFA binary mixture (00G40C) had the longest initial and final setting times. Whereas the GGF binary mixture (40G00C) had the shortest setting times.
The inclusion of GGF in the ternary mixture (20G20C) had shortened the initial and final setting times by 18%, and 39%, respectively, compared to 00G40C. The measured setting times and the induction periods obtained by running the isothermal calorimetry test showed high correlation.

Table 4-4 Results of setting time.

<table>
<thead>
<tr>
<th>Label</th>
<th>Vicat Apparatus</th>
<th>Isothermal Calorimetry-Based Dormant Period, mins</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial, mins</td>
<td>Final, mins</td>
</tr>
<tr>
<td>Control</td>
<td>270</td>
<td>375</td>
</tr>
<tr>
<td>00G40C</td>
<td>445</td>
<td>600</td>
</tr>
<tr>
<td>20G20C</td>
<td>365</td>
<td>430</td>
</tr>
<tr>
<td>40G00C</td>
<td>235</td>
<td>330</td>
</tr>
</tbody>
</table>

**Flow Behavior Results**

The water requirement of each mixture to achieve a similar flow as the control mixture is shown in Table 4-3. Also, the flow values for the mixtures with a constant w/b ratio (0.485) are reported in Table 3. From these results, it is evident that 40% GGF mixture (40G00C) required slightly more water than control mixture to get the same flow as a direct result of the finer particles and the higher specific surface area of GGF. However, the water requirement decreased for the other blends, where CFA was used with or without GGF. The trends observed in the flow test are consistent with those of water requirement, as the 40G00C had similar flow as control, and the flow of other mixtures was noticeably higher than control as the fly ash dosage increased at the same w/b ratio. Although GGF is an extremely fine particulate material, its presence in mixtures, with or without CFA, did not affect the flow of the mixtures, which was possibly due to the smooth surface texture of GGF particles.
**Drying Shrinkage Results**

The performance of the tested mixtures in terms of drying shrinkage is illustrated in Figure 4-4. At an early age all the tested mixtures had higher shrinkage than the control, which was made of 100% cement. However, at 28 days, the 10G30C and 20G20C mixtures were the only mixtures that had drying shrinkage less than the control. Both mixtures continued to shrink less than the control, and they were less by 15% and 10.6%, respectively, at the end of the test duration (as shown in Figure 4-4b), which was added for further clarification of Figure 4-4a at 28 days and 98 days.

As it can be seen in Figure 4-4, the mixtures 10G30C and 20G20C showed the lowest drying shrinkage. The better performance of these two mixtures in comparison with mixtures 40GC00 and 30G10C could most likely be attributed to the lower water to binder ratios of 10G30 and 20G20C mixtures (see Test Methods - Drying Shrinkage for w/b ratios). Additionally, the higher fineness of 40G00C and 30G10C, because of having more GGF content, could have possibly led to the higher drying shrinkage as compared with the other test mixtures. According to Hu et al. [45], the higher the w/b ratio, the larger the pore diameter and hence the moisture loss and drying shrinkage. Further, the better performance of these two mixtures in comparison with 00G40C can be attributed to the lack of micro-reinforcement within the paste structure. As shown in Figure 4-1, GGF particles are dense solid particles. It is likely that a portion of GGF particles remains unreacted in the paste; thus, acting as micro-aggregates and stiffening the paste. However, some fly ash particles tend to be hollow (cenospheres) and hence may not be able to act as micro-aggregates. Finally, the lower drying shrinkage of mixtures having different levels of SCMs, except 40% GGF, in comparison to the control mixture can be attributed to the
denser packing of the particles and the pozzolanic effect, which would refine the pore structure, thereby reducing the shrinkage [45].
**ASR Test Results**

**Accelerated Mortar Bar Test (AMBT)**

The AMBT expansion results for all the tested mixtures are shown in Figure 4-5. The expansion of the control mixture was 0.90% at 14 days, supporting the previously determined expansion using the same reactive aggregate and mixture materials [24]. It should be noted that in this study, even 40% replacement of cement with CFA did not yield a satisfactory performance to mitigate ASR. However, even when as little as 10% GGF was added (10G30C), the 14-day expansion reduced to well below the 0.10% limit. Increasingly better performance was observed upon utilizing higher levels of GGF - in other mixtures. Additionally, the excellent performance of GGF to mitigate ASR, which was observed by Rashidian-Dezfouli and Rangaraju [24], was confirmed here; as the 40G00C mixture had the lowest expansion. Finally, the AMBT bars were visually inspected after the end of the test; there were no significant cracks in any of the GGF-containing mixtures, whereas the control mixture was severely cracked.
The better performance of GGF-containing mixtures can be ascribed to the pozzolanic reactivity of the combined blend of GGF and CFA, which was supported by the SAI values shown in Table 4-3. As more CH is consumed, the pore solution has a lesser amount of free Ca\(^{++}\) ions, and thus, the ASR gel is less expansive. Additionally, as more C-S-H gel is produced due to the pozzolanic reaction, the alkalinity level of pore solution would likely drop to a level at which the ASR reaction would be unsustainable.

Moreover, since GGF was found to work very well in geopolymer mortar and concrete [46], it is possible that the unreacted GGF particles could have been alkaline activated, especially because of the elevated temperature used in the AMBT procedure. Further studies are needed to investigate the mechanism by which GGF suppresses ASR. Lastly, the combination of 10% to 20% of GGF with 20% to 30% of CFA seems to be the optimum proportion to mitigate ASR. This is probably due to better particle packing and denser microstructure for the blend, as the GGF particles are finer than CFA particles.

**Miniature Concrete Prism Test (MCPT)**

The results of the MCPT expansions are shown in Figure 4-6. As can be seen, the MCPT results are in total agreement with the AMBT results. The mixture with 40% CFA (00G40C) failed the test after having expanded more than 0.020% at 56 days of NaOH solution exposure. Both test mixtures of 40G00C and 20G20C had a substantially lower expansion than the control, with the former performing slightly better than the latter. Although only four data points are used to plot the correlation between the AMBT
expansion at 14 days and the MCPT expansion at 56 days, as shown in Figure 4-6-b, they show a good correlation.
Resistance to Sulfate Attack Results

The performance of the mixtures in the sulfate attack study is presented in Figure 4-7. The two combinations that were tested were able to reduce the expansion caused by sulfate attack, with the mixture having 10% GGF (10G30C) performing slightly better than 20% GGF (20G20C). However, both these mixtures passed the requirement of expansion
less than 0.05% at 6 months, as per ASTM C618 specification. The 10G30C and 20G20C combinations showed a reduction in expansion by 89% and 74%, respectively, as compared with control at the end of the test period. The better performance of these two GGF-containing mixtures can most likely be attributed to their better pozzolanic activity, as evidenced by the SAI values for these two mixtures (Table 4-3). The better pozzolanic reactivity would reduce CH in the paste, leaving less CH to react with sulfate and forming less expansive products. Also, the smaller particle size of GGF would densify the hardened paste, making it less permeable, which provides better resistance to liquid ingress.

![Figure 4-7. Sulfate attack test results.](image)

**Conclusions**

Based on the work conducted in this study on binary and ternary blends of GGF and CFA, the following conclusions can be drawn:

1- Based on TGA and SAI test results, the pozzolanic activity of the GGF and CFA in the ternary mixtures increased the compressive strength.
2- Even though GGF is an extremely fine particulate material, its presence in mixtures, with or without CFA, did not negatively affect the flow of the mixtures.

3- Ternary mixtures experienced less drying shrinkage, than control mixture at later ages (28 days and after). Additionally, the early age strength of GGF-containing mixtures was higher compared with both the control and binary CFA mixture.

4- The ternary blends of GGF and CFA substantially outperformed the binary mixtures with CFA in mitigating ASR and in improving resistance to sulfate attack.

5- The combinations of 10% GGF with 30% CFA and 20% GGF with 20% CFA appear to be the optimal blending levels to improve performance in terms of SAI, drying shrinkage, resistance to ASR and sulfate attack.

**Recommendations**

The use of GGF to partially replace CFA at high replacement levels (as much as 50% in the SCM blend, with an overall replacement level of cement at 40%) appears to be a viable option to account for the dwindling supplies of fly ash and to boost the performance of CFA in mitigating ASR and sulfate attack. Although the beneficial effects of GGF in mitigating ASR and sulfate attack are proven in this study, additional research is needed to determine the precise mechanism involved.
References


Chapter 5

DURABILITY PERFORMANCE OF CONCRETE CONTAINING BLENDS OF GROUND GLASS FIBERS AND CLASS C FLY ASH

Abstract

Class C fly ash (CFA) has been used widely as a supplementary cementitious material (SCM) to partially replace ordinary Portland cement (OPC) in concrete. However, there are some concerns such as slower strength gain with its use at high dosage levels that are necessary to meet durability demands. Typically, higher amounts of CFA are required when CFA is used as an SCM to mitigate alkali-silica reaction (ASR). Moreover, the increasing scarcity of fly ash in the US, due to the decreased dependence on coal to produce power at power plants, is forcing the construction industry to look for alternative sources of SCMs. The fiber glass manufacturing process results in significant amounts of off-spec material that is typically landfilled. Previous studies have shown that ground glass fibers (GGF) could be very effective SCM from a strength and durability perspective if it is properly processed and ground.

This study explores the performance of concrete containing GGF and CFA, individually and combined, at two dosage levels (20% and 40% by mass). Thermogravimetric analysis (TGA) was first carried out to investigate the pozzolanic activity of the combinations and the results were supported by conducting the strength activity index. Performance of concrete mixtures based on these blends was evaluated in terms of mechanical properties, alkali-silica reaction, and chloride penetration. The durability of concrete has been correlated with non-destructive techniques including ultrasonic pulse velocity and surface resistivity. Results showed superior performance of mixtures containing GGF compared to CFA at both dosage levels that were evaluated.
Additionally, blending GGF with CFA could significantly lessen the weaknesses of CFA, both in terms of strength and durability.

**Introduction**

The utilization of fly ash in concrete enhances its mechanical properties and durability. Additionally, fly ash use in concrete offers sustainability in two ways: first, to manage the coal combustion wastes produced at coal-burning-based power plants, and second, to replace portion of cement whose manufacturing process is responsible for about 8% of CO2 emissions [1]. However, since coal is a finite resource that soon will need to be substituted with other energy resources, fly ash supplies have been dwindling and the availability of quality fly ash is diminishing. Due to the increasing number of power plants switching to other sources to generate power, the consumption of coal has reduced by 50% in the past nine years (from one billion tons in 2010 to 0.5 billion tons in 2019) [2]. Therefore, optimizing the use of fly ash in concrete is important for construction industry.

Other than the dwindling supply of fly ash, there are some negative aspects associated with the use of class C fly ash (CFA) in concrete. These negative attributes include the higher dosages that are required to meet the concrete durability demands. For example, to mitigate alkali-silica reaction (ASR), usually more than 30% replacement ratio is required [3], which would negatively affect strength development and setting at early ages [4], [5]. Moreover, CFA may contain appreciable levels of free calcium Oxide (CaO), C₃A and anhydrous calcium sulfate which increases the possibility of unsoundness and affects the durability of concrete [5]. Thus, there is a need to improve the performance of CFA, especially at higher levels of cement replacement.

As a way of counterbalancing the aforementioned negative aspects of CFA in concrete, this work suggests the use of ternary blends in which CFA is combined with a
better-quality material. The literature showed that previous studies had investigated the use of several materials along with CFA, such as slag [6,7], rice husk ash [8], glass powder [9], meta-kaolin [7, 10–12], silica fume [13–15]. However, none of these studies had examined the use of ground glass fibers (GGF) with CFA, which is the focus of this study.

The GGF was chosen in this study due to several advantages and motivations that it offers. During production, the glass fibers are thoroughly examined for deficiencies. Therefore, Glass fiber is extremely consistent in terms of the chemical composition and physical properties. However, a significant quantity of glass fibers that does not meet the required physical quality standards, in terms of filament continuity within a strand, is disposed-off as an off-spec glass fiber (≈25% of produced glass fibers is landfilled). The demand for glass fiber products is vastly increasing [16], and the glass fiber industry has been growing fast [17]. In the US alone, 500,000 tons of waste glass fibers can annually be allocated for beneficiating [18]. Moreover, the glass fibers waste will increase in the next few decades as some of the products that extensively rely on glass fibers, such as wind turbine blades, have a very short life span [19], and the options for recycling are very limited [20]. The construction industry is a vital sector where a major percentage of the waste glass fibers can be consumed. It should be mentioned that a new STM standard has been issued this year, ASTM C1866 [21] – Standard Specification for Ground-Glass Pozzolan for Use in Concrete. The ground glass fiber (GGF), explored in this study, is compliant with the Type GE glass identified in ASTM C1866.

Most importantly, the GGF was chosen for its ability to enhance concrete durability, which has been proven in several studies [22–24]. The first use of ground glass from a glass fiber processing plant as a supplementary cementitious material was in 2004 [18], wherein the ground glass was referred to as VCAS pozzolan, that stands for Vitreous
Calcium-Aluminate-Silicate [18]. It has been found that the VCAS improved the fresh and hardened properties of OPC concrete. The inclusion of 20% OPC replacement by VCAS was found to improve the flowability of the mix by more than 130%, strength activity index of 123% at 7 days, and was capable of suppressing sulfate attack and ASR damages significantly [18]. The report estimated the environmental benefits of recycling glass fibers waste and stated that for each ton of recycled glass fibers, about 5 BTU (British Thermal Unit) energy could be saved annually.

Rashidian-Dezfouli and Rangaraju [22] further investigated the feasibility of using GGF as pozzolan in concrete. The pozzolanic activity, fresh and hardened concrete properties and potential for use as an SCM to mitigate ASR, sulfate attack, and chloride penetration were all explored in their study. They concluded that the use of GGF up to 30% replacement did not affect the mechanical properties of concrete. Also, the performance of mixtures containing GGF in mitigating ASR and sulfate attack was excellent at both 20% and 30%.

Based on this background, the objectives of this work are to explore the use of GGF to improve the shortcomings of using CFA in concrete. To achieve this objective, first the performance of CFA and GGF in binary mortar and concrete mixtures was compared. Then, the synergetic effect of a ternary blend at 40% replacement of cement with CFA+GGF was studied and compared with the binary based mixtures.

**Experimental Program**

**Materials**

**Cement**

Two types of ordinary portland cements meeting ASTM C150 [25] were used in this study: A Type I/II ordinary portland cement (OPC) ($\text{Na}_2\text{O}_{eq} = 0.38\%$) that was obtained
from Argos cement company, SC, and a Type I high alkali portland cement (Na₂O_{eq} = 1.00%) from Lehigh Cement company, PA. The Type I/II OPC was used for most of the tests, while the high alkali cement was used only in the miniature concrete prism test (MCPT) (AASHTO T380). The chemical compositions and physical properties of portland cement are presented in Table 5-1.

**Ground Glass Fibers (GGF)**

The Ground Glass Fiber (GGF) used in this study was prepared by milling the off-spec glass fibers in a ball mill to a fine powder, white in color, with an average particle size of 4 microns. The chemical compositions and physical properties of GGF are presented in Table 5-1.

**Class C Fly Ash (CFA)**

A high-calcium fly ash (CaO = 24.2%) with a specific gravity of 2.50 was used and the chemical composition is given in Table 5-1.

**Table 5-1: Chemical composition and physical properties for the materials.**

<table>
<thead>
<tr>
<th>Material</th>
<th>Physical Properties</th>
<th>Chemical Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Specific Gravity</td>
<td>LOI</td>
</tr>
<tr>
<td>Type I cement</td>
<td>3.15</td>
<td>2.6%</td>
</tr>
<tr>
<td>High alkali cement</td>
<td>3.15</td>
<td>–</td>
</tr>
<tr>
<td>CFA</td>
<td>2.50</td>
<td>1.6%</td>
</tr>
<tr>
<td>GGF</td>
<td>2.60</td>
<td>1.0%</td>
</tr>
</tbody>
</table>
Fine Aggregate (Siliceous Sand)

A non-reactive siliceous natural river sand from Glasscock Co. in Sumter, SC with an oven-dry specific gravity of 2.63, an absorption ratio of 0.35% and a fineness modulus of 2.60 was used in this study.

Non-Reactive Coarse Aggregate

Size 67 crushed stone from Liberty, SC provided by Vulcan Materials Company was used in this study for concrete mixtures. The specific gravity and absorption of this aggregate were 2.65 and 1.0% respectively. The dry rodded unit weight of this aggregate was 1550 Kg/m³.

Reactive Coarse Aggregate

Highly reactive rhyolitic aggregate, Las Placitas gravel from New Mexico (NM) was used for testing ASR. The specific gravity and percent absorption of this aggregate were 2.6 and 1.1%, respectively. This aggregate was crushed and graded in accordance with AASHTO T380 [26] for use in miniature Concrete Prism Test (MCPT).

Sodium Hydroxide

Sodium hydroxide pellets with 97% minimum assay were acquired from Fisher Chemicals. These pellets were used to prepare the alkali solution that is used in ASR testing. They were also used to increase the alkali level of concrete mixes for MCPT test method as required by AASHTO T380 [26].

Mixture Proportions

All tested mixtures are shown in Table 5-2. Water to cementitious materials ratio (w/c) of 0.4 was used for all paste and mortar mixtures. The paste mixtures were used for TGA, while mortar mixtures were used to test the strength activity index (SAI). For concrete
mixtures, the volume of dry rodded coarse aggregate per unit volume of concrete was 0.68. Cementitious materials content was fixed at 410 Kg/m³ while water to cementitious materials ratio (w/c) was maintained at 0.45. No chemical admixtures were used in any of the tested mixtures.

The individual contribution of GGF and CFA to mechanical and durability properties of mortar and concrete was examined in the binary mixtures at a replacement level of 20% and 40%. Additionally, the combined effect of using both GGF and CFA on the concrete properties was examined in the ternary mixture at 40% total replacement.

Table 5-2 Cementitious materials proportion for all the mixtures.

<table>
<thead>
<tr>
<th>Mix Label</th>
<th>Cement, %</th>
<th>CFA, %</th>
<th>GGF, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20C00G</td>
<td>80</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>00C20G</td>
<td>80</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>40C00G</td>
<td>60</td>
<td>40</td>
<td>0</td>
</tr>
<tr>
<td>20C20G</td>
<td>60</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>00C40G</td>
<td>60</td>
<td>0</td>
<td>40</td>
</tr>
</tbody>
</table>

Test Methods

Pozzolanic Activity by Thermo-Gravimetric Analysis (TGA)

TGA is a commonly used experiment to determine the degree of hydration of cementitious materials. The basic principle of the TGA test is to first, gradually heat a sample taken from the hardened paste of cementitious material and monitor the weight loss caused by evaporation and the decomposition of chemical elements.

The purpose of this test was to determine the extent of fly ash’s pozzolanic reactivity with cement by measuring the content of Calcium Hydroxide (CH). CH along with C-S-H gel are among the main products of cement hydration. C-S-H gel gives the strength of the hardened cement paste, while CH does not contribute much to strength. When using fly ash as a SCM, the silica in fly ash reacts with the CH resulting in more C-
S-H gel and ultimately more strength. The calcium hydroxide (CH) content was estimated by measuring the weight loss that occurred between 400 °C and 500 °C, at which the decomposition of CH (Ca(OH)$_2$ → CaO + H$_2$O) occurs, and between 600 °C to 800 °C, at which calcium carbonate (CaCO$_3$) decomposes [27]. Once the CH% is determined, whether fly ash has pozzolanic reactivity can be verified.

Ground hardened paste samples of about 40 mg, with hydration stopped using isopropyl alcohol and diethyl ether, was tested at a temperature ramp of 10 °C/min with nitrogen gas purge of 30 ml/min. The prepared samples underwent TGA testing by using an AutoTGA 2950 V5.4A instrument up to 800 °C.

**Strength-Activity Index (SAI) test (ASTM C311)**

The pozzolanic reactivity was measured by testing the compressive strength of 2 in. cubes at 7 and 28 days. Two mixtures were prepared according to ASTM C311-18 [28], the first mixture is the control using cement only, and the second is the test mixture using 20% replacement with SCM. For the fly ash, according to ASTM C311-18, a minimum of 75% SAI at both 7 and 28 days is required for test samples in order to consider the tested fly ash as an effective pozzolan. For GGF, however, ASTM C1866 stipulate a minimum SAI of 75% at 7 days and a minimum of 85% at 28 days.

- **Compressive Strength of Concrete (ASTM C39)**

Compressive strength of the concrete samples was measured in accordance with (ASTM C39). For this test, 4 in. by 8 in. concrete cylinders were cast for each of the tested mixtures, demolded the following day and cured in a moist room with a relative humidity of 100% and temperature of 23 °C ± 2 °C. The compressive strength then was tested at 7 and 28 days.
- **Splitting Tensile Strength (ASTM C496)**

  For each mixture, splitting tensile strength was measured at 28, and 56 days in accordance with ASTM C496. The horizontally oriented 3 in. by 6 in. concrete cylinder was loaded at a loading rate of 100-200 psi/min continuously until failure. The ultimate load reached can then be used to calculate the splitting tensile strength (modulus of rupture) of concrete.

- **Alkali-Silica Reaction (ASR)**

  **Miniature Concrete Prism Test (AASHTO T380, MCPT)**

  To investigate the effectiveness of the tested SCMs in mitigating ASR in concrete, AASHTO T380 [26] Miniature Concrete Prism Test (MCPT) was conducted. This test was chosen as it provides a faster indication of ASR mitigation than the well-known ASTM C1293 test method [29]; the maximum period of this test is 84 days compared to two years of ASTM C1293 test method. It is worth mentioning that a good correlation was established by some studies between both MCPT and ASTM C1293 for a variety of reactive coarse and fine aggregates [30], [31].

  In this study, a non-reactive quartz fine aggregate was used along with a reactive coarse aggregate—graded in accordance to AASHTO T380 [26]—in preparing the samples. After demolding, the samples were conditioned as per the test method and stored in a sealed plastic container. The plastic container was placed in a water bath adjusted to a temperature of 60 °C for the remainder of the test duration. When mitigation measures are to be evaluated, the Portland cement is replaced with SCM and the alkali content of the mix is boosted to 1.25% by mass of cement in the mixture. AASHTO T380 requires a level of expansion of less than 0.02% at 56 days for the tested proportion to be considered as effective in ASR mitigation.
At the end of the ASR expansion measurements, samples were cut from the center of the prisms and manually ground using mortar and pestle to a fineness of less than 1mm. TGA test was performed on powdered sample with hydration stopped using solvent exchange methods. For each specimen, approximately 50 mg of sample was loaded in the crucible and analyzed at a temperature ramp of 10°C/min with nitrogen gas purge of 30 mL/min.

**Dynamic Modulus of Elasticity**

The dynamic modulus of elasticity DME of the concrete prisms was relatively measured throughout the MCPT testing period to further monitor the physical distress arising in concrete due to ASR. The DME values were determined using the resonant frequency method based on impulse excitation technique. W. Lemmens, Inc., Belgium instrument was used to determine the resonant frequencies of the concrete prisms right after taking the length change readings on 0, 7, 14, 28, 56, and 84 days of NaOH solution exposure. Changes in the relative DME values were correlated with ASR-related expansion measurements.

**Ultrasonic Pulse Velocity**

When a short and strong electrical signal is sent to a transformer, which makes it vibrate according to the resonance frequency, the vibration of the transformer is propagated to the concrete through contact media such as grease and a rubber couplant, and this is sensed by the receiving transformer on the opposite side. Because the time spent by the wave from start to arrival is recorded by an electrical device, the wave velocity can be calculated when the distance the wave travels is known. Besides the concrete strength, the wave velocity is influenced by the water content and reinforcement. When
the status of concrete changes from dry to saturated, the wave velocity increases by about 5%.

- Rapid Chloride Penetration Test (RCPT - ASTM C1202)

To evaluate the chloride permeability of concrete mixtures, one cured concrete cylinder was saw cut in accordance with ASTM C1202 to produce three disks of 2 in thickness and 4 in. diameter one day prior to the test date. After the samples were dried at room temperature, the sides of the disks were sealed using epoxy-based coating. After that, the disks were placed in a vacuum desiccator under a vacuum pump with a pressure less than 50 millibar for three hours followed by one hour under saturation. At least 18 hours later, the RCPT test was performed.

In this test, a 60 V potential difference is applied between the ends of the disc for 6 hours during which the charge through the disc is measured. The total charge, measured in coulombs, that passes through the specimen is used to indicate the level of risk of chloride penetration as per ASTM C1202.

Water Sorptivity Test (ASTM C1585)

The rate of absorption by capillary action into the concrete pores was assessed by conducting the sorptivity test in accordance with ASTM C1585 at 28 days. Concrete discs with dimensions of 2 in. thickness and 4 in. diameter were cut from a concrete cylinder. Next, they were conditioned by a vacuum desiccation for 3 hours followed by vacuum saturation for one hour. After that, the discs were placed in a sealed container and put in an environmental chamber at 50 C and 80% RH for 3 days followed by a minimum of 15 days storage at 23 C. The side of the discs were, then, epoxy coated, and the top surface was wrapped by a plastic sheet to prevent moisture loss. After that, the absorption procedure started, where the discs were placed on supports in a pan with water covering
from 1 mm to 3 mm from the bottom of the disc (above the supports). Subsequent measurements of the mass of each disc were taken at certain times up to 8 days, as specified in ASTM C1585. The mass of water absorbed throughout the test period is divided by the density of water and the surface area that was exposed to water. The measured values are plotted against the square root of time and two absorption rates are measured: the initial absorption and the secondary absorption, in unit of length per time to the power of half \((L/T^{1/2})\). The initial absorption is represented by the slope of the straight line that best fits the data collected from the start of the absorption procedure to the end of the first 6 hours. Whereas the secondary absorption rate is the slope of the best fitted straight line representing the rest of the data until the end of the test. The initial rate of absorption is typically considered by the capillary suction of the pores, while the secondary rate is affected by not only the capillary pores but by other aspects such as filling air voids and larger pores \[32\].

**Results and Discussions**

**Pozzolanic Activity**

The pozzolanic activity test results by TGA are shown in Figure 5-1. In this figure, the relative CH content for each tested mixture was calculated relative to that of Control mixture. The CH content was assessed by examining the weight loss caused by CH decomposition. The performance of CFA and GGF was similar at 20% replacement, with GGF containing mixture \((00C20G)\) slightly higher values especially at 7 days; meaning that they had higher content of CH. This increase in CH content can be attributed to the dilution effect of cement as more water is available for cement to react and produce more CH. Additionally, the surface of both materials may have acted as nucleation sites and facilitated the cement hydration reaction \[33\], with GGF providing larger surface being
finer. The pozzolanic reactivity is clearly proven at the higher replacement ratio of 40%. All values of $\text{CH}_{\text{mix}}/\text{CH}_{\text{control}}$ were less than the dilution lines except for 40G00C at 7 days, which again can be explained by the combined effect of dilution of cement and higher surface area for nucleating. If the tested mixtures were ordered according to the lowest CH content at 28 days, the order will be as follows: 40C00G, 20C20G, 00C40G, 20C00G, 00C20G, and Control.

The ternary blend of 20G20C did not show different performance here compared to the binary blend of each material. However, when the same combinations were tested for SAI, as shown in Table 5-3, higher SAI values were obtained for the ternary mixture of 20C20G at both 7 and 28 days. The inclusion of GGF into the binary CFA mixture improved the SAI values. Also, the SAI values of GGF binary mixtures were much higher than those of CFA binary mixtures. It should be noted that the minimum SAI value as per
ASTM C311 for fly ash is met here at both replacement levels of 20% and 40%. Also, the binary GGF mixtures had a much higher SAI than the limit imposed by ASTM C1866.

Table 5-3 Strength activity index test results.

<table>
<thead>
<tr>
<th>Mixture Label</th>
<th>SAI, %</th>
<th>7-day</th>
<th>28-day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>100.00</td>
<td>100.00</td>
<td></td>
</tr>
<tr>
<td>20C00G</td>
<td>79.30</td>
<td>88.20</td>
<td></td>
</tr>
<tr>
<td>00C20G</td>
<td>105.00</td>
<td>106.00</td>
<td></td>
</tr>
<tr>
<td>40C00G</td>
<td>75.11</td>
<td>87.61</td>
<td></td>
</tr>
<tr>
<td>20C20G</td>
<td>77.80</td>
<td>98.60</td>
<td></td>
</tr>
<tr>
<td>00C40G</td>
<td>98.00</td>
<td>102.00</td>
<td></td>
</tr>
</tbody>
</table>

Besides its excellent pozzolanic activity, the GGF particles are much stronger than the fly ash particles [34]. Thus, the unreacted GGF particles could have behaved as microaggregate filling the voids and adding to the strength. To further examine the hardness of GGF particles, 30 grams of each material retained on standard sieve No. 80 and passing standard sieve No. 40 were ground in a ball mill using 1:4 ratio of material to steel balls by mass (i.e. 120 grams of steel balls). The ball mill was run at 250 RPM for 30 minutes. After milling, each material was sieved on standard sieve No. 80 and the percent weight loss was calculated. The mass losses were 42% and 75% for GGF and CFA, respectively, suggesting the stronger nature of GGF particles over CFA particles.

**Compressive Strength and Splitting Tensile Strength**

The results of compressive strength of the concrete mixtures are presented in Figure 5-2a. Also, a comparison between the performance of the binary mixtures of CFA and GGF at the tested dosage levels is shown in Figure 5-2b. At 20% replacement, the binary GGF mixture outperformed the binary CFA mixture at each test age. The double action of pozzolanic activity and the microaggregate-like behavior of GGF was the most-
likely reason of the superiority of GGF performance. This is also true at 40% replacement, as the GGF binary mixture had a 28-day strength that was significantly higher by 33% than the CFA binary mixture. The 40C00G had even less strength than the Control at all ages, which is clearly attributed to the high replacement ratio and the nature of slow rate of hydration for CFA. The ternary mixture of 20C20G, however, had a middle performance between GGF and CFA binary mixture, which evidently suggests a synergetic effect of the inclusion of GGF into the mix on improving the strength.

Figure 5-2 a) Compressive strength of concrete mixtures; b) comparison of the binary CFA and GGF mixtures.

The resulting denser structure of concrete, because of the fineness of GGF and CFA and their contribution in pozzolanic activity, increased the strength of concrete. Although this study did not examine the microstructure of concrete directly, but measurements of ultrasonic pulse velocity (UPV) were taken for the concrete cylinders prior to testing 28-day compressive strength. It is been established that the UPV values relate very well to the density and compressive strength of concrete [35], [36]. The UPV values measured for all the concrete mixtures are shown in Table 5-4. There is a good correlation between the UPV values and the compressive strength at 28 days ($R^2 = 0.852$). The measured UPV values also relatively agree with the findings of Hong et al., 2015 [35] in which a relationship was
established between UPV and compressive strength, but with underestimation of strength ranged from 11% to 40% of the actual strength. Nevertheless, the GGF-containing mixtures of 20% and 40% had the highest UPV value followed by 20C00G and 20C20G indicating a denser structure. All mixtures had UPV values higher than the control mixture except the 40C00G which could imply higher porosity as a result of the high replacement ratio and the slower rate of pozzolanic activity of CFA.

Table 5-4 Ultrasonic pulse velocity measurements of concrete cylinders.

<table>
<thead>
<tr>
<th>Label</th>
<th>28-day strength, psi</th>
<th>28-day strength, MPa</th>
<th>UPV, m/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>6020</td>
<td>41.5</td>
<td>4200</td>
</tr>
<tr>
<td>20C00G</td>
<td>7130</td>
<td>49.2</td>
<td>4550</td>
</tr>
<tr>
<td>00C20G</td>
<td>7720</td>
<td>53.2</td>
<td>4620</td>
</tr>
<tr>
<td>40C00G</td>
<td>5920</td>
<td>40.8</td>
<td>4045</td>
</tr>
<tr>
<td>20C20G</td>
<td>7250</td>
<td>50</td>
<td>4320</td>
</tr>
<tr>
<td>00C40G</td>
<td>7870</td>
<td>54.3</td>
<td>4630</td>
</tr>
</tbody>
</table>

The splitting tensile test results at 28 and 56 days for the tested concrete mixtures are shown in Figure 5-3. All SCM containing concrete mixtures had a higher tensile strength than the control mixture except 40C00G. Once again, the binary GGF mixtures performed better than the CFA binary mixtures at both test ages. Additionally, the ternary mixture of 20C20G had the highest tensile strength among all mixtures. Correlation of these results with compressive strengths at 28 and 56 days yielded R-squared values of 0.79 and 0.86, respectively. Results from this study provided weak correlation (0.45) with the previously mentioned UPV values at 28 days of age.
**Alkali-Silica Reaction (ASR)**

The ASR-induced expansion is plotted versus time of exposure to the 1N NaOH solution and shown in Figure 5-4. In these prisms, reactive coarse aggregate and non-reactive silicious fine aggregate were used along with high alkali cement that was replaced by 20% and 40% of each material (CFA and GGF). In addition, a ternary mixture of 20%CFA and 20%GGF was also tested to investigate the combined effect of both SCMs. The 56-day expansion limit in AASHTO T380 is 0.02% below which the tested dosage and type of SCM is considered effective to mitigate ASR-induced damage.

As shown in Figure 5-4, 20%CFA and 40%CFA were able to lower the concrete expansion at 56 days compared to Control by 11.7% and 85%, respectively. However, both CFA-binary mixtures failed to properly mitigate ASR having a higher 56-day expansion than 0.02%. As it was discussed earlier that one of the negative aspects associated with the use of CFA is the high dosage level necessary to meet durability demands. At 20% replacement of CFA, not only did it fail to mitigate ASR, but also it had caused even more expansion than that if cement diluted by 20%. Studies showed that most CFAs have a
pessimum effect around 15% to 20% [7], [37]. These experimental results of ASR expansion are in agreement with the findings of Malvar and Lenke, 2006 [38] whose study investigated the effectiveness of fly ash in mitigating ASR based on its chemical compositions and other factors. They came up with an equation that can be used along with some figures to estimate the minimum fly ash replacement to suppress ASR expansions. Based on their findings, and using the data from the chemical composition of CFA and cement, shown in Table 5-1, and the 14-day expansion from ASTM C1260 (done by the author elsewhere) at 90% reliability level, the calculations revealed that at least 47% of this CFA is required to properly mitigate ASR below the expansion limit of 0.1% as per ASTM C1567.

In contrast, all the GGF-containing mixtures had much smaller expansions and all are considered effective to mitigate ASR. The use of only 20% of GGF was able to mitigate ASR and reduce the expansion by 96% as compared to the Control mixture. These results are in line with the work of Rashidian-Dezfouli and Rangaraju in which the investigated the use of GGF as SCM up to 30% replacement [39]. Moreover, 40% replacement of GGF has substantially mitigated ASR to a very low level. Finally, the ternary GGF and CFA blended mixture showed a similar performance of the 40% GGF mixture in suppressing ASR, which confirms the combined effect of the blend.
The ASR mitigation mechanism by the use of SCMs in general and fly ash and GGF in specific has been well explained and investigated in several studies [22], [40]–[42]. The pozzolanic activity of the SCM consumes CH and bound it into the stable C-S-H gel. Otherwise, this CH reacts with the newly formed ASR gel producing a higher viscosity ASR gel that has higher susceptibility to expansion upon absorbing moisture [42]. To assess the CH content in the tested ASR samples, the TGA test was performed on pulverized samples sectioned from the ASR prisms. The CH content measurements were: Control=6.78%, 20C00G=6.18%, 00C20G=4.85%, 40C00G=5.8%, 00C40G=4.63%, and 20C20G=4.74%. These results correlate well with the MCPT 56-Day expansions, shown on Figure 5-4, which indicated a higher consumption of CH for the GGF-containing binary and ternary mixtures.

The excellent ASR mitigation of GGF-containing mixtures can be attributed to the excellent pozzolanic reactivity of the binary and ternary blend of GGF and CFA, which was endorsed by the SAI values shown in Table 5-3. As more CH is consumed, pore solution
would have lesser amount of free Ca+ ions and thus the formed ASR gel would have lesser Ca/Si ratio and lower ability to expand [40]. Additionally, by consuming CH and producing more C-S-H gel through pozzolanic action, the pH of pore solution will be dropped to a degree at which ASR reaction would be untenable. On the other hand, based on the fact that GGF is proven to be an superb precursor for geopolymer concrete [43], it is likely that the unreacted GGF particles were alkaline activated, which further lowered the pH of pore solution, especially with the heat curing associated with the MCPT.

Finally, the MCPT prisms were visually inspected for cracks and deterioration signs due to ASR, there were no visible distress on any of the GGF-containing mixtures, while there existed cracks ranged from mild for CFA-binary mixtures to heavy for the control mixture. Referring to the splitting tensile strength results shown in Figure 5-3, and along with the mentioned ASR mitigation justifications for the GGF-including mixtures, it can also be noted that the increase of tensile strength of these mixes had contributed to resisting the internal distresses caused by ASR gel expansion. Although 20C00G had expanded only 11% less than Control, it had a mild network of cracks compared to control, which may be attributed to higher tensile strength.

For further investigation of the distress induced by ASR on the tested concrete mixtures, the dynamic modulus of elasticity (DME) was monitored at specific ages during MCPT test. The relative DME was calculated for each mixture individually based on their zero readings, and the results are shown in Figure 5-5. It is clear that both control and 20C00G mixtures had showed a continuous reduction in DME. Although the 20C00G had a lower rate of reduction than the control mixture in the first two weeks of exposure, they both ended up having about 40% reduction of DME. The 40C00G mixture showed a relatively high increase in the first week of exposure that might have been an outlier, but
it started to drop in the second week reaching about 10% total reduction at the end of the MCPT test. However, all of the GGF-containing mixtures had no reduction at all in DME, proving that there was no distress of any type due to the ASR reactions. These results are in total agreement with the ASR test results.

![Relative Dynamic Modulus of Elasticity for MCPT prisms](image)

**Figure 5-5** Relative DME for the concrete prisms tested in MCPT.

**Sorptivity and Rapid Chloride Penetration Test (RCPT)**

The CH produced during the cement hydration is soluble in water and it can leach out of concrete creating voids. These voids increase permeability and thus facilitate the ingress of chloride ions [44]. The pozzolanic activity therefore reduces the leaching of CH by turning it into C-S-H gel and ultimately reduces the permeability.
The resulting denser structure of concrete, because of the fineness of GGF and CFA and their contribution in pozzolanic activity, reduced the permeability. Although this study did not examine the permeability of concrete directly, but measurements of surface resistivity were taken. It is been established that the electrical surface resistivity is linked to the pore structure of concrete and help predict its durability \[45\]. As expected, the lowest surface resistivity was measured for the control mixture, as shown in Figure 5-6. The GGF-containing mixtures, both binary and ternary mixtures, had the highest resistivity followed by the CFA-binary mixtures. ACI 222R-01 suggests a minimum resistivity of 20 KΩ.cm to ensure a low corrosion rate of rebars in concrete, in other words, lower chloride penetration \[46\]. The measured resistivity of the GGF-containing mixtures averaged at about 20 KΩ.cm and all these mixtures have shown a very low chloride permeability. In contrast, the CFA-containing mixtures had lower resistivity and a lower performance in RCPT.
The results of sorptivity are shown in Table 5-5. Also, a correlation between the RCPT results and sorptivity is shown in the same table for both the initial and secondary absorption rates. The mixtures were ordered in a way such to list the GGF-binary mixtures first then CFA mixtures. As it can be seen, for GGF-mixtures, the results of the RCPT highly correlate with both the initial and secondary sorptivity. However, once the CFA binary mix of 20C00G enters the correlation order, the R2 value drops to 0.5 for the initial sorptivity, while it is still showing high correlation with the secondary sorptivity. The overall correlation of all the results was very weak for both initial and secondary sorptivity having R2 of 0.51, and 0.35, respectively.
Even though the RCPT method is widely used to determine the resistance of blended concrete to the penetration of chloride ions, it has a low accuracy in predicting the resistance of fly ash blended concrete to chloride penetration. It has been argued that the charge affects several ions even though the target is chloride ions [47], [48]. Concretes blended with fly ash consists of various ions which when exposed to chemical additives a reduction in alkalinity occurs. As a result, the electrical conductivity of the concrete is reduced [47], [48] and a false positive RCPT result is achieved. Furthermore, the electrical charge may be altered as a result of possible change of the sample temperature due to the applied potential difference [47]. All these facts are most likely the reasons why the correlation was weak between the sorptivity and RCPT.

Finally, the inclusion of GGF has been proved to enhance the performance of the CFA-based mixtures in resisting the chloride ion penetration. The 20% and 40% GGF
binary mixtures’ results presented in this study agree with those achieved by Rashidian-Dezfouli and Rangaraju, 2017 [22] in terms of the higher the GGF content the lower the charge passed through the samples. The superiority of GGF mixtures to resist chloride ion ingress can be, in part, attributed to the lower permeability due the refined pore structure filled with pozzolanic action products. Also, this was evidenced by the higher values obtained for the electrical resistivity of GGF-containing mixtures. Furthermore, it is been argued that the increase in the binding capacity is attributed to the aluminum content of SCM [49]–[51]. Although fly ashes contain higher amounts of alumina, it is mostly crystalline and very stable to react. Whereas for GGF, the aluminum content is lower than fly ash but it is in amorphous state which facilitates the reaction with chloride ions and immobilize them.

**Conclusions**

1. Based on TGA and SAI test results, the pozzolanic activity of the ternary blends of GGF and CFA mixtures was improved significantly compared to the binary mixtures containing CFA.

2. The ternary blends of GGF and CFA showed significant improvement in mitigating ASR compared to control mixtures.

3. Ternary blends of GGF and CFA showed significantly better ability to reduce chloride ion permeability, compared to binary mixtures containing Class C fly ash, even at 40% dosage levels.

4. The use of GGF along with CFA is a feasible option to alleviate the declining supplies of fly ash and to enhance the durability performance of CFA-containing concrete mixtures.
References


Chapter 6

COMPARISON OF CHLORIDE PERMEABILITY PERFORMANCE OF CONCRETES CONTAINING BINARY AND TERNARY BLENDS OF FLY ASH AND GROUND GLASS FIBERS

Introduction

Concrete is one of the most used man-made materials in the construction industry across the globe. The wide usage of concrete is due to its versatility and low cost [1], [2]. In addition, if properly cured concrete has enormous strength and is durable [3]. The strength of concrete, however, deteriorates rapidly when exposed to extreme environments. This includes exposure to marine conditions and de-icing salts [4]. Moreover, corrosion of reinforcement induced by chloride causes severe degradation of reinforced concrete structures. The rapid deterioration of concrete structures exposed to extreme conditions renders its use unsustainable. This is because the production of cement, an important constituent of concrete, is energy-intensive and contributes to increased release of carbon into the atmosphere [2], [5]. An increased emission of carbon is associated with global warming which is perhaps the greatest challenge of the world today. Nonetheless, research indicates that the strength and sustainability of concrete can be improved by incorporation of industrial byproducts such as fly ash [2], [4].

Resistance of Fly Ash Blended Concrete to Chloride Penetration

Fly ash is an industrial waste that is generated from the combustion of coal. The use of fly ash to enhance the strength and durability of concrete dates back to the 1930s. This was in response to corrosion of reinforced concrete structures and the need to minimize deposition of ash generated in power plants and coal-powered factories into the
environment [6]. The disposal of fly ash into landfills is associated with environmental pollution [6], [7]. Research however indicates that the addition of fly ash to concrete enhances the resistance to chloride penetration and thus reduces deterioration of steel reinforcements in concrete structures [2], [6]–[9].

Fly ash reduces the permeability and chloride ingress into concrete structures [6], [7], [10]. The principle reason for this is the reaction of silica and alumina in fly ash with calcium hydroxide from Portland cement to produce stable hydrates that reduce the porosity of concrete. When fly ash undergoes pozzolanic reaction it not only reduce calcium hydroxide, which is a water soluble compound and may leach out leaving porosity in concrete, but also it reduces the permeability of concrete [11]. Low permeability of concrete blended with fly ash improves resistance to chloride penetration.

A literature study carried out by Marks et al., 2015 [10] revealed that chloride penetration in concrete structures is reduced by addition of fly ash. They also noted that fly ash enhances chloride-binding effect of concrete [10]. As a result, they concluded that that incorporating fly ash in concrete protects steel reinforcements from chloride-induced corrosion. In a related study, Bremseth, 2010 [6] reported that the permeability of concrete is influenced by several factors including the quantity of SCM and efficiency of the curing process.

In an experimental study that was carried out by Dhir et al., 1997 [12], using an equilibrium method, they reported that the binding capacity of chloride to cement increased when 50 percent fly ash is added to cement paste. The increase in the binding capacity is attributed to the alumina content of fly ash [2], [9], [13]. Aluminates that are found in fly ash bind and immobilize chloride [11].
In comparison to conventional cement concrete, fly ash blended concrete contains up to 5 times aluminates [11]. In addition, Shi et al., 2012 [2] suggests that the increase in chloride binding capacity of concrete could be a result of the generation of C-A-S-H gel which is similar to the C-S-H gel when the aluminous compounds react with calcium hydroxide (CH). This C-A-S-H gel enhances the adsorption of chloride ions in concrete, as a result, the ingress of chloride ions into concrete is limited [2], [9]. The resistance to chloride penetration in concrete is therefore improved with the adsorption of chloride ions.

Considering that fly ash is made up of tiny particles that fill up most of the voids in the binder phase, these fly ash particles act to seal off contiguous void spaces in concrete, hence reducing the penetration of water molecules and other chemicals including chloride ions into concrete [6]. When these voids are filled there is a corresponding increase in the density of concrete [6]. An increase in the density of concrete improves its resistance to chloride penetration.

Shi et al., [2] concluded that an increase of fly ash content of concrete reduces both its permeability and chloride penetration. Parande et al., 2011 [14] confirmed that when fly ash is added to Portland cement the compressive strength of concrete is increased whilst its permeability to chloride ions is significantly reduced in comparison to ordinary cement concrete. Furthermore, Shi et al., 2012 [2] and Saraswathy and Song, 2006 [11] argued that addition of fly ash to concrete is significantly effective to minimize the corrosion of steel reinforcements in concrete structures.

Research indicates that the resistance of concrete to chloride penetration is influenced by the amount of fly ash that is added. Bremseth, 2010 [6] noted that concrete with a high content of fly ash has a higher resistance to chloride penetration in comparison
to concrete with a low content of fly ash. Conventional concrete has the least resistance to the penetration of chloride ions [6]. According to the performance tests carried out by Bremseth (2010) [6], a comparison of concrete with different amounts of fly ash shows that resistance to chloride penetration is directly proportional to the amount of fly ash that is added to concrete. Figure 6-1 below shows that concrete with 50% fly ash (C25) is more resistant to the penetration of chloride in comparison to a higher strength concrete (C45) which has no fly ash added to it. The study by Bremseth, 2010 [6] confirms an earlier study by Bouzoubaâ et al., 1998 [15] in which they made two concretes with different amounts of fly ash and a control. The concrete structures were exposed to a tidal zone for 10 years. The results obtained confirmed that the resistance to the penetration of chloride ions was higher in the concrete samples that had the highest fly ash [15]. It is therefore irrefutable that fly ash helps to reduce the penetration of chloride ions significantly.

![Figure 6-1: Resistance to chloride penetration after a 10-year exposure to a tidal zone (From [6]).](image)

Investigations carried out at Canada Centre for Mineral and Energy Technology (CANMET) showed that concrete blended with a high amount of fly ash had a higher resistance to chloride penetration in comparison to conventional concrete [11], [16].
Furthermore, concrete blended with fly ash has a high potential to limit the movement of chloride ions [11].

Although several studies confirm that fly ash blended concrete has a higher resistance to chloride penetration, a few studies contradict this. Nagataki et al., 1993 [17] noted that an increase in the amount of fly ash to 30 percent in cementitious paste reduces the capacity to bind and immobilize external chlorides. Another study by Ampadu et al., 1999 [18] reported that the benefits of adding fly ash to concrete only reduces diffusion of chloride ions at final phases of curing. In addition, they argued that resistance to chloride penetration is only effective when the amount of fly ash is 40% [18]. Thomas argued that an increase in fly ash content of concrete exposed to marine environment decreases chloride threshold values. Nonetheless, the resistance to chloride penetration in fly ash blended concrete structures remained significantly high [11].

**Chloride Permeability of Fly Ash Incorporated Concrete – Standard Test Methods**

Conventional concrete allows penetration of chloride ions when exposed to marine environments. One way of increasing the resistance of concrete to penetration of chloride ions is to blend it with fly ash. The resistance of blended concrete to penetration by chloride can be determined by various methods, *viz*, are the Rapid Chloride Penetration Test (RCPT) standardized in ASTM C1202 [19] and the Rapid Migration Test (RMT) standardized in NT build 492 [20]. The two methods use different transport processes that is diffusion for the former whilst the latter uses electromigration [21].

The RCPT method involves determination of the amount of electric charge passing through cylinders slices of 100 mm nominal diameter and 50 mm thick over a 6-hour period under an applied voltage of 60 V [19]. One end of the specimen is exposed to 3%
sodium chloride solution and the other end in a 0.3N sodium hydroxide solution. The resistance to chloride penetration is represented by the electrical charge passing through the specimen. In the RMT method, the penetration of chloride ions into concrete is determined by using electrical migration to accelerate the displacement of ions in a specimen [20]. A colorimetric indicator measures the resistance to the penetration of chloride ions. Chloride ions are forced to move into the test sample by an external potential that is applied across the sample over a predetermined period [20].

The RCPT method is widely used to determine the resistance of blended concrete to the penetration of chloride ions. This test is preferred because it is relatively quick and less laborious [21]. Nonetheless, the RCPT method has a low accuracy in predicting the resistance of fly ash blended concrete to chloride penetration. It has been argued that the charge affects several ions even though the target is chloride ions [21], [22]. As a result, the electrical conductivity of the concrete is reduced [21], [22]. Furthermore, the potential difference applied to the test specimen increases its temperature and alters the electrical charge [21]. Moreover, concrete admixed with calcium nitrite produces high Coulomb values representing a low resistance to the penetration of chloride [19].

The RMT method is widely used in Europe as a quality assessment tool because of its inherently higher accuracy in comparison to RCPT [23]. The accuracy of this test is higher because the process is not affected by corrosion inhibitors [24]. Moreover, the applied potential difference is quite low hence does not induce an increase in temperature in the specimen [24]. The accuracy of the RMT method is also improved due to the fact that the test measures actual penetration of chloride ions in concrete. In addition, the RMT method is used in research because of its short duration [23].
**Objectives of This Study**

This study examined and compare the performance of concrete in resisting chloride ion penetration incorporating class C fly ash (CFA) and class F fly ash (FFA), and ground glass fibers (GGF). Two replacement ratios were compared, 20% and 40% of each SCM in binary blends. Also, a ternary blended concrete at 40% replacement was tested using CFA+GGF and FFA+GGF to explore the effect of adding GGF to FA in the concrete system. The strength activity index was first determined for the mortar of all the tested mixtures in order to compare the reactivity of the tested SCMs. After that, the slump of the fresh concrete and the mechanical properties of the hardened concrete including compressive strength and splitting tensile strength were investigated. To explore the permeability of the hardened concrete, both water absorption test and the sorptivity test were conducted. The resistance of concrete to chloride penetration was assessed by running both ASTM C1202 Rapid Chloride Penetration Test (RCPT) and the NT Build 492 the Rapid Migration Test (RMT).

**Experimental Program**

**Materials**

Type I/II ordinary portland cements (OPC) (Na$_2$O$_{eq}$ = 0.38%) meeting ASTM C150 [25] obtained from Argos cement company, SC, was used in this study. A high-calcium class C fly ash (CFA) with CaO content of 24.2% and a specific gravity of 2.77 was used, and the Blaine’s fineness of this CFA was . For class F fly ash (FFA), the specific gravity was 2.25 and the average particle size was 28 microns. The Ground Glass Fiber (GGF) used in this study was prepared by milling the off-spec glass fibers to a fine white powder with an average particle size of 4 microns. The chemical compositions and physical properties of all of the materials are presented in Table 6-1.
Table 6-1 Chemical composition and physical properties for the materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific Gravity</th>
<th>LOI</th>
<th>Blaine’s Fineness, kg/m²</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>SO₃</th>
<th>Alkali eq.</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>3.15</td>
<td>2.6%</td>
<td>417.5</td>
<td>19.93</td>
<td>4.77</td>
<td>3.13</td>
<td>62.27</td>
<td>2.70</td>
<td>0.06</td>
<td>0.48</td>
<td>2.95</td>
<td>0.38</td>
</tr>
<tr>
<td>CFA</td>
<td>2.50</td>
<td>1.6%</td>
<td>468.8</td>
<td>37.60</td>
<td>18.80</td>
<td>6.00</td>
<td>24.20</td>
<td>4.50</td>
<td>2.30</td>
<td>1.90</td>
<td>2.30</td>
<td>1.99</td>
</tr>
<tr>
<td>FFA</td>
<td>2.25</td>
<td>–</td>
<td>348.5</td>
<td>50.70</td>
<td>25.1</td>
<td>12.5</td>
<td>3.3</td>
<td>1.1</td>
<td>0.51</td>
<td>2.27</td>
<td>–</td>
<td>dddd</td>
</tr>
<tr>
<td>GGF</td>
<td>2.60</td>
<td>1.0%</td>
<td>701.2</td>
<td>47.72</td>
<td>10.36</td>
<td>0.34</td>
<td>19.62</td>
<td>2.27</td>
<td>0.67</td>
<td>0.10</td>
<td>–</td>
<td>dddd</td>
</tr>
</tbody>
</table>

For the mortar and concrete mixtures, a non-reactive siliceous natural river sand from Glasscock Co. in Sumter, SC with an oven-dry specific gravity of 2.63, an absorption ratio of 0.35% and a fineness modulus of 2.60 was used in this study. The coarse aggregate used in the concrete mixtures was Size 67 crushed stone from Liberty quarry in SC provided by Vulcan Materials Company. The specific gravity and absorption of this aggregate were 2.65 and 1.0% respectively. The dry rodded unit weight of this aggregate was 1550 Kg/m³.

**Mixture Proportions**

All tested mixtures are shown in Table 6-2. Water to cementitious materials ratio (w/c) of 0.40 was used for all mortar mixtures. The mortar mixtures were used to test the strength activity index (SAI) and the compressive strength of mortar. For concrete mixtures, the volume of dry rodded coarse aggregate per unit volume of concrete was 0.68. Cementitious materials content was fixed at 410 Kg/m³ while water to cementitious materials ratio (w/c) was maintained at 0.45. No chemical admixtures were used in any of the tested mixtures.

The individual contribution of CFA, FFA, and GGF to mechanical and durability properties of mortar and concrete was examined in the binary mixtures at a replacement level of 20% and 40%. Additionally, the combined effect of using both CFA and GGF or FFA and GGF
on the concrete properties was inspected in the ternary mixtures at 40% total cement replacement.

Table 6-2 Relative proportions in the binder.

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>Cement</th>
<th>CFA</th>
<th>FFA</th>
<th>GGF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20C</td>
<td>80</td>
<td>20</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20F</td>
<td>80</td>
<td>0</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>20G</td>
<td>80</td>
<td>0</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>40C</td>
<td>60</td>
<td>40</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>40F</td>
<td>60</td>
<td>0</td>
<td>40</td>
<td>0</td>
</tr>
<tr>
<td>40G</td>
<td>60</td>
<td>0</td>
<td>0</td>
<td>40</td>
</tr>
<tr>
<td>20C20G</td>
<td>60</td>
<td>20</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>20F20G</td>
<td>60</td>
<td>0</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>

**Test Methods**

**Strength-Activity Index (SAI) Test (ASTM C311)**

The pozzolanic reactivity was measured by testing the compressive strength of 2 in. cubes at 7 and 28 days. Two mixtures were prepared according to ASTM C311-18 [26], the first mixture is the control using cement only, and the second is the test mixture using 20% replacement with SCM. For the fly ash, according to ASTM C311-18, a minimum of 75% SAI at both 7 and 28 days is required for test samples in order to consider the tested fly ash as an effective pozzolan. For GGF, however, ASTM C1866 stipulates a minimum SAI of 75% at 7 days and a minimum of 85% at 28 days.

**Compressive Strength of Concrete (ASTM C39)**

Compressive strength of the concrete samples was measured in accordance with (ASTM C39). For this test, 4 in. by 8 in. concrete cylinders were cast for each of the tested mixtures, demolded the following day and cured in a moist room with a relative humidity
of 100% and temperature of 23 °C ± 2 °C. The compressive strength then was tested at 7, 28 and 70 days.

- **Splitting Tensile Strength (ASTM C496)**

  For each mixture, splitting tensile strength was measured at 28, and 56 days in accordance with ASTM C496. The horizontally oriented 3 in. by 6 in. concrete cylinder was loaded at a loading rate of 100-200 psi/min continuously until failure. The ultimate load reached can then be used to calculate the splitting tensile strength (modulus of rupture) of concrete.

**Sorptivity and Water Absorption**

In this study, water absorption and sorptivity tests were performed. The volume of permeable pores was investigated in accordance with ASTM C642 [27] and the rate of water absorption by capillary suction was measured in accordance with ASTM C1585 [28]. In the water absorption test, broken chunks of concrete that are free of cracks are chosen to be the test samples as long as their volume is larger than 300 cc (about 800 g for normal concrete). The samples are first dried in oven at 110 °C until they are completely dry, and then the dry masses are taken. After that, the samples are saturated for at least 48 hours to ensure full saturation of the voids, then the SSD masses are taken. Next, the samples are boiled in water for 5 hours and then cooled at room temperature for at least 14 hours after which the SSD masses for the boiled samples are taken. Lastly, the submerged weights are taken and then the density, voids, and absorption of the concrete samples can be calculated as prescribed in ASTM C642.

For the sorptivity test, Concrete discs with dimensions of 2 in. thickness and 4 in. diameter were cut from a concrete cylinder. Next, they were conditioned by vacuum desiccation for 3 hours followed by vacuum saturation for one hour. After that, the discs
were placed in sealed container and put in an environmental chamber at 50 °C and 80% RH for 3 days followed by a minimum of 15 days storage at 23 °C. The side of the discs were, then, epoxy coated, and the top surface was wrapped by a plastic sheet to prevent moisture loss. After that, the absorption procedure started, where the discs were placed on supports in a pan with water covering from 1 mm to 3 mm from the bottom of the disc (above the supports), as shown in Figure 6-2. Subsequent measurements of the mass of each disc were taken at certain times up to 8 days, as specified in ASTM C1585. The mass of water absorbed throughout the test period is divided by the density of water and the surface area that was exposed to water. The measured values are plotted against the square root of time and two absorption rates are measured: the initial absorption and the secondary absorption, in unit of length per time raised to the power of half ($L/T^{1/2}$). The initial absorption is represented by the slope of the straight line that best fits the data collected from the start of the absorption procedures to the end of the first 6 hours. Whereas the secondary absorption rate is the slope of the best fitted straight line representing the rest of the data until the end of the test. The initial rate of absorption is typically reflected by the capillary suction of the pores, while the secondary rate is affected by not only the capillary pores but by other aspects such as filling the air voids and larger pores [29].
The standard ASTM C1202 was employed to assess the permeability of chloride ions through concrete. 4in diameter by 8in long concrete cylinders were cast and cured for 28 days. After that, each concrete cylinder was cut by a water-cooled saw into three discs of 2in thickness. Then, the sides of the samples were epoxy coated after they were dried at room temperature. The samples are then conditioned as per ASTM C1202 by vacuum desiccator for three hours then they were saturated under vacuuming for another hour. At least 18 hours later, the prepared samples were placed in the RCPT cells where the reservoir at one side was filled with a 3% NaCl solution and the other side’s reservoir was filled with a 0.3N NaOH solution. The test was then initiated by applying the 60 V potential for 6 hours and readings for the current and charge were taken every half hour. The total charge (coulombs) passed through the samples are averaged and used to indicate how resistant the concrete is to chloride ingress. Figure 6-3 shows the device and the cells used in RCPT test.
Rapid Migration Test (RMT)

This test measures the non-steady state migration coefficient ($D_{nssm}$) to assess the chloride permeability in concrete. The samples used for this test are prepared and conditioned in a matter similar to that of the RCPT. The test is standardized in NT Build 492 and it is considered a simple and a quick tool to evaluate the chloride ingress in concrete. The concrete samples are placed in a rubber or plastic sleeve tightly clamped on the sample to prevent leakage of solutions, then the samples are placed in a plastic reservoir in a way that they are inclined 32 degrees to the horizontal line by placing a plastic support at the base of the reservoir. The reservoir is filled with 10% NaCl solution (catholyte) and the upper side of the specimen (the rubber sleeve) is filled with 300 ml of 0.3 NaOH (anolyte). Both sides are connected to a power supply capable of applying up to 60 V DC voltage. The test is initiated by applying 30 V potential difference and recording the resulted current passing through the sample. Based on the recorded current, the final applied potential and the duration of the test are determined as per the standard [20]. After the test is over, the samples are taken out of the sleeves and cut into two halves. One
half is sprayed with 0.1N silver nitrate on the split section. Next, the chloride ingress is measured by a caliper or a roller and average of at least 5 readings is used in the calculations of \( D_{\text{nsm}} \).

![Figure 6-4](image)

Figure 6-4 Rapid migration test setup: (a) plastic cylinders were modified to serve as the rubber sleeve prescribed in NT Build 492; (b) Measurement of chloride penetration after the test; (c) The cathode and anode connections; (d) The plastic reservoir and the support of the cylinders at an angle of 32 degrees; (e) Silicon was used to seal the sides of the sample from top and bottom.

### Results and Discussion

**Strength Activity Index (SAI) Results**

The results of the SAI test are shown in Table 6-3. All tested mixtures, except the binary mixtures of 40F, passed the minimum SAI of 75%, specified by ASTM C618 [30]. Additionally, all of the binary GGF-containing mixtures passed the minimum SAI requirements of ASTM C1866 for type GE pozzolan, which is 85%. Moreover, both ternary
mixtures achieved a 28-day SAI values of more than 90%, which was significantly better than that of binary fly ash-based mixtures having the same replacement level. Both the extreme fineness of the GGF and the amorphous structure were the most likely triggers to improve the pozzolanic reaction and yield high SAI values. Likewise, since the particle size of GGF is smaller than that of fly ash, they provided a better packing of the particles, which may suggest a filling effect and could impact the SAI test results. However, in the previous study, TGA results showed high consumption of CH at 28 days for 40G, which had the highest content of GGF among the mixtures tested for TGA. Therefore, the pozzolanic activity of the GGF with each of CFA and FFA in the ternary mixtures increased the strength, and that was clearly reflected in the SAI values.

Table 6-3 Strength activity index for all mixtures.

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>7-Day SAI%</th>
<th>28-Day SAI%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>20C</td>
<td>77.0</td>
<td>93.0</td>
</tr>
<tr>
<td>20F</td>
<td>90.0</td>
<td>88.0</td>
</tr>
<tr>
<td>20G</td>
<td>109.0</td>
<td>113.0</td>
</tr>
<tr>
<td>40C</td>
<td>73.0</td>
<td>88.0</td>
</tr>
<tr>
<td>20G20G</td>
<td>93.0</td>
<td>101.0</td>
</tr>
<tr>
<td>40G</td>
<td>100.0</td>
<td>115.0</td>
</tr>
<tr>
<td>40F</td>
<td>65.0</td>
<td>70.0</td>
</tr>
<tr>
<td>20F20G</td>
<td>102.0</td>
<td>113.0</td>
</tr>
</tbody>
</table>

Although the binary mixture having 40% dosage of FFA did not pass the SAI test, it was included in the rest of the test plan for comparison reasons.

**Compressive Strength of Concrete**

The results of compressive strength at 7, 28, and 70 days for all the tested mixtures are shown in Figure 6-5. Additionally, the performance of the binary blended mixtures based on each tested SCM is represented in Figure 6-6. The GGF-based binary mixtures
outperformed both fly ash based binary mixtures at all ages. In fact, at 40% GGF dosage, which is a relatively high replacement for cement, the compressive strength is higher than that of the control mixture. In the ternary mixtures, the inclusion of GGF with CFA and FFA at 40% replacement level has boosted the compressive strength by 22.5% and 130%, respectively at 28 days, which shows the clear advantage of the ternary blends of GGF and fly ash. The incorporation of GGF in particular and fly ashes in general into the cementitious system may have facilitated the nucleation sites and provided more spaces for precipitation for the hydrates to form. This resulted in better performance of the ternary mixtures than the binary fly ash counterparts. The fineness of GGF particles may also provided better particles packing. The unreacted GGF particles may have also served as microaggregate adding on the strength and density of concrete. The GGF particles are strong and solid as was proven elsewhere [31].
The FFA-binary mixture of 40% that previously had failed the SAI test requirements did not perform well in concrete too. As it can be seen, even after 70 days of age the strength was only 54% of the strength of control. Whereas at 20%, the strength at 7 days was very low compared to the CFA and GGF binary mixtures. Although this study did not examine the reactivity of this FFA, but its low performance can be attributed to its low reactivity as pozzolan.

Figure 6-6 shows a comparison between the binary mixtures of each SCM tested here. The early age strength for the 20% replacement level was lower for FFA than control, whereas it was higher for CFA and GGF, with GGF having the highest early age strength. However, the high level of replacement at 40% has reduced the early strength of CFA compared with control. GGF-containing mixtures had higher compressive strength than control at all ages and replacement levels, which agrees with the SAI values that indicated high pozzolanic reactivity of GGF.
Rapid Chloride Permeability Test (RCPT) Results

The results of the RCPT test are presented in Figure 6-7. As it can be seen, the mixtures of 40C and control had the lowest resistance to chloride penetration followed by 20C. From the performance of binary fly ash mixtures, it is apparent that the FFA containing mixtures outperformed the CFA containing mixtures in resisting chloride penetration. For FFA containing mixtures, the 20% replacement level has higher resistance to chloride ingress than the 40% replacement. As mentioned earlier, the FFA used in this study might have been low in pozzolanic reactivity and thus the 40% replacement ratio is high for such fly ash.

The CH produced during the cement hydration is soluble in water and it can leach out of concrete creating voids. These voids increase permeability and thus facilitate the ingress of chloride ions [6]. The pozzolanic activity therefore reduces the leaching of CH.
by turning it into C-S-H gel and ultimately reduces the permeability. The resulting denser structure of concrete, due to the fineness of GGF and both fly ashes and their contribution in pozzolanic activity, reduced the permeability. To investigate the permeability of the tested concrete, measurements of electrical resistivity were taken for the concrete cylinders. It is been established that the electrical surface resistivity is linked to the pore structure of concrete and help predict its durability [32], [33]. As expected, the lowest surface resistivity was measured for the control mixture, as shown in Figure 6-8. The GGF-containing mixtures, both binary and ternary mixtures, had the highest resistivity followed by the FFA-binary mixtures. While the CFA containing mixtures did not experience a significant increase in electrical resistivity as compared to the control.

Based on the surface resistivity (SR) of concrete, ACI 222R-01 provides classification for corrosion rate and for chloride permeability resistance. The classification specifies the risk of chloride ingress as following: high if SR<12 KΩ.cm, moderate for SR between 12-21, low for SR between 21-37, very low for SR between 37-254, and negligible beyond that [34]. Therefore, for the tested concrete mixtures in this study, The 40% GGF mixtures had a low risk of chloride ingress, while the other mixtures had a moderate risk except control and 40C where the risk is high.
As discussed earlier, the alumina content of an SCM plays an important role in the mechanism of suppressing chloride ions movement. Although the alumina content in both CFA and FFA was higher than that of GGF, the crystalline nature restrained the release of alumina into the paste. In contrast, the GGF is a highly amorphous material and the relatively high amount of alumina must have contributed to its superior performance in resisting chloride ingress.

**Rapid Migration Test (RMT) Results**

The chloride penetration resistance of the tested concrete mixtures was further examined by conducting the RMT test in accordance with NT Build 492. The non-steady state migration coefficient was calculated for each tested mixture using the simplified equation listed in the NT Build 492 standards. The results of this test are presented in Figure 6-9. The RMT results are highly correlated with the RCPT results with coefficient of determination of 0.93. The migration coefficient was highest for the control and 40C mixtures, which happened to also perform worst among other mixtures in RCPT, Followed by 20C and 40F in both tests. Whereas the GGF-based binary mixtures and the ternary blends of GGF and the fly ashes had the lowest migration coefficient. The correlation between RMT and surface resistivity values shown in Figure 6-8 was lower than that between RCPT and surface resistivity ($R^2 = 0.8$ compared to 0.91).
To compare the depth of chloride ingress for both RCPT and RMT test, all the tested samples were cut into halves after the test and the cut surface was sprayed by 0.1N silver nitrate. All the tested concrete discs are shown in Table 6-4. The depths obtained by both tests as shown are very comparable.
Table 6-4 Comparison between the tested RCPT and RMT samples for the depth of chloride penetration.

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>RCPT</th>
<th>RMT</th>
<th>Mix ID</th>
<th>RCPT</th>
<th>RMT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td><img src="image" alt="Control" /></td>
<td><img src="image" alt="Control" /></td>
<td>40F</td>
<td><img src="image" alt="40F" /></td>
<td><img src="image" alt="40F" /></td>
</tr>
<tr>
<td>20C</td>
<td><img src="image" alt="20C" /></td>
<td><img src="image" alt="20C" /></td>
<td>40G</td>
<td><img src="image" alt="40G" /></td>
<td><img src="image" alt="40G" /></td>
</tr>
<tr>
<td>20F</td>
<td><img src="image" alt="20F" /></td>
<td><img src="image" alt="20F" /></td>
<td>20C20G</td>
<td><img src="image" alt="20C20G" /></td>
<td><img src="image" alt="20C20G" /></td>
</tr>
<tr>
<td>20G</td>
<td><img src="image" alt="20G" /></td>
<td><img src="image" alt="20G" /></td>
<td>20F20G</td>
<td><img src="image" alt="20F20G" /></td>
<td><img src="image" alt="20F20G" /></td>
</tr>
<tr>
<td>40C</td>
<td><img src="image" alt="40C" /></td>
<td><img src="image" alt="40C" /></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Water Absorption and Sorptivity**

The CH produced during the cement hydration is soluble in water and it can leach out of concrete creating voids. These voids increase permeability and thus facilitate the ingress of chloride ions [6]. The pozzolanic activity therefore reduces the leaching of CH.
by turning it into C-S-H gel and ultimately reduces the permeability. In this study, the permeability of hardened concrete was investigated by conducting the water absorption test and the sorptivity test. Permeability has been shown to have a direct relationship with water absorption and sorptivity as they depend on factors such as capillary pores sizes and their continuity in the concrete matrix [33].

The results of sorptivity are shown in Figure 6-10. Overall, the results of RCPT and sorptivity are very weakly correlated. However, when the correlation is performed only for GGF-based binary mixtures, it yields a very high correlation with $R^2$ values of 0.98 for both the initial and secondary sorptivity. In contrast, both tested fly ashes had sorptivity results that are not in any way related to the RCPT results. For example, 40C performed worse than 40F in RCPT but in sorptivity it had a higher value than 40F. The reason might be the possibility of false negative results discussed earlier. In comparison with the correlation between RCPT results and initial and secondary sorptivity, it was found that the secondary sorptivity had a higher correlation than the initial sorptivity. Although some studies expected that the secondary sorptivity should not be taken as an indicator of concrete resistance to chloride penetration due to possible inaccuracy [29], the results in this study have shown stronger correlation with the secondary sorptivity than the initial one. A good correlation was also obtained in the study by Obla et al., 2014 [35] between the secondary absorption, RCPT, and RMT with chloride diffusion coefficient, while the initial absorption had a weak correlation, similar to this study with RCPT & RMT.
Figure 6-10 Sorptivity test results.

![Sorptivity test results](image)

Figure 6-11 Water absorption test results.

![Volume of Permeable pore space, %](image)

The porosity was assessed by carrying out water absorption test for which the results are shown in Figure 6-11. The test was conducted on concrete chunks at a later age of about 90 days. The volume of the permeable pore space was maximum for both FFA-based binary mixtures, with 40% being the highest. Although what would one expect in
this case is that the control mixture would have the maximum permeability, but the test indicated otherwise. This also another reason that supports that the FFA used in this study is of a lower quality and has no tangible pozzolanic activity. Nevertheless, the 40G mixture had the lowest porosity because of the excellent pozzolanic activity and fineness of GGF which resulted in pore structure refinement. The other mixtures had porosity comparable to that of the control.

Conclusions

In comparing the performance of GGF with CFA and FFA, it is evident that the GGF superiorly outperformed the fly ashes in all the tested properties in this study. GGF has high pozzolanic reactivity as suggested by the SAI values obtained in this study and as other studies revealed [36]. The GGF-containing mixtures had higher early compressive strength even at high replacement ratio of 40%. The use of GGF to account for the shortcomings of fly ash performance in concrete is promising. The ternary blend of cement with GGF and either CFA or FFA has substantially enhanced the concrete strength and durability in terms of chloride ion permeability. In assessing the chloride penetration of concrete, both tested methods which were the Rapid Chloride Penetration Test (RCPT) and the Rapid Migration Test (RMT) have shown comparable results. The RCPT and RMT results were highly correlated with the surface resistivity of concrete samples.
References


Chapter 7

EXPERIMENTAL INVESTIGATION ON THE EFFECT OF USING A BLEND OF OFF-SPEC FLY ASH AND GROUND GLASS FIBERS ON THE MECHANICAL PROPERTIES AND DURABILITY OF CONCRETE

Abstract

Vast quantities of ashes produced by burning coal in power plants are disposed-off in long-term storage facilities known as storage ponds, and the stored ash is referred to as ponded ash. Ponded ash has negatively affected the environment in several instances, including groundwater contamination through leaching of hazardous heavy metals, which necessitates an immediate need to find beneficial applications for these ashes. Ponded ash often fails to meet the limit on the loss on ignition (LOI), which determines the content of unburnt carbon. A high LOI ash usually increases the water-demand and negatively impacts the durability of concrete, affecting mainly the quality and the quantity of air entrainment meant for freeze-thaw protection of concrete.

The objective of this study is to investigate the possibility of making beneficial use of ponded ash in ordinary Portland cement (OPC) and geopolymer concrete by blending it with another pozzolan that can alleviate its negative impacts. In this study, blends of high LOI fly ash with ground glass fibers (GGF) were investigated. For this purpose, the experimental work encompassed four stages — first, the characterization of the selected ponded ash for the chemical and mineralogical composition and physical properties. Second, investigation of the pozzolanic activity of the chosen ponded ash individually and in combination with GGF. Third, the evaluation of properties of fresh and hardened mortar and concrete with binary and ternary blends of cementitious materials in both OPC and geopolymer systems. The final step included testing the durability of OPC and geopolymer concrete, prepared using the optimum combinations from the previous stage,
against freeze-thaw durability, alkali-silica reaction (ASR), and rapid chloride permeability test (RCPT). The results from this study thus far prove the effectiveness of using GGF with high LOI fly ash to improve the performance of ponded ash in both OPC and geopolymer systems.

**Introduction**

Fly ash is a complex anthropogenic byproduct produced in significant abundance during the combustion of coal in thermal power plants. As global demand for energy increases, so too has coal combustion and the amount of fly ash produced. Proper disposal of fly ash is required to reduce the impact of this material on the environment. If fly ash is not properly remediated, it can pose a substantial environmental threat, contaminating soil and water while also disrupting ecosystems [1]. Although aggressive efforts are being made to find novel and sustainable methods for recycling and reusing fly ash, most of this byproduct is currently stored in ash ponds which include surface impoundments and landfills [2]. Unfortunately, these storage methods have proven to be unsustainable as various reports of pond leakage, malfunction, and subsequent adverse environmental impacts have been reported with increasing frequency [3].

The alarming environmental impacts of ash ponds has triggered the necessity of finding beneficial uses of the ponded ash. However, the qualities set by standards for fly ash to suit the use as supplementary cementitious material (SCM) in concrete has limited its usage in the construction industry. ASTM C618 stipulates certain physical and chemical requirements that fly ash must meet. One of the requirements that the ponded fly ash most likely fails to meet is unburnt carbon content represented by the loss on ignition (LOI) property.
In coal-based power plants, the boilers are run at reduced power during seasons of lower demand for energy to save on cost. But once demand increases, they are required to be placed back to full power operation. However, it takes a long time to raise the boilers' performance to full power and power plants always inject oil into the furnace to accelerate the process [4]. During this boosting process, the fly ash is produced with higher LOI. Also, high-rank types of coal, such as anthracite, are challenging to combust and result in higher LOI content [4], [5].

The ASTM C618-19 specification places a limit on LOI of 6% for fly ash to be suitable for concrete usage. A value of LOI up to 12% is allowed, as per the footnote mentioned in ASTM C618-19 under table 2, when satisfactory laboratory results are obtained using such fly ashes. As such, power plants that are not functional at full load year-round have ash ponds full of high LOI ashes awaiting proper disposal or beneficial usage.

The high LOI affects the water demand for concrete. An increase by 4% in LOI would require about 5% more of water to account for the slump reduction of concrete [6]. Which would affect the strength of concrete, pore sizes, and permeability. The high-LOI fly ash is also known to absorb the air-entraining agents (AEA) that are meant for providing resistance to freeze-thaw, which negatively impacts the air content in high-LOI FA-including concrete[5], [7]. The mechanism of how the AEA stabilizes the air bubbles in cement pastes is that the polymers of AEA have two ends with one being hydrophilic and the other hydrophobic. The hydrophilic ends stick to cement particles while the other ends stabilize the air bubbles around the cement particles. But when the carbon grains are present, and with their adsorptive nature, there are not enough AEA to stabilize the air bubbles [7]. Therefore, when using a high-LOI fly ash in concrete, higher AEA dosages are
required to provide the designed air content of the concrete mixture. However, high dosages of AEA affect concrete strength. for each 1% of AEA (usually measured as a ratio of cement mass), there is a 5% reduction in concrete strength [8].

It is imperative, therefore, to find ways to optimize and facilitate the use of the long-stored high LOI ponded ash into construction industry. For this purpose, this work suggests blending the high LOI fly ash with ground glass fibers (GGF) to reduce the effect of high LOI on the mechanical properties of concrete and enhance its durability. At the same time, this would encourage the industry to harvest the long-stored fly ashes in the ash ponds. The glass fiber industry has substantial amount of waste resulting from either being off the desired qualities or during processing the glass fibers filaments.

Previous Studies have utilized ponded ash and off-spec fly ashes as a replacement of fine aggregate [9], [10] or cement [10]–[12], for artificial aggregate production [13], for soil stabilization [14], [15], and for embankment [16]. Most of the properties that these off-spec fly ashes failed to meet in these studies were the LOI and the sulfate content. However, not much effort has been made to blend the off-spec fly ash with another industrial byproduct, especially the off-spec landfilled glass fibers.

The objectives of this study and the expected outcomes of blending off-spec fly ash and off-spec glass fibers are:

- Reduce the water demand of mortar and concrete that contain high LOI fly ash, and thus, it will increase the compressive strength and enhance concrete durability.
- It should neutralize the effect of high LOI on the air content of concrete and therefore, it should enhance the resistance of concrete to freezing and thawing.
- It will help reduce vast amounts of off-specification fly ash that has been stored for long time in ash ponds.
- Most importantly, reducing the environmental and social impacts of ash ponds and landfills and an opportunity of economic benefits.

**Experimental Program**

**Materials**

**Cement**

Two types of ordinary portland cements meeting ASTM C150 [17] were used in this study: A Type I/II ordinary portland cement (OPC) (Na_eq = 0.38%), and a Type I high alkali portland cement (Na_eq = 1%). The Type I/II OPC was used for most of the tests, while the high alkali cement was used only in tests related to ASR, i.e., the miniature concrete prism test (MCPT) (AASHTO T380). The chemical compositions and physical properties of portland cement are presented in Table 7-1.

**High LOI Fly Ash**

High-LOI fly ash was brought from a local ash pond in North Carolina. Throughout this study, the high LOI fly ash will be referred to by RFA. Full characterization for the physical and chemical properties was carried out for this fly ash. A summary of the physical properties and chemical composition is provided in Table 7-1. The chemical compositions of RFA by XRF in the majority are silica, alumina and iron oxides (SiO_2 + Al_2O_3 + Fe_2O_3) with 87.12% by mass. Also, Figure 7-7-1 provides an SEM images of RFA showing different sizes of rough-surface spherical particles as well as dark irregular particles for the unburnt carbon. While Figure 7-2 (b) shows the X-Ray Diffraction (XRD) analysis for the RFA. The main mineralogical constituents are quartz, mullite, and hematite. After quantitively identifying the crystalline phases of the RFA, an amorphous
content of about 70% has been estimated. This amorphous structure would help facilitate the pozzolanic activity of the RFA. The particle size distribution of RFA has been analyzed by Laser Diffraction and the results are represented in Figure 7-3. It should be noted that only the fly ash portion of the as-received ash was used in this study by employing only the particles that are finer than 75 microns. The ponded ash was first dried at 110 °C for at least 24 hours, then sieved on standard sieve No. 200. The PSD of the as-received ponded ash showed that about 70% of the total particles are finer than 75 microns. The average particle size of RFA is 44 microns.

Ground Glass Fibers (GGF)

The Ground Glass Fiber (GGF) used in this study had an average particle size of 4 microns. The chemical composition and physical properties of GGF are presented in Table 7-1. Morphological characteristics of GGF are shown in a scanning electron microscopy (SEM) image provided in Figure 7-7-1d. The GGF particles are angular with fine texture, with Blaine’s fineness of 701.2 m²/kg. It is worth mentioning that there has been a new standard for the use of GGF as pozzolan, which is ASTM C1866 [18]; Standard Specification for Ground-Glass Pozzolan for Use in Concrete. The ground glass fiber (GGF), explored in this study, is what ASTM refers to as type GE.
Figure 7-1 SEM image for (a), (b), and (c) RFA at different magnification levels, d) GGF

Figure 7-2 XRD Analysis for a) GGF b) RFA
Figure 7-3 Particle size distribution of RFA in both original state and sieved state, and GGF.

**Fine Aggregate (Siliceous Sand)**

A non-reactive siliceous natural river sand from Glasscock Co. in Sumter, SC with an oven-dry specific gravity of 2.63, an absorption ratio of 0.35%, and a fineness modulus of 2.6 was used in this study.

**Reactive Coarse Aggregate**

Highly reactive rhyolitic aggregate, Las Placitas gravel from New Mexico (NM), was used for testing ASR. The specific gravity and percent absorption of this aggregate were 2.6 and 1%, respectively. This aggregate was either pulverized to be used as a fine aggregate graded as per ASTM C1260 [19] and ASTM C1567 [20] or crushed to be used as a coarse aggregate graded as per AASHTO T380 [21].
Table 7-1. Chemical composition and physical properties for the materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific Gravity</th>
<th>LOI</th>
<th>Average Particle size, µ</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>SO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>3.15</td>
<td>2.6%</td>
<td>17</td>
<td>19.93</td>
<td>4.77</td>
<td>3.13</td>
<td>62.27</td>
<td>2.70</td>
<td>0.06</td>
<td>0.48</td>
<td>3.23</td>
</tr>
<tr>
<td>RFA</td>
<td>2.50</td>
<td>20.54%</td>
<td>44</td>
<td>48.33</td>
<td>24.93</td>
<td>13.86</td>
<td>3.51</td>
<td>1.36</td>
<td>0.15</td>
<td>1.87</td>
<td>4.52</td>
</tr>
<tr>
<td>GGF</td>
<td>2.60</td>
<td>1.0%</td>
<td>4</td>
<td>56.50</td>
<td>12.48</td>
<td>0.37</td>
<td>22.06</td>
<td>2.60</td>
<td>0.75</td>
<td>0.10</td>
<td>0.03</td>
</tr>
</tbody>
</table>

**Mixture Proportion**

For the cementitious mixtures, different combinations of RFA and GGF were used to replace from 20% to 50% at 10% increments, of cement by mass. The mixtures employed in this study can be divided into three categories: first, binary mixtures based on cement and RFA, second, binary mixtures based on cement and GGF, and finally, ternary mixtures based on cement, RFA, and GGF. The mixture proportions of the mortar mixtures followed the requirements for each test method. The mixture proportion and the test methods employed in this study are shown in Table 7-2.

As for the geopolymer mixtures, the RFA was blended with GGF in 10% increments up to 50%. The blend was activated using sodium hydroxide solution and the mixtures were designed to have Na₂O concentration in the activator to binder ratio of 10% based on a previous study in which this ratio was found to be optimal [22]. The geopolymer paste volume to the total volume of the geopolymer mortar was maintained at 45%. The water to binder ratio was 40% for all the mixtures. It should be noted that trial mixtures were carried out first in which a combination of NaOH solution and 40% sodium silicate solution were used to activate the blends of RFA and GGF. However, all the trial mixtures resulted in a very sticky mortar that was so difficult to work with and cast into the molds. Therefore, it was decided to use only NaOH solution. Table 7-3 shows the geopolymer mixtures with the design parameters and the results for casting 6 of 2 in. mortar cubes. All
the cast geopolymer mortar cubes were placed in an air-tight container after casting and cured for 24 hours at 60 °C. The purpose of this part of the work was only to investigate the possibility of producing geopolymer mortar with good fresh properties and compressive strength, but they were not tested further for durability.

Table 7-2. Mixture proportions and test methods.

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>Control</th>
<th>20R00G</th>
<th>10R10G</th>
<th>00R20G</th>
<th>30R00G</th>
<th>15R15G</th>
<th>00R30G</th>
<th>40R00G</th>
<th>20R20G</th>
<th>00R40G</th>
<th>30R30G</th>
<th>25R25G</th>
<th>00R50G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>100</td>
<td>80</td>
<td>80</td>
<td>70</td>
<td>70</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>GGF</td>
<td>0</td>
<td>0</td>
<td>10</td>
<td>20</td>
<td>15</td>
<td>30</td>
<td>0</td>
<td>20</td>
<td>40</td>
<td>0</td>
<td>25</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>RFA</td>
<td>0</td>
<td>20</td>
<td>10</td>
<td>0</td>
<td>30</td>
<td>15</td>
<td>0</td>
<td>40</td>
<td>20</td>
<td>0</td>
<td>50</td>
<td>25</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Test methods performed and the followed standards</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isothermal Calorimetry ASTM C1679 &amp; ASTM C1702</td>
</tr>
<tr>
<td>Setting Time ASTM C191</td>
</tr>
<tr>
<td>TGA</td>
</tr>
<tr>
<td>Flow test ASTM C1437</td>
</tr>
<tr>
<td>Water Demand ASTM C311</td>
</tr>
<tr>
<td>SAI ASTM C311</td>
</tr>
<tr>
<td>Drying Shrinkage ASTM C596</td>
</tr>
<tr>
<td>AMBT ASTM C1260 &amp; C1567</td>
</tr>
<tr>
<td>MCPT AASHTO T380</td>
</tr>
<tr>
<td>Foam Index Test</td>
</tr>
<tr>
<td>Compressive Strength</td>
</tr>
<tr>
<td>Freezing and Thawing</td>
</tr>
</tbody>
</table>

√, ×: The corresponding mixture was, or was not, tested for the corresponding test.
√* the corresponding mixtures were tested with and without AEA.
Table 7-3 geopolymer mixtures proportions.

<table>
<thead>
<tr>
<th>Label</th>
<th>100R00G</th>
<th>90R10G</th>
<th>80R20G</th>
<th>70R30G</th>
<th>60R40G</th>
<th>50R50G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na2O/binder%</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Water/binder%</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Filler %</td>
<td>55</td>
<td>55</td>
<td>55</td>
<td>55</td>
<td>55</td>
<td>55</td>
</tr>
<tr>
<td>Sand, g</td>
<td>1200</td>
<td>1200</td>
<td>1200</td>
<td>1200</td>
<td>1200</td>
<td>1200</td>
</tr>
<tr>
<td>RFA</td>
<td>440</td>
<td>396</td>
<td>352</td>
<td>308</td>
<td>264</td>
<td>220</td>
</tr>
<tr>
<td>GGF</td>
<td>0</td>
<td>44</td>
<td>88</td>
<td>132</td>
<td>176</td>
<td>220</td>
</tr>
<tr>
<td>Water, g</td>
<td>176</td>
<td>176</td>
<td>176</td>
<td>176</td>
<td>176</td>
<td>176</td>
</tr>
<tr>
<td>NaOH pellets, g</td>
<td>57</td>
<td>57</td>
<td>57</td>
<td>57</td>
<td>57</td>
<td>57</td>
</tr>
</tbody>
</table>

**Test Methods**

**Isothermal Calorimetry**

In this study, Calmetrix iCal HPC 4000 isothermal calorimeter was used to evaluate the heat evolution in mixtures with 20% and 40% replacements of binary and ternary blends of RFA and GGF and compare it with that of OPC control mixture. The instrument was calibrated using a standard Portland cement sample of known heat evolution. The cement, water, and SCMs were preconditioned to 23 °C and hand-mixed in a plastic vial (150 mL), using water to cementitious materials ratio of 0.40, and placed in the calorimeter for the analysis. All the measurements were carried out at 23 °C.

**Thermo Gravimetric Analysis (TGA)**

In order to investigate the pozzolanic reactivity of the binary and ternary blends of GGF and RFA with OPC, the thermogravimetric analysis (TGA) was conducted on the four mixtures shown in Table 7-2 (at 20% replacement). At the age of 7 days and 28 days, the hardened paste samples were crushed and manually ground using mortar and pestle to a fineness of less than 177µm (No. 80 standard sieve). The calcium hydroxide (CH) content in the samples was estimated by measuring the weight loss that occurred between 400 °C and 500 °C, at which the decomposition of CH (Ca(OH)₂ → CaO + H₂O) occurs, and
between 600 °C to 800 °C, at which calcium carbonate (CaCO₃) decomposes to CaO and
CO₂ [39]. TGA test was performed using a TA instrument, Q5000, in a platinum crucible
heated up to 1000 °C. Approximately 50 mg of powdered hardened paste samples, with
hydration stopped using solvent exchange methods (i.e. diethyl ether and isopropyl
alcohol), was loaded in the crucible and analyzed at a temperature ramp of 10 °C/min with
nitrogen gas purge of 30 ml /min. While TGA was only carried out for the control mixture
and at 20% replacement of binary and ternary mixtures of RFA and GGF, the pozzolanic
activity of all the mixtures was tested by the strength activity index test.

**Strength Activity Index (SAI)**

In this study, the strength activity index (SAI) values were determined for all the
mix proportions according to ASTM C311 [24]. The purpose of this test was to further
check the pozzolanic activity of the blend of RFA and GGF and compare it with that of the
control and the binary mixtures. The control mixture, as per ASTM C311, consisted of 500
g cement, 1375 g sand, and 242 g water, while the test mixtures, shown in Table 7-2, had
the same amount of cement and sand but just enough water to produce a flow equal to that
of control ± 5%. The SAI values were determined at the ages of 7 and 28 days, during which
mortar cubes were cured in saturated lime water in a standard moist room. ASTM C311
requires SAI values of 75% or higher at both 7 and 28 days as the accepted criteria for the
suitability of using the fly ash as an SCM. Mixtures that failed to pass this test were
excluded from any further testing.

**Setting Time**

To investigate the effect of the binary and ternary blends of RFA and GGF on the
setting time of the cementitious paste, the setting time was measured for the control and
the 20% replacement mixtures, as shown in Table 7-2. The test was performed using Vicat
needle apparatus and following ASTM C191 [25] procedures. However, the setting time was not measured for mixtures at normal consistency. Instead, w/b ratio of 0.4 was used exactly as the paste samples that were tested for isothermal calorimetry and TGA.

**Flow Behavior**

The flowability of each mixture was measured and compared with that of the control mixture. In addition, the results of flowability tests that were performed on mortar mixtures during the strength activity index test were used to determine the water requirement of each mixture. The flow was measured following ASTM C1437 [26], and the water requirement was determined according to ASTM C311 [24].

**Drying Shrinkage**

Incorporating GGF with the fly ash in replacing the OPC, as suggested in this work, increases the fineness of the total cementitious materials. Drying Shrinkage is the largest part of the total shrinkage, and it is the main trigger of cracks in concrete [27]. In order to evaluate the drying shrinkage behavior of the binary and ternary RFA and GGF mixtures, mortar bars were prepared and cured according to ASTM C596 [28]. The mixtures, which had a total of 750 g of binder and 1500 g of sand, were designed to achieve similar flow of 110 ± 5 % as per ASTM C596. Length change measurements of mortar bars were taken over a 60-day period, during which the mortar bars were kept at 23 °C and 50% relative humidity. It is worth mentioning that the ASTM C618 optionally specifies a maximum difference in shrinkage at 28 days of 0.03% from control.

**Resistance to Alkali-Silica Reaction (ASR)**

**Accelerated Mortar Bar Test (AMBT)**

Accelerated mortar bar tests (AMBT) (ASTM C1260 [19] and C1567 [20]) were conducted to evaluate the effectiveness of the tested blends of GGF and RFA to suppress
ASR-induced expansion. In this investigation, rhyolitic gravel from Las Placitas gravel pit was employed as the reactive aggregate. The test was performed for all tested mixtures listed in Table 7-2.

In each test, four 1 in. × 1 in. × 11.25 in. (25 × 25 × 285-mm) mortar bars were cast with an embedded stainless-steel gage stud at each end of the mortar bar. After demolding, the specimens were kept in water at 80 °C for 24 hours, and then they were placed in 1 N NaOH solution at 80 °C as per the specification. Length change of the mortar bars was measured at periodic intervals over a test duration of 28 days. The specification requires a mortar bar expansion of less than 0.10 % at 14 days of exposure in 1N NaOH solution for the tested SCM dosage to be considered as an effective ASR mitigation.

**Miniature Concrete Prism Test (MCPT)**

AMBT test was conducted on mortar samples. However, to investigate the effectiveness of the binary and ternary blends in mitigating ASR in concrete, AASHTO T380 [21] Miniature Concrete Prism Test (MCPT) was also conducted. Although there is a well-known and more reliable method to test ASR, which is ASTM C1293 [29], it takes two years to check ASR mitigation, whereas in MCPT, it only takes up to 84 days. Also, studies have shown a good correlation between both MCPT and ASTM C1293 for a variety of reactive aggregate [30], [31].

In this test, three 2 in. x 2 in. x 11.25 in. (50 × 50 × 285-mm) concrete prisms are cast using a high alkali cement (0.9±0.1% Na₂Oeq.) with additional boosting of alkalis to 1.25% Na₂Oeq. by mass of cement, with either a reactive fine and non-reactive coarse aggregate or contrariwise, depending on which reactive aggregate is being evaluated. Once prisms are cast, they are cured for 24 hours in a fog room at 23 °C before demolding the next day. For the next 24 hours, the demolded prisms are soaked in water at a 60 °C before
placing them in a 60 °C 1N NaOH solution. Length change measurements are observed periodically up to 56 or 84 days, depending on the level of expansion detected in the prisms. When mitigation measures are to be evaluated, the Portland cement is replaced with SCM, and the alkali content of the mix is boosted to 1.25% by mass of Portland cement. AASHTO T380 specifies a level of expansion of less than 0.020% at 56 days for the tested proportion to be considered as effective in ASR mitigation.

In this study, a non-reactive quartz fine aggregate was used along with a reactive coarse aggregate - graded per AASHTO T380 [21]- in preparing the samples. The test was performed on four mixtures, as listed in Table 7-2. After demolding, the samples were conditioned as per the test method and stored in a sealed plastic container. The plastic container was placed in a water bath adjusted to a temperature of 60 °C for the remainder of the test duration.

**Foam Index Test**

To evaluate the effect of the high-LOI fly ash on the air entraining agent (AEA) performance, the foam index test was conducted. In this test, a known concentration of AEA is added to the slurry of cement and fly ash that is placed in a plastic bottle in similar amounts of drops with known volume. After that, the bottle is shaken for the same period for all mixtures. Once the shaking is stopped, the foam formed on the surface of the paste is observed for whether it covers the whole surface and can persist for some time on the surface. If the foam was not stable, the procedure is repeated by adding more drops of AEA solution, until a “stable” foam layer stays for 15 seconds or more. Once a stable foam layer is achieved, the total number of the added AEA solution is recorded.

According to the recommendations set by Harris et al., 2008, [32], the following test criteria were used:
- the bottle shake method was chosen, a 5 cm diameter and 10 cm tall (200 ml) plastic bottle with a screw-on lid was used.
- Volume of tested paste was 100 ml with w/c = 2.0 and SCM/c = 0.2
- Air Entraining Agent (AEA) used was Sika-AEA-14 with concentration between 5 and 10%.
- Each drop was 0.15 ml of AEA.
- Test Procedures: 45 second initial shaking, add 5 drops, followed by 10 seconds shaking with 4 shakes per second, followed by 30 second rest period. Observe the formed foam and repeat until stable foam achieved.

Results and Discussion

Hydration Kinetics

Figure 7-4 (a) and (b) show the heat flow and heat release of systems with different blends of RFA and GGF namely Control, 20R00G, 10R10G, 00R20G, 20R20G, and 00R40G. The initial thermal power of 00R40G was much higher than the control which can be explained by the high surface area of GGF and probably because there is higher amount of water available for cement for the initial reactions. According to ASTM C1679, the time taken to reach half of the maximum power in the main hydration peak can be taken as the setting time. The results show that this duration is 5.43h for control, 5.35h, 5.40h, 5.22h, 5.04h, and 4.88h for 20R00G, 10R10G, 00R20G, 20R20G, and 00R40G, respectively. Based on these values, there was no significant effect of the ternary RFA+GGF mixture (10R10G) on the setting period as compared to control, whereas it was reduced for the ternary blended mixture at 40% replacement. The heat release curve indicates that the control produced the highest amount of heat at 334 J per each gram of
binder, followed by 00R20G at 275 J/g, 10R10G at 271 J/g, 262 J/g for 20R00G, and about 230 J/g of heat for both 00R40G and 20R20G.

Figure 7-4 a) Heat flow; and b) Heat release curves (w/c = 0.40) @ 23 °C.

**Pozzolanic Activity by TGA**

The TGA curves at 7 and 28 days and the ratio of CH content in the test mixtures relative to that of the control mixture are shown in Figure 7-5 a, b, and c, respectively. As a result of replacing 20% and 40% of cement with the RFA and GGF, it can be assumed that pozzolanic activity is established if the ratio of CH\textsubscript{test}/CH\textsubscript{control}, shown in Figure 7-7-5c, is less than 80% and 60%, correspondingly. The results evidently indicate a consumption
of CH by SCM to produce C-S-H gel because its content for all the tested mixtures was reduced compared to the CH content of control. Expectedly, a lesser CH content was determined at the age of 28 days than that of 7 days, proving the pozzolanic activity of the tested SCM. The tested mixtures can be arranged in a descending order by the CH content as Control, 20R00G, 10R10G, 00R20G, 20R20G, and 00R40G at 28 days. To compare the performance of the two tested SCM in binary in ternary mixtures, the CH content was reduced by 9.5% in 00R20G compared to 20R00G, while the ternary mixture of 10R10G had about 5% reduction in CH content relative to the binary 20R00G. This suggests that the inclusion of GGF with the high LOI fly ash is clearly beneficial.

It should be noted that when OPC is replaced by SCM, the amount of water available to react with OPC is higher at the same w/b ratio. Therefore, higher amounts of CH could be produced and react with the replacing SCM. Also, the use of finer SCMs such as GGF can act as nucleating agents for accelerated reaction of OPC. These two phenomena are the likely reasons to explain the higher ratio of CH_{test}/CH_{control} above the corresponding dilution lines for some of the GGF-containing mixtures, especially at 40% replacement at early age of 7 days. The pozzolanic activity is further evaluated by measuring the strength activity index.
Strength Activity Index (SAI)

The results of the SAI test are shown in Table 7-4. All tested mixtures, except the binary mixtures of 40R00G and 50R00G, passed the minimum SAI of 75%, specified by ASTM C618 [33]. In addition, all the binary GGF-containing mixtures highly passed the minimum SAI requirements of ASTM C1866 for type GE pozzolan, which is 85%. Moreover, all the ternary mixtures achieved a 28-day SAI values of more than 90%, which was significantly better than that of binary RFA-based mixtures. Both the fineness of the GGF and the amorphous structure most likely helped improve the pozzolanic reaction. Likewise, since the particle size of GGF is smaller than that of fly ash, they provided a better packing of the particles, which may suggest a filling effect and could impact the SAI test results. However, the TGA results showed a high consumption of CH at 28 days for 00R40G, which had the highest content of GGF among the mixtures tested for TGA. Therefore, the pozzolanic activity of the GGF and RFA in the ternary mixtures increased the strength, which clearly is reflected on the SAI values.
Table 7-4 Fresh and hardened mortar test results.

<table>
<thead>
<tr>
<th>Tested Property</th>
<th>Control</th>
<th>20R00G</th>
<th>10R10G</th>
<th>00R20G</th>
<th>30R00G</th>
<th>15R15G</th>
<th>00R30G</th>
<th>40R00G</th>
<th>20R20G</th>
<th>00R40G</th>
<th>50R00G</th>
<th>25R25G</th>
<th>00R50G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow, % (at a constant w/b = 0.485)</td>
<td>126</td>
<td>110</td>
<td>117</td>
<td>124</td>
<td>96</td>
<td>115</td>
<td>125</td>
<td>100</td>
<td>128</td>
<td>116</td>
<td>89</td>
<td>103</td>
<td>120</td>
</tr>
<tr>
<td>Water requirements, % to achieve same flow as control</td>
<td>100</td>
<td>112.07</td>
<td>107.76</td>
<td>99.14</td>
<td>116.38</td>
<td>107.76</td>
<td>101.72</td>
<td>116.38</td>
<td>112.07</td>
<td>103.45</td>
<td>120.69</td>
<td>112.07</td>
<td>106.03</td>
</tr>
<tr>
<td>7-Day SAI (%)</td>
<td>100</td>
<td>96.93</td>
<td>102.6</td>
<td>117.97</td>
<td>73.76</td>
<td>94.09</td>
<td>102.13</td>
<td>61.7</td>
<td>75.65</td>
<td>104.49</td>
<td>43.97</td>
<td>71.16</td>
<td>88.18</td>
</tr>
<tr>
<td>28-Day SAI (%)</td>
<td>100</td>
<td>94.94</td>
<td>107.75</td>
<td>117.79</td>
<td>84.64</td>
<td>106.74</td>
<td>114.61</td>
<td>69.29</td>
<td>95.88</td>
<td>118.16</td>
<td>52.81</td>
<td>94.57</td>
<td>102.25</td>
</tr>
<tr>
<td>7-Day Mortar Compressive Strength, psi</td>
<td>5620</td>
<td>4550</td>
<td>5020</td>
<td>5540</td>
<td>3740</td>
<td>4880</td>
<td>5320</td>
<td>3310</td>
<td>2570</td>
<td>5240</td>
<td>2570</td>
<td>3490</td>
<td>5070</td>
</tr>
<tr>
<td>28-Day Mortar Compressive Strength, psi</td>
<td>5920</td>
<td>6790</td>
<td>7690</td>
<td>7210</td>
<td>5220</td>
<td>7230</td>
<td>7290</td>
<td>4950</td>
<td>4490</td>
<td>7030</td>
<td>3880</td>
<td>5440</td>
<td>6640</td>
</tr>
<tr>
<td>56-Day Mortar Compressive Strength, psi</td>
<td>6680</td>
<td>7600</td>
<td>8110</td>
<td>7550</td>
<td>5370</td>
<td>7680</td>
<td>7770</td>
<td>5490</td>
<td>5270</td>
<td>8940</td>
<td>4330</td>
<td>6320</td>
<td>7680</td>
</tr>
</tbody>
</table>

a) RFA Binary Mixtures Compressive Strength Results

b) GGF Binary Mixtures Compressive Strength Results
The Compressive Strength of Geopolymer Mortar

The results of compressive strength of geopolymer mortar based on combinations of RFA and GGF activated by NaOH solution and heat cured at 60 °C for 24 hours are shown in Table 7-5. As it can be clearly observed, the strength increased with the increase of GGF in the mixture. Additionally, the early-age strength of the heat cured geopolymer improved as the GGF content increased. The compressive strength was better as GGF dosages of 40% or more of the total binder mass. Also, there was no significant increase between the 7- and 90-day strength for the last two mixtures shown in Table 7-5, meaning higher degree of reaction was observed as higher amount of GGF is introduced.

Table 7-5 Compressive Strength of RFA+GGF-based Geopolymer

<table>
<thead>
<tr>
<th>Mix Label</th>
<th>7-Day strength, psi</th>
<th>28-day strength, psi</th>
<th>90-day strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>100R00G</td>
<td>330</td>
<td>440</td>
<td>1330</td>
</tr>
<tr>
<td>90R10G</td>
<td>1230</td>
<td>1630</td>
<td>2200</td>
</tr>
<tr>
<td>80R20G</td>
<td>1820</td>
<td>2390</td>
<td>2590</td>
</tr>
<tr>
<td>70R30G</td>
<td>3400</td>
<td>2920</td>
<td>3230</td>
</tr>
<tr>
<td>60R40G</td>
<td>5300</td>
<td>5350</td>
<td>5600</td>
</tr>
<tr>
<td>50R50G</td>
<td>6250</td>
<td>6330</td>
<td>6730</td>
</tr>
</tbody>
</table>

The inclusion of GGF into the RFA mixtures negated the need for the use of SS and accelerated the geopolymerization reaction. The improvements of RFA geopolymer when
the GGF was blended in the binder is most likely attributed to the particles size and the amorphous structure of GGF. The particle size is essential for the source material of geopolymer and GGF having very fine particles enhanced the performance of the total blend. The dissolution rate of Si and Al is faster in GGF because of the amorphous structure, which makes up for soluble Si from SS solution. Additionally, the GGF particles being solid, angular, and strong, the unfixed GGF particles in geopolymer matrix may have behaved as reinforcement to the mortar, which added to the compressive strength. It is worth mentioning that the mixture of 50R50G initially was selected for additional investigation for mortar and concrete durability, but the circumstances surrounding the spread of the pandemic prevented the continuation of this work.

**Setting Time**

The results of setting time of the six tested mixtures are shown in Table 7-5. As it can clearly be observed, the RFA binary mixture (20R00G) had the longest initial setting times, about 8% longer than the control. Whereas the GGF binary mixture (00R40G) had the shortest setting times. The inclusion of GGF in the ternary mixture (10R10G) had slightly shortened the initial setting times compared to 20R00G.

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>Vicat Apparatus Initial, mins</th>
<th>Final, mins</th>
<th>Isothermal Calorimetry-Based setting time, mins</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>240</td>
<td>375</td>
<td>325</td>
</tr>
<tr>
<td>20R00G</td>
<td>260</td>
<td>385</td>
<td>320</td>
</tr>
<tr>
<td>10R10G</td>
<td>255</td>
<td>385</td>
<td>325</td>
</tr>
<tr>
<td>00R20G</td>
<td>250</td>
<td>375</td>
<td>313</td>
</tr>
<tr>
<td>20R20G</td>
<td>245</td>
<td>370</td>
<td>302</td>
</tr>
<tr>
<td>00R40G</td>
<td>235</td>
<td>355</td>
<td>292</td>
</tr>
</tbody>
</table>

Table 7-6 Setting Times of RFA+GGF Binary and Ternary Mixtures.
as it was mentioned, according to ASTM C1679, the time taken to reach half of the maximum power in the main hydration peak can be taken as the setting time. The measured setting times by Vicat needle and the values obtained by running the isothermal calorimetry test showed good correlation.

**Flow Behavior**

The water requirement of each mixture to achieve a similar flow as the control mixture is shown in Table 7-4. Also, the flow values for the mixtures with a constant w/b ratio (0.485) are reported in the same table. For the GGF-based binary mixtures, it is evident that 40% and 50% GGF mixture required relatively higher amount of water than control mixture to get the same flow as a direct result of the finer particles and the higher specific surface area of GGF. However, the water requirements were about the same as control for 20% and 30% GGF. The trends observed in the flow test are consistent with those of water requirement, similar flow at lower replacement ratios and lower flow as the GGF content increases. Whereas for the RFA-based binary mixtures, and as expected, the water requirements are much higher as a result of the high LOI present in the fly ash. Once GGF was included in the ternary mixtures, the flow and the water requirements were enhanced significantly, which can be again attributed to the fineness and the smooth surface texture of GGF.

**Foam Index Test**

The foam index for each tested combination is shown in Figure 7-7. As it can be seen, the general tendency of an increase in foam index with increasing LOI stands, as the 20R00G resulted in exactly double the dosage for the Control mixture. However, once GGF is introduced into the mix, the required AEA dosage for stable foam on the surface of the paste dropped to almost similar amount to that of the control mixture. It is known that
the use of high dosage of AEA negatively affects the strength and durability of concrete. Therefore, the use of the RFA alone even at low replacement ratio is not recommended in application where AEA admixtures are to be used.

**Figure 7-7 Foam index test results.**

![Foam index test results](image)

**Drying Shrinkage of Cement Mortar**

The performance of the tested mixtures in terms of drying shrinkage is illustrated in Figure 7-8. At an early age all the tested mixtures had higher shrinkage than the control except those with high amount of RFA, namely 40R00G, 50R00G, and 25R25G. At the end of the test period, all tested mixtures had higher drying shrinkage than that of the control except the binary 00R20G mixture that had a slightly lower shrinkage than control.

The drying shrinkage of the tested mixtures relative to that of the control at the end of the test period (60 days) is shown in Figure 7-7-8b. as it can be seen, the performance of the GGF-binary mixtures highly outperformed the binary RFA mixtures and the ternary blended mixtures. Additionally, the figure shows slight improvement in drying shrinkage when the GGF included in the ternary mixtures as compared to the
binary RFA mixtures. This improvement is more apparent at higher cement replacement ratio.

The higher fineness of GGF could have possibly led to a higher drying shrinkage as compared with the other tested mixtures. According to Hu et al. [34], the higher the w/b ratio, the larger the pore diameter and hence the moisture loss and drying shrinkage. However, the GGF-containing mixtures had less shrinkage and that could be attributed to the lack of micro-reinforcement within the paste structure in the RFA binary mixtures. As shown in Figure 7-1, GGF particles are irregular particles and they were proved to be dense solid particles. It is likely that a portion of GGF particles remains unreacted in the paste; thus, acting as micro-aggregates and stiffening the paste. However, some fly ash particles tend to be hollow (cenospheres) and hence may not be able to act as micro-aggregates. Finally, the denser packing of the particles and the pozzolanic effect most likely have refined the pore structure and reduced the shrinkage [34].

![Drying Shrinkage of All Mixtures](image)
Fresh Properties and Compressive Strength of Concrete Mixtures

The fresh properties and compressive strength of the cement concrete mixtures for both non-air entrained concrete and air-entrained (starred) are presented in Table 7-6 and Figure 7-9, respectively. As expected, the use of RFA at 20% cement replacement ratio reduced the workability of concrete because of the absorption nature of RFA. However, the inclusion of GGF improved the performance and resulted in higher slump. The AEA dosage amounts were based on the foam index test results relative to the dosage that was added to the control mixture. The amount of AEA that was added to the control mixture was just enough to provide about 6% of air content, which is a typical value for concrete to resist mild to severe exposure to freezing and thawing cycles. As it can clearly be seen, basing the AEA dosages on the results of the foam index test did not provide the targeted air content for the mixtures containing RFA. For 20R00G, the air content of the non-AE concrete was reduced to less than half of that of the control, whereas there was no difference in the air content of 00R20G compared with the control. For the AE-concrete...
mixtures, the air content was still very low for 20R00G despite the AEA dosage that was added. It should be noted that the AEA dosage that was added to 20R00G exceeded the maximum recommended dosage and yet it did not provide adequate air content.

As for the compressive strength results, the binary GGF mixture outperformed the binary RFA mixture by 8.2% and 17.6% at 7 and 28 days, respectively. The double-action of pozzolanic activity of the reacted GGF particles and the microaggregate-like behavior of the unreacted GGF particles was the most likely reason for GGF performance's superiority. In fact, the 20R00G had even less strength than the Control at both ages, which is most likely attributed to the lower pozzolanic activity of RFA. The ternary mixture of 10R10G, however, had a middle performance between GGF and RFA binary mixture, which evidently suggests a synergetic effect of the inclusion of GGF into the mix on improving the strength. When comparing the non-AE concrete and the AE concrete, there was 6% and 4% reduction in the 7- and 28-day strength of 20R00G mixture because of the high AEA dosage that was added. However, both the control mixture and the 00R20G experienced even higher strength loss as it was more than 25% at both ages. The ternary mixture of 10R10G had a reduction of 20% and 10.8% in strength at 7 and 28 days, respectively after adding the AEA dosage.

Table 7-7 Fresh Properties of Cement Concrete Mixtures.

<table>
<thead>
<tr>
<th>label</th>
<th>Non-Air Entrained Concrete</th>
<th>Air Entrained Concrete</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Slump, in</td>
<td>UW, kg/m³</td>
</tr>
<tr>
<td>Control</td>
<td>6.75</td>
<td>16651</td>
</tr>
<tr>
<td>20R00G</td>
<td>6.5</td>
<td>16786</td>
</tr>
<tr>
<td>10R10G</td>
<td>7.5</td>
<td>16686</td>
</tr>
<tr>
<td>00R20G</td>
<td>7.75</td>
<td>16558</td>
</tr>
</tbody>
</table>
Figure 7-9 Compressive strength of concrete mixtures.

**ASR Test Results**

**Accelerated Mortar Bar Test (AMBT)**

The AMBT expansion results for all the tested mixtures are shown in Figure 7-10. The expansion of the control mixture was 0.90% at 14 days, supporting the previously determined expansion using the same reactive aggregate and mixture materials [35]. Both mixtures of 20R00G and 10R10G failed the test having had a higher 14-day expansion than the ASTM expansion limit of 0.1% at 14 days of exposure to the NaOH solution. However, even when as little as 10% GGF was added (10G30C), the 14-day expansion reduced to well below the 0.10% limit. Increasingly better performance was observed for all the GGF-containing mixtures even at the lowest tested replacement ratio of 20% which confirms the results obtained by Rashidian-Dezfouli and Rangaraju [35]. Finally, the AMBT bars were visually inspected after the end of the test; there were no significant cracks in any of the GGF-containing mixtures, whereas the control mixture was severely cracked.
The better performance of GGF-containing mixtures can be ascribed to the pozzolanic reactivity of the combined blend of GGF and RFA, which was supported by the SAI values shown in Table 7-3. As more CH is consumed, the pore solution has a lesser amount of free Ca++ ions, and thus, the ASR gel is less expansive. Additionally, as more C-S-H gel is produced due to the pozzolanic reaction, the alkalinity level of pore solution would likely drop to a level at which the ASR reaction would be unsustainable. Moreover, since GGF was found to work very well in geopolymer mortar and concrete [22], it is possible that the unreacted GGF particles could have been alkaline activated, especially because of the elevated temperature used in the AMBT procedure. Further studies are needed to investigate the mechanism by which GGF suppresses ASR. Lastly, the better particle packing and denser microstructure for the blended mixtures must have also contributed to the better ASR mitigation performance.
Miniature Concrete Prism Test (MCPT)

The results of the MCPT expansions for the binary and ternary mixtures are shown in Figure 7-11a, b, and c. As can be seen, the MCPT results are in total agreement with the AMBT results except that the mixture of 10R10G had a lower expansion than the 56-day expansion limit imposed by AASHTO T380 which is 0.02% (the expansion was 0.0195%). Again, all the GGF-containing mixtures as shown in part b in the figure successfully mitigated ASR expansion. The AMBT expansions at 14 days and the MCPT expansions at 56 days, as shown in Figure 7-11d, are very well correlated.
Figure 7-11. ASR MCPT results, showing the expansion values at 56 days for a) RFA binary mixtures, b) GGF binary mixtures, c) RFA+GGF ternary mixtures, and d) Correlation between MCPT and AMBT test results.

**Resistance to Chloride Penetration**

The resistance to chloride ion penetration was assessed by conducting the rapid chloride penetration test (RCPT) and the rapid migration test (RMT). The results of both tests are presented in Table 7-7. The chloride ion permeability performance based on the RCPT test results was moderate, low and very low for the control, 20R00G, and both 10R10G and 00R20G, respectively. It is clearly advantageous to include the GGF into the binary RFA mixture as the total charge dropped by 51.5%. Also, the migration coefficient calculated by the RMT test was reduced by 72% for the ternary mixture compared with the binary RFA mixture. According to Zych, 2014, the resistance to chloride ion penetration based on the RMT results is considered unacceptable if the migration coefficient is more than $16 \times 10^{-12} \text{ m}^2/\text{s}$, acceptable if it was between $(8-16) \times 10^{-12} \text{ m}^2/\text{s}$, and good if it was between $(2-8) \times 10^{-12} \text{ m}^2/\text{s}$. Based on that, the performance was unacceptable of 20R00G, acceptable for the control, and good performance for both 10R10G and 00R20G. The correlation between the results of both tests is shown in Table 7-7. The possible reasons why the correlation was low is because the RCPT lacks accuracy when it is used to evaluate fly ash-based concrete mixtures. The RMT is considered more accurate than RCPT when concrete containing fly ash is being evaluated.

<table>
<thead>
<tr>
<th>Label</th>
<th>Total Charge, Coulombs</th>
<th>Chloride Ion Permeability</th>
<th>Avg. $D_{nsmr} \times 10^{12}$ m²/s</th>
<th>Correlation RCPT &amp; RMT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>3162</td>
<td>Moderate</td>
<td>15.59</td>
<td></td>
</tr>
<tr>
<td>20R00G</td>
<td>1682</td>
<td>Low</td>
<td>17.30</td>
<td></td>
</tr>
<tr>
<td>10R10G</td>
<td>816</td>
<td>Very Low</td>
<td>4.83</td>
<td></td>
</tr>
<tr>
<td>00R20G</td>
<td>460</td>
<td>Very Low</td>
<td>2.07</td>
<td>0.66</td>
</tr>
</tbody>
</table>
Conclusions

Based on the work conducted in this study on binary and ternary blends of GGF and RFA, the following conclusions can be drawn:

1- The combination of GGF and fly ash with high LOI resulted in better performance in both cementitious and geopolymer mortar as a result of the high pozzolanic activity of GGF and its fine particles and amorphous structure. Both fresh properties represented in flow of mortar and slump of concrete and the hardened properties represented in SAI and compressive strength of concrete are all improved.

2- The inclusion of GGF enhanced the pozzolanic activity of the ternary mixtures. In fact, the 40R00G did not pass the SAI test while when GGF was included in 20R20G the result improved and passed the minimum requirements. The TGA test results supported the SAI test results.

3- The drying shrinkage of the ternary blended RFA and GGF was not noticeably different than the binary RFA mixture, but the performance of GGF-based binary mixtures was the best in reducing drying shrinkage.

4- The combination of high LOI fly ash and GGF improved the performance of ASR mitigation even at a low dosage of GGF. The mixture 10R10G which had only 20% replacement of cement by the combined blend of RFA and GGF was able to fully mitigate ASR in MCPT test.

5- Based on the foam index test, the combined blend of 10R10G required less AEA to achieve the same air content in concrete than the binary RFA. This would help increase the resistance to freeze and thaw cycles and at the same time, it did not significantly affect the compressive strength adding smaller amounts of AEA. However, the use of the foam index test to predict the AEA required
for concrete containing high LOI fly ash is not accurate. The ternary blended mixture of RFA+GGF experienced a significant improvement in terms of air content as compared with the binary RFA mixture.

6- Based on the evaluation of chloride ion penetration resistance, the binary fly ash mixture of 20R00G had an unacceptable performance. However, the performance substantially improved with the inclusion of GGF.

Finally, this study helps reduce the environmental burdens of the ash that has long stored in ash ponds and promotes its use in concrete to reduce the cement and the associated carbon emissions.

References


[22] H. Rashidian-Dezfouli and P. R. Rangaraju, “Comparison of strength and durability characteristics of a geopolymer produced from fly ash, ground glass fiber and glass


[35] H. Rashidian-Dezfouli and P. R. Rangaraju, “Role of Ground Glass Fiber as a Pozzolan in Portland Cement Concrete,” *Transportation Research Record: Journal of the*
Chapter 8

EVALUATION OF GEOPOLYMER MORTAR BASED ON A BLEND OF PONDED FLY ASH AND GROUND GLASS FIBERS ACTIVATED BY A SODIUM SILICATE-FREE ACTIVATOR

Abstract

Geopolymer-based binders have gained extensive attention in the last two decades as a sustainable alternative to Ordinary Portland Cement (OPC)-based binders. The carbon footprint of geopolymers is largely based on the type of the alkaline activator used in the mixture. Geopolymers mixtures that require sodium silicate-based activators provide a lower reduction in the carbon footprint in comparison to the OPC systems. However, for class F flash (FFA)-based geopolymer mixtures, the use of sodium silicate and the high temperature curing (i.e. 60°C - 80°C) is essential to achieve a good compressive strength. On the other hand, recent studies on ground glass fibers (GGF)-based geopolymers have shown that an excellent compressive strengths can be achieved without using sodium silicate solution, while specimens were only cured at moderate temperatures. Therefore, the objective of the current work is to investigate the effect of using sodium silicate-free activators on the activation and geopolymerization process of binary geopolymer mixtures that contain different levels of FFA and GGF and are heat cured at different temperatures. To this end, the use of GGF up to 50% replacement of FFA by mass have been investigated. The results have shown the superior performance of the FFA+GGF-based geopolymer specimens that are activated solely with NaOH solution in comparison to fly ashes-based geopolymer specimens that are activated with a combination of NaOH and sodium silicate solutions.
Introduction

Achieving sustainability of construction materials is an important goal in the construction industry. Cement manufacturing process is aggressive to the environment in terms of the associated high ratio of CO₂ emissions. While there are many avenues to achieve sustainability in the construction industry, one of the most important is provided through the beneficiating of long stored and eco-unfriendly industrial wastes to replace the necessity of using cement as the main world-wide binder.

One of the prominent and promising material to replace the use of cement is the vastly developed alkali-activated binder or geopolymer. Geopolymer has been identified by many researchers as the best sustainable substitute to the cement-based binders. Geopolymer is the product of the reaction between aluminosilicate materials, either natural or based on industrial waste, and alkaline solution. Most of the studies performed on geopolymer have used a combination of sodium silicate solution (water glass) and sodium hydroxide solution [1]–[4]. However, these procedures have been noted to affect the carbon footprint of the geopolymer. It has been established that the use of sodium silicate solution as the alkaline activator is the most contributing factor towards the total carbon footprint of the geopolymer concrete by 75% of the total carbon footprint [5]. Additionally, in general the cost of sodium silicate is higher than the cost of NaOH, which further obstructs the achievement of sustainability. In this regard, it has been suggested that eliminating the use of the sodium silicate alkaline solution, while still maintaining good quality performance by the material is one of the ways that would significantly reduce the geopolymer concrete carbon footprint. Nonetheless, some precursors that lack the amorphous silica, such as fly ash, the use of the water glass as well as heat curing become essential to obtain acceptable levels of performance.
Fly ash is a byproduct of coal burning at coal-based thermal power plants. Coal has been the main power supply for decades and as a result loads of ashes have been produced. There are two methods to dispose of the ash produced at power plants: first, the dry method, in which the fly ash is collected by electrostatic precipitators and transported to landfills or indoor storage areas. The second method is the wet disposal, in which both fly and bottom ashes are mixed with the water to facilitate pumping all the resulted slurry out of the power station into open storage facilities called ash ponds. These ash ponds are very detrimental to the environment in many ways, such as affecting the surface and ground water by leaching through the soil or if natural disaster occurs, such as Hurricanes. Additionally, so many cases of ash spill from ash ponds have been recorded, such as the incident of Dan river spill in 2014 in NC. Therefore, it is imperative to find beneficial uses for the ponded ash.

Another industrial waste that has not been fully considered for recycling is the waste glass fibers. The manufacturing process of glass fibers has about 25% of the produced glass fibers as waste. This stream of the waste usually gets ground to decrease the cost of the transportation to the landfills by reducing its volume. Recently, researchers have investigated the feasibility of using the ground glass fibers as a cement replacement and as a precursor for producing geopolymer concrete [6]–[9]. The results have shown that GGF can be considered a vital option to use as pozzolan in Portland cement concrete and as a source material in geopolymer concrete. The excellent performance of GGF was attributed to the highly amorphous structure and the particle fineness which facilitate its reaction in both concrete systems mentioned. Also, GGF particles liberate a relatively higher amount of silica when activated by NaOH solution in comparison to fly ash particles [7].
One of the factors that affect geopolymerization is the release rate of Si and Al species. The release rate is important because it affects the type of network formed and thus the strength. The Si-rich gel help most in the strength of geopolymer than the al-rich gel. Therefore, the ratio of Si to al (or SiO$_2$ to Al$_2$O$_3$) is important parameter in the geopolymer process and the resulted compressive strength [7]. Because of the stable crystal nature of Silica in fly ash making it difficult to be released, the soluble Si is usually supplied in the system by the sodium silicate (SS) solution. However, The GGF has significant content of amorphous silica that can easily be released into the system without the need for SS solution [7]. Furthermore, GGF can also provide other elements that are not present in SS solution and are important for geopolymerization process, mainly Al and Ca.

The presence of Ca in the geopolymer system affects its properties at both the fresh and hardened state. The calcium oxide (CaO) accelerates the setting time of geopolymer [10], [11]. Additionally, the CaO react with the geopolymer products to form calcium silicate hydrate (C-H-S) like gel which is calcium aluminosilicate hydrate (C-A-S-H) [12], [13]. this product densifies the geopolymer structure and contribute to the Mechanical properties of geopolymer concrete. Since the ponded ash usually are low calcium, blending it with GGF would make the CaO available in the system and it will most likely enhance the produced geopolymer properties.

The physical properties of precursors also play an important role in geopolymer. It is been established that the fineness of precursor affect the compressive strength of geopolymer [14], [15]. Mostly attributed to the increase of specific surface area of the source material and the resulting small size pores in the produced geopolymer. The GGF is significantly fine when compared to fly ash. therefore, if blended with fly ash, the
fineness of the total blend will increase, and this should positively reflect on the strength of the geopolymer. Moreover, the GGF particles are much stronger than the fly ash particles, which means that even the unreacted GGF particles in the system will boost the strength acting as micro reinforcement to the geopolymer system.

Several previous studies have investigated alternatives for sodium silicate in order to produce a greener geopolymer concrete. Bernal et al. [16] mixed silica fume or rice husk (as the silica providers) with NaOH solution to replace the use of silicate-based activator. Rice husk was also utilized by several other studies as a source of silica [17]–[20]. Some other studies used waste glass to produce the silicate-based activator necessary to activate slag [21], [22], and metakaolin [23].

The objective of this study is to investigate the feasibility of producing geopolymer based on the blends of ponded ash and GGF and using sodium hydroxide solution as the only activator. Sustainability is affirmed here by using two industrial wastes to produce a greener alternative for the cement by using a lesser carbon footprint activator.

Experimental Program

Materials

Ponded Ash

The ponded ash was brought from an ash pond located in NC. The label CSFA will be used henceforth to denote the ponded ash. the ponded ash was fully characterized for its physical, chemical, and mineralogical properties. The characterization results are shown in the results and discussion section.

Ground Glass Fibers (GGF)

The Ground Glass Fiber (GGF) was obtained from PPG Industries, in NC. The GGF was made by grinding the off-spec glass fiber into a fine powder with an average particle
size of 4 microns. The chemical compositions and physical properties of GGF are presented in Table 8-2. Besides, a scanning electron microscopy (SEM) image for GGF particles is provided in Figure 5-1. The GGF particles are angular and very fine, having Blaine’s fineness of 600 m²/kg, as shown in Table 10-2. GGF has a medium content of SiO₂ and CaO as compared to class C fly ash and class F fly ash, while it has a lower content of Al₂O₃. Figure 8-1 shows a ternary diagram comparing the chemical composition of GGF with other cementitious materials. The GGF was also found to be highly amorphous based on the X-ray diffraction studies performed by Rashidian-Dezfouli and Rangaraju [6].

![Figure 8-1 Chemical composition of GGF compared to cement and some other cementitious materials.](image)

**Fine Aggregate (Siliceous Sand)**

A non-reactive siliceous natural river sand from Glasscock Co. in Sumter, SC with an oven-dry specific gravity of 2.63, an absorption ratio of 0.35% and a fineness modulus of 2.6 was used in this study.
Non-Reactive Coarse Aggregate

Crushed stone graded to ASTM C33 size 67 were used to cast the geopolymer concrete cylinders for testing the compressive strength and splitting tensile strength of geopolymer based on GGF, fly ash and an even blend of both.

Reactive Coarse Aggregate

Highly reactive rhyolitic aggregate, Las Placitas gravel from New Mexico (NM), was used for testing ASR. The specific gravity and percent absorption of this aggregate were 2.6 and 1%, respectively. This aggregate was crushed and pulverized to be used as a fine aggregate graded as per ASTM C1260 [24] and ASTM C1567 [25].

Alkaline Activator

Sodium Hydroxide (NaOH) pellets were used to produce the NaOH solution according to each mixture proportions and design. Most of the mixture design when the Alkali Modulus (AM), which is the ratio of silica to sodium oxide in the activator (SiO₂/Na₂O), required about an 8N NaOH solution. For the tests that utilize the geopolymer pastes, 8N NaOH solution was used directly to prepare the paste. In addition, 40% sodium silicate solution was used along with NaOH solution for some mixtures as explained in Mixture Design and proportions section.

Mixture Design and Proportions

a- The first set of geopolymer mortar mixtures (using sodium silicate-free activator)

The purpose of preparing these mixtures is to investigate the performance of the blended CSFA/GGF based geopolymer in comparison with the geopolymer mixture produced with each of the individual material. The design of these geopolymer mixtures was based on a previous study by Rashidian-Dezfouli et al. [7] in which the optimum
Na₂O-to-binder ratio associated to the highest compressive strength was 10%. Therefore, the Na₂O-to-binder ratio was fixed at 10% for all the produced geopolymer mixtures. The sand content by volume was also fixed at 55% of the total volume of the geopolymer mortar mixture. As for the water-to binder (w/b) ratio, a little higher value than that used in the above study was used here to account for the slightly high LOI of the fly ash. The higher LOI materials demand higher w/b to render a workable mortar. Therefore, a w/b value of 0.4 was used in this study. The alkaline activator used for these mixtures was NaOH solution only, i.e. no sodium silicate solution was utilized and thus the activator modulus equaled to zero. These mixtures were heat cured at three different temperatures: ambient curing temperature, 40 °C, and 60 °C to study the effect of curing temperature on the compressive strength performance.

b- The second set of geopolymer mortar mixtures (with the use of SS)

In this set of mixtures, the alkaline modulus was varied from 0% to 1.5% at 0.5% increments by adding dosages of the sodium silicate solution to the sodium hydroxide activator. The other mix design parameters remained the same (i.e. Na₂O/binder ratio of 10%, w/b = 0.4 and sand volume = 55%). The purpose of making these mixtures was to compare the performance with the previous set of mixtures and evaluate the use of GGF as a replacement to the use of SS solution. The mixtures here consisted of 100% CSFA, 100% GGF, and an even blend of both. It should be noted that these mixtures were only used to test the compressive strength of the geopolymer mortar, and they were not a part of any other test methods in this investigation.

c- Geopolymer concrete mixture proportion (no SS)

The geopolymer concrete mixtures utilized the same quantities that would have been used for a 4000 psi ACI 211-based mixture design. The binder content (the CSFA
and/or the GGF) was 430 kg/m³, the water content was 193 kg/m³, the coarse aggregate content was 995 kg/m³, and the fine aggregate content was 800 kg/m³. The NaOH pellets were used to prepare the alkaline solution based on Na₂O to binder ratio of 10% and no sodium silicate was used in the concrete mixtures. The alkaline solution was prepared and left to cool down to the room temperature before mixing the geopolymer concrete.

All mixtures are shown in Table 8-1. The first and last mixtures were synthesized with the pure fly ash and the pure GGF, respectively. The purpose of preparation of these two mixtures was to compare their performance with the binary CSFA/GGF mixtures in which fly ash was replaced by GGF at a 10%-increment up to 50%.

Table 8-1 Labels, mixture proportions and test methods.

<table>
<thead>
<tr>
<th>Mix label</th>
<th>Binder</th>
<th>Test Methods</th>
<th>Geopolymer Paste</th>
<th>Geopolymer Mortar</th>
<th>Geopolymer Concrete</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CSFA</td>
<td>GGF</td>
<td>Setting Time</td>
<td>Isothermal Calorimetry</td>
<td>Water Demand</td>
</tr>
<tr>
<td>100CS00G</td>
<td>100</td>
<td>0</td>
<td>√</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>100CS00G</td>
<td>100</td>
<td>0</td>
<td>×</td>
<td>√</td>
<td>×</td>
</tr>
<tr>
<td>90CS10G</td>
<td>90</td>
<td>10</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>80CS20G</td>
<td>80</td>
<td>20</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>70CS30G</td>
<td>70</td>
<td>30</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>60CS40G</td>
<td>60</td>
<td>40</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>50CS50G</td>
<td>50</td>
<td>50</td>
<td>√</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>00CS100G</td>
<td>0</td>
<td>100</td>
<td>√</td>
<td>√</td>
<td>√</td>
</tr>
</tbody>
</table>

Proportioned by weight.

**Test methods**

The particle size distribution for both CSFA and GGF was determined using a Shimadzu SALD-2300 Particle Size Analyzer. X-ray fluorescence (XRF) and X-ray
diffraction (XRD) techniques were utilized to analyze the chemical composition and mineralogical composition of CSFA. The mineralogical phases of the geopolymer pastes of the mixtures were also evaluated using X-Ray Diffraction (XRD).

All the test methods performed on the geopolymer paste, mortar, and concrete are shown in Table 8-1. The setting time was measured according to ASTM C191 using Humboldt Vicat consistency apparatus. For the purpose of this test the geopolymer pastes were prepared with amount of 8N NaOH solution enough to yield normal consistency as per ASTM C187. The 8N NaOH solution was chosen based on the mixture design that was used to test the compressive strength of the geopolymer mortar. After that, the paste was mixed, and the solution was added gradually while mixing until normal consistency was achieved. The setting time was measured at both the room temperature and 60 °C heat curing.

The compressive strength of geopolymer mortar and concrete was performed in accordance to ASTM C109 and ASTM C39, respectively. For the geopolymer mortar, 2 in. cubes were cast in copper molds, then the molds were placed in air tight containers and cured at different temperatures (ambient, 40 °C and 60 °C) for 24 hours, then demolded and left at room temperature until tested. For the concrete mixtures, 3 in. by 6 in. cylinders were cast in and cured only at 60 °C.

Results and Discussion

Ponded Ash Characterization

Chemical composition of the ponded fly ash was determined by x-ray fluorescence (XRF) and the results are shown in Table 8-2. The sum of the oxides was well above 70% specified for class F fly ash as per ASTM C618 [26]. However, the loss on ignition (LOI) value was slightly higher than the maximum required by the same specification. The
chemical composition of GGF in comparison to the OPC and other cementitious materials is shown in Figure 8-1. The particle shape is angular for GGF compared to the spherical particles of CSFA as shown in Figure 8-1. The laser diffraction results for particle size distribution of both materials are shown in Figure 8-3. As it can be seen, the GGF particles are much finer than the CSFA particles. Blaine’s fineness test was conducted according to ASTM C204 [27], and the results, as shown in Table 8-2, confirmed that GGF particles are much finer than the CSFA’s particles. In this study, it was decided to utilize only the ash portion passing the standard No. 200 sieve (75 microns), as shown by the curve CSFA-sieved in Figure 8-3. It should be noted that more than 85% of the as-received ponded ash was finer than 75 microns. The as-received ash was dried out in an oven with a temperature of 110 °C for 24 hours then sieved.

Table 8-2 Physical properties and chemical composition of CSFA and GGF.

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific Gravity</th>
<th>LOI</th>
<th>Average Particle size, µ</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>SO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>3.15</td>
<td>2.6%</td>
<td>17.0</td>
<td>19.93</td>
<td>04.77</td>
<td>03.13</td>
<td>62.27</td>
<td>2.70</td>
<td>0.06</td>
<td>0.4</td>
<td>3.23</td>
</tr>
<tr>
<td>CSFA</td>
<td>2.25</td>
<td>6.1%</td>
<td>20.1</td>
<td>52.79</td>
<td>25.01</td>
<td>09.28</td>
<td>06.02</td>
<td>1.05</td>
<td>0.56</td>
<td>2.58</td>
<td>0.9</td>
</tr>
<tr>
<td>GGF</td>
<td>2.50</td>
<td>1.0%</td>
<td>4.0</td>
<td>56.50</td>
<td>12.48</td>
<td>00.37</td>
<td>22.06</td>
<td>2.60</td>
<td>0.75</td>
<td>0.10</td>
<td>0.03</td>
</tr>
</tbody>
</table>
Figure 8-2. SEM image for a) CSFA, b) GGF.
Water Demand, and Workability

The water demand can be determined from the values of solution-to-binder ratio found to yield normal consistency of geopolymer paste. For the mixtures of 100CS00G, 50CS50G, and 00CS100G, the solution-to-binder ratios were: 0.33, 0.27, and 0.26, respectively. The inclusion of GGF into the fly ash mixtures helped reduce the amount of
solution needed to obtain a workable paste. This can certainly be attributed to the smooth texture and the smaller size of GGF particles. Also, the inclusion of GGF reduced the total LOI in the binder which has a direct impact on the amount of water needed to yield a workable paste or mortar. The flow of each mortar mix is shown in Table 8-3. There was no a general trend observed in the workability of the mortar mixtures. However, the introduction of GGF into the blend helped increase the workability compared to the pure fly ash based geopolymer mixture.

Table 8-3 The flow results of the tested geopolymer mortar.

<table>
<thead>
<tr>
<th>Mix label</th>
<th>100CS00G</th>
<th>90CS10G</th>
<th>80CS20G</th>
<th>70CS30G</th>
<th>60CS40G</th>
<th>50CS50G</th>
<th>00CS100G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow, %</td>
<td>60</td>
<td>75</td>
<td>69</td>
<td>77</td>
<td>67</td>
<td>70</td>
<td>71</td>
</tr>
</tbody>
</table>

Isothermal Calorimetry Results

This test was performed on geopolymer pastes based on pure fly ash, pure GGF, and an even blend of both. Additionally, a pure fly ash pastes was activated using both NaOH and SS for comparison reasons. All the results are plotted and shown in Figure 8-5. When the test was initiated, the 100CS00G-SS, which is the mixture of pure CSFA activated by both NaOH and SS, released the highest heat, followed by 100CS00G and 00CS100G. For 00CS100G, the heat was released in a slow and steady rate and continued constantly until the test ended after 160 hours. The first narrow peaks are associated with the dissolution of solids in the alkaline activator [28], in which the aluminosilicates dissolve into the monomers of Si and Al. It can be clearly seen that the sodium silicate for fly ash-based geopolymer produced significantly higher heat than the fly ash-based geopolymer that was activated solely by NaOH solution, but both released heats were less than the GGF-containing mixtures. In fact, the curve for evenly blended GGF and CSFA based geopolymer had a cumulative heat that was average between GGF based geopolymer
and CSFA based geopolymer without SS. For both fly ash mixtures (100CS00G-SS and 100CS00G), the heat release was reduced significantly after the initial peaks. However, when GGF was introduced to the geopolymer mixtures, the reaction continued which can be revealed by the uninterrupted heat evolution throughout the test period. The performance of these mixtures in isothermal calorimetry correlate very well with the results of the mortar compressive strength at ambient temperature as will be shown later. In mixtures containing GGF, a second peak is noticed, whereas no such peak is shown for both pure CSFA-based geopolymers. This peak is associated with the polymerization and condensation of the species [29]. It should be noted that this test was only performed at 23 °C, it is recommended to be performed at higher temperature for better understanding for the reaction kinetics.

![Cumulative Heat Release](image)

**Cumulative Heat Release**

![Heat Flow](image)

**Heat Flow**

Figure 8-5 Isothermal calorimetry test result on geopolymer paste.

**Setting Time of Geopolymer paste**

Table 8-4 shows the results of setting time of the tested mixtures. The slow rate of reaction in the geopolymer paste containing CSFA only as the precursor and without heat curing resulted in a very long setting time. While the equally blended GGF and SCFA geopolymer paste had a significantly shorter setting time at the ambient temperature. This
can be attributed to the better performance of GGF as a geopolymer precursor due to its amorphous structure and very finely divided particles. The setting time resulting from the heat conditioning of the geopolymer paste was not different for the GGF based geopolymer and the binary CSFA and GGF based geopolymer. While for the mixtures that were cured at the ambient temperature, the inclusion of GGF was capable of reducing the initial setting time by 44% in comparison to the CSFA based geopolymer.

<table>
<thead>
<tr>
<th>Mix label</th>
<th>W/b for Normal Consistency</th>
<th>60 C Heat Curing</th>
<th>Ambient Curing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Initial Setting, min (hrs)</td>
<td>Final Setting, min (hrs)</td>
</tr>
<tr>
<td>100CS00G</td>
<td>0.33</td>
<td>150 (2.5)</td>
<td>225 (3.75)</td>
</tr>
<tr>
<td>50CS50G</td>
<td>0.27</td>
<td>100 (1.67)</td>
<td>135 (2.25)</td>
</tr>
<tr>
<td>00CS100G</td>
<td>0.26</td>
<td>100 (1.67)</td>
<td>135 (2.25)</td>
</tr>
</tbody>
</table>

**Table 8-4 Setting time results.**

*Compressive Strength of the First Set of Geopolymer Mortar*

All the results of testing compressive strength of geopolymer mortar are shown in Figure 8-6. Compressive strength increased as the GGF dosage and curing temperature increased. For 100CS00G, which was based on pure fly ash, the mortar cubes were crumbled when tested at 7 days for both the ambient and 40 °C cured mixtures; that was why they were not shown in the figure. It can also be seen that there was not much change between 7-Day and 28-Day strengths when cured at 60 °C indicating no further geopolymerization reactions were occurring. Whereas the difference is noticeable in the cases of ambient and 40 °C cured mixtures. The strength of the even GGF/CSFA blend was able to reach 41%, 52%, and 67% of the pure GGF-based geopolymer strength at 28 days for the ambient, 40 °C and 60 °C curing regimes, respectively.
Compressive Strength of the Second Set of Geopolymer Mortar

As it was mentioned, the purpose of this set of mixtures is to check the performance of the mortar mixtures if a sodium silicate solution was also used along with the NaOH solution for activation. Table 8-5 shows the results of the compressive strength of (SS+NaOH)-activating geopolymer mixtures at a variable alkali modulus ranging from 0% to 1.5%.

It should be noted that the mixtures containing SS in the activator, especially the 100CS00G, become highly sticky and difficult to handle as well as they set faster if not cast during the first five minutes after mixing. This probably was due to the way the SS was introduced to the mixtures, as it was mixed with the NaOH solution and the mix water
before adding the binder. It probably could have been better if the SS were added after mixing the mortar. The reasoning beyond that is thought to be relevant to the readily presence of Si ions floating in the SS solution, which along with the Na from the NaOH solution initiate the geopolymer reaction by first releasing Al from the fly ash. The presence of all these species may render a sticky paste. This was the reason these mixtures were only tested for compressive strength and were not involved in other testing except the isothermal calorimetry.

Table 8-5 7-day compressive strength results for the second set of mixtures.

<table>
<thead>
<tr>
<th>SiO₂/Na₂O</th>
<th>100CS00G</th>
<th>50CS50G</th>
<th>00CS100G</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1770</td>
<td>8580</td>
<td>11750</td>
<td>Taken from the first set of mixtures</td>
</tr>
<tr>
<td>0.5</td>
<td>1790</td>
<td>8310</td>
<td>11300</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1950</td>
<td>8120</td>
<td>10845</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>1385</td>
<td>7430</td>
<td>10320</td>
<td></td>
</tr>
</tbody>
</table>

In comparing the results from the two set of mixtures, it can be concluded that the addition of GGF even at a low level to fly ash has significantly increased the strength of geopolymer mortar, whereas the use of SS solution was only able to increase the strength up to 10% for the pure fly ash mixture of 100CS00G. Therefore, the use of GGF to enhance the fly ash-based geopolymer performance is more advantageous than the use of SS, and this would result in a more sustainable fly ash-based geopolymer by eliminating the need for the SS solution.

Figure 8-7 shows the relationship between the alkali modulus and the compressive strength of the tested geopolymer mortars. For the CSFA based geopolymer, there was a slight enhancement when the SS was introduced into the alkali activator up to alkali modulus of 1.0%, then there was a drop in the compressive strength at AM of 1.5%. The increase in strength when changing the alkali modulus from 0% to 1% is in agreement with
the results obtained in the study by Rashidian-Dezfouli et al., 2018 [7], while the drop in strength after AM of 1% is in agreement with the study by Rattanasak and Chindaprasirt, 2009 [10]. To explain the drop in the strength, a study done by Asif et al., 2014 [30] that investigated the effect of Si/Al ratio on the mechanical properties of geopolymer revealed that the optimum Si/Al ratio was 2.0 after which there was steep drop in the strength of geopolymer. For this study, the Si/Al ratio was calculated for the tested mixtures by running SEM/EDX analysis. The values were 2.24, 2.32, 3.88 for 100CS00G, 50CS50G, and 00CS100G, respectively, as SiO2/Na2O ratio of 0%. Additionally, according to Rashidian-Dezfouli, 2018 [7], the presence of soluble Si from SS negatively affects the solubility of GGF particles and leads to strength reduction.

Unlike the 100CS00G mixture, the compressive strength of the other two tested mixtures, 50CS50G and 00CS100G, decreased when the SS was used in the activator. This indicates that the use of SS is not necessary in the GGF-containing mixtures. The inclusion of GGF into the CSFA mixtures negated the need for the use of SS to facilitate the geopolymerization reaction. The improvements of CSFA geopolymer when the GGF was blended in the binder is most likely attributed to the particles size and the amorphous structure of GGF. The particle size is essential for the source material of geopolymer [31] and GGF having very fine particles enhanced the performance of the total blend. Additionally, the GGF particles being solid, angular, and strong, the unfixed GGF particles in geopolymer matrix may have behaved as reinforcement to the mortar [7], which added to the compressive strength.
Figure 8-7: The effect of variable alkali modulus on the compressive strength of geopolymer mortar.

**Thermogravimetric Analysis (TGA)**

Figure 8-8 shows the results of TGA test for the geopolymer pastes made with pure fly ash, even blend of fly ash and GGF, and pure GGF (i.e. 100CS00G, 50CS50G, and 00CS100G, respectively). As expected, the release of evaporable water from the geopolymer paste caused the sharp weight loss up to the temperature of 200 °C. All DTG curves peaked at around 90 °C. The weight losses, however, were 17.79%, 17.04%, and 13.52% for 100CS00G, 50CS50G, and 00CS100G, respectively. One possible reason to justify the lower weight loss in 00CS100G is the higher amount of Ca in GGF in comparison to fly ash. This can lead to the formation of C-S-H gel in addition to geopolymers chains, which means that some water will be used during the hydration process and will be bound in the hardened matrix.

The weight loss, after that, was steady up to 700 °C. It continued to be stabilized for 100CS00G and 50CS50G up to 1000 °C, but 00CS100G experienced a higher rate of weight loss between 700 °C and 1000 °C, which indicates carbonation. Bernal, et al. [32] justified the higher resistance of fly ash-based geopolymer to carbonation identifying the
main reaction products. They detected that N-A-S-H is the main product in fly ash based geopolymer and this product cannot be affected by carbonation, whereas the C-A-S-H product, based on their slag-based geopolymer, can highly be decalcified. Similar observation was obtained from the study by Li and Li [33] that fly ash-based geopolymer has a high resistance to carbonation. Therefore, it is thought in this study that GGF-based geopolymer is more vulnerable to carbonation than fly ash-based geopolymer as was sensed from the TGA results.

![TGA results for geopolymer pastes.](image)

**SEM/EDX Results**

A semi-quantitative analysis was obtained by conducting SEM/EDX analysis on hardened cut and polished geopolymer paste samples. The results of both analyses are shown in Figure 8-9 and Table 8-6.

When the GGF is introduced into the fly ash mixtures, there is an increase in Ca and decrease in Na and Al concentrations. The Si was dropped for 50CS50G then it was increased in the pure GGF mixture. The increase in Ca concentration as GGF is introduced might be an indicator of forming C-A-S-H network rather than N-A-S-H observed in fly
ash-based geopolymer in several studies [32]. Also, the higher concentration of Na in the pure fly ash mixture of 100CS00G supports that N-A-S-H is forming.

Table 8-6 EDX analysis results.

<table>
<thead>
<tr>
<th></th>
<th>Ca</th>
<th>Si</th>
<th>Na</th>
<th>Al</th>
<th>Mg</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>100CS00G</td>
<td>7.67</td>
<td>17.71</td>
<td>4.06</td>
<td>7.89</td>
<td>1.56</td>
<td>1.64</td>
</tr>
<tr>
<td>50CS50G</td>
<td>8.89</td>
<td>15.40</td>
<td>3.45</td>
<td>6.65</td>
<td>0.91</td>
<td>2.65</td>
</tr>
<tr>
<td>00CS100G</td>
<td>10.28</td>
<td>19.34</td>
<td>3.27</td>
<td>4.99</td>
<td>1.07</td>
<td>0.55</td>
</tr>
</tbody>
</table>

![SEM Images of the geopolymer pastes.](image)

Figure 8-9 SEM Images of the geopolymer pastes.
**XRD Results of Geopolymer Pastes**

The XRD test was conducted on powdered geopolymer pastes for samples that were cured at ambient temperature, and the results are shown in Figure 8-10. From the XRD results, 00CS100G appears to be amorphous, characterized by the broad hump centered around 30 degrees in 2-theta. While 50CS50G still has some of this amorphous character but shows the emergence of quartz and mullite crystalline phases which originated from the fly ash. The 100CS00G features somewhat more pronounced (more highly crystalline, and/or perhaps forming in greater quantity) quartz and mullite peaks, at the expense of the amorphous contribution. There is another set of generally weak peaks that at 2-theta = 19, 29, 32, and 34 degrees that were not identified in this analysis.

![Figure 8-10 XRD test results for the geopolymer pastes.](image)

**Dissolution of Geopolymer Paste in HCl**

The results of the paste dissolution in HCl are shown in Table 8-7. The residue percent (unreacted particles) after the geopolymerization products were dissolved and filtered out show that the reaction was better when GGF was included in the binary blend
of CSFA and GGF compared to the CSFA based geopolymer. It can also be inferred that
the heat curing facilitated the geopolymerization reaction for all the tested mixtures as the
amount of residues decreased when the test was conducted at 60 °C. It should be noted
that the results of this test correlated well with the data from the compressive strength test
(correlation factor of 0.916). It is worth mentioning that this test, along with the test of
extent of dissolution, could serve as good indicators of the performance of different
precursors in geopolymer.

Table 8-7 Results of dissolution of geopolymer paste in HCl.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Residue @ ambient, %</th>
<th>Residue at 60 °C, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>100CS00G</td>
<td>43.87</td>
<td>38.55</td>
</tr>
<tr>
<td>50CS50G</td>
<td>37.5</td>
<td>33.63</td>
</tr>
<tr>
<td>00CS100G</td>
<td>32.82</td>
<td>30.5</td>
</tr>
</tbody>
</table>

**Extent of Dissolution**

The results of testing the extent of dissolution of precursors in a high alkali
medium (5N NaOH solution) are shown in Table 8-8. The test was conducted at both
ambient temperature and at 60 °C heat curing. The results show clearly how the heat
curing facilitated the dissolution rate of Si and Al in the alkaline solution. The
concentration of Si has increased more than 358% when heat curing was utilized, while
the concentration of Al increased by 292%. The Al is strongly bound in the fly ash as
concluded by Rashidian Dezfooli et al. [7]. However, the concentration of calcium ions was
decreased for all the mixtures when they were heat cured for the test period, especially for
50CS50G. This could indicate a faster reaction rate as more calcium is fixed in the
geopolymerization product.

Table 8-8 Results of testing the extent of dissolution of precursors.

<table>
<thead>
<tr>
<th>Mixture ID</th>
<th>at Ambient</th>
<th>at 60 °C</th>
</tr>
</thead>
</table>

256
The compressive strength and splitting tensile strength of the geopolymer concrete mixtures cured at 60 °C are shown in Table 8-9. There is a high correlation between the compressive strength of the tested geopolymer mortar and concrete, with the strength of geopolymer concrete mixtures being about 50% of that of the corresponding mortar mixtures. There was no significant increase in strength between 7 and 28 days which shows that the heat curing accelerated the geopolymerization process. By utilizing an even blend of CSFA and GGF, the compressive strength was increased by 232.5% at 28 days compared with pure CSFA based geopolymer strength. The splitting tensile strength of the geopolymer concrete ranged from 7.5% and 9% of the compressive strength for the tested geopolymer concrete mixtures.

Table 8-9 Results of compressive strength and splitting tensile strength of geopolymer concrete.

<table>
<thead>
<tr>
<th>Mixture ID</th>
<th>Compressive Strength, psi</th>
<th>Splitting Tensile Strength, psi</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7-day</td>
<td>28-day</td>
</tr>
<tr>
<td>100CS00G</td>
<td>850</td>
<td>1120</td>
</tr>
<tr>
<td>50CS50G</td>
<td>3680</td>
<td>3725</td>
</tr>
<tr>
<td>00CS100G</td>
<td>5295</td>
<td>5365</td>
</tr>
</tbody>
</table>

**Alkali-Silica Reaction**

The Alkali-Silica Reaction (ASR) was investigated for the three geopolymer mortars indicated in Table 8-1. The purpose of this test is to further investigate and compare the performance of fly ash and GGF geopolymers in resisting ASR. In general, the geopolymer is more capable of suppressing ASR than conventional concrete. The accelerated mortar bar test (AMBT) was conducted in accordance with ASTM C1260 and...
the results are shown in Figure 8-11. The performance of all the three tested geopolymer mixtures is similar and all mortar bars have experienced expansions that were less than the expansion limit set by ASTM C1260, which is 0.1%.

Conclusions

- Fly Ash-based geopolymer requires the use of sodium silicate solution in addition to sodium hydroxide to increase the compressive strength.
- The combination of GGF and the investigated ponded fly ash (CSFA) that has a slightly higher LOI than ASTM C618 requirements resulted in a high compressive strength as compared to only fly ash based geopolymer mixtures.
- The use of GGF to replace the necessity of using sodium silicate solution with fly ash geopolymer mixtures has been proved successful. At 60 °C curing for 24 hours, a percent increase in strength from 44% to 220% were achieved for 10% to 50% replacement ratios.
References


Chapter 9

EVALUATION OF COAL ASH AS A SUPPLEMENTARY CEMENTITIOUS MATERIAL FOR APPLICATION IN FULL-DEPTH RECLAMATION OF ASPHALT PAVEMENTS

Abstract

Full Depth Reclamation (FDR) is a rapid means to rehabilitate existing pavement by blending the reclaimed asphalt and base materials with ordinary portland cement (OPC). Compacting the blend provides a stable base upon which a new layer of asphalt pavement can be constructed. The South Carolina Department of Transportation has employed FDR as a standard rehabilitation operation in maintaining the state’s large network of roads. However, the huge demand for OPC in the FDR projects, coupled with the relatively tight supply of OPC, is forcing the construction industry to explore the use of industrial by-products as supplementary cementitious materials (SCMs).

In this study, four different coal-combustion residues (coal ashes) from four Duke Energy power plants were evaluated for use in FDR projects. The fly ash (FA) portion of each coal ash was used as pozzolan to replace up to 40% of cement by mass. For this purpose, the chosen SCMs were analyzed for their chemical and mineralogical composition and physical properties. The pozzolanic reactivity, relevant mechanical and durability aspects of the blended cementitious materials, at selected dosage levels, were investigated. The results show that all FAs can be used, with relative performance, as pozzolans to partially replace cement for base stabilization; however, the FA produced at power plant B, due to its low LOI, high fineness, and amorphous structure, performed better in stabilizing the base materials. This project highlights the beneficial utilization of industrial by-products as valuable construction materials that otherwise would be landfilled as solid wastes.

Introduction

Full Depth Reclamation (FDR) is a rapid means to rehabilitate existing pavements by mixing the pulverized asphalt and base materials with ordinary portland cement (OPC). Compacting the resulting blend at optimum moisture content provides a stable base upon which a new layer of asphalt pavement can be constructed. This technique has been implemented since the 1980s [1] and it has been extensively performed by many transportation agencies. The advantages that have aided the rapid rise of FDR are [1]–[4]

- Cost-effective method.
- Uses 100% recycled materials, reducing the impact on environment.
- Ability to rehabilitate severely distressed roads.
- Fully carried out in situ with minimal traffic interruption.
- Provides a high resistance for cracks, decreasing the reflected cracks on the pavement layer, and
- The new stable base boosts the structural performance of the new pavement.

Cement is the most frequently used stabilizer in the FDR process. In addition, Class C fly ash, hydrated lime, asphalt emulsion, and foamed asphalt, have been used in FDR [1], [5]. Class C fly ash is not abundantly available in the state of SC. The use of lime and asphalt-based stabilizers results in a lower initial strength and more susceptibility to moisture than cement-based stabilization [4]. In addition, the use of cement is suitable for a wider range of soil types than any other stabilizers [4].

Over the last decade, South Carolina Department of Transportation (SCDOT) has successfully used OPC in pavement rehabilitation projects using FDR. As a result of this on-going success, SCDOT is progressively ramping up the use of FDR in its pavement rehabilitation operations. The pavement condition of over 50% of state-maintained
roadways is rated as poor and very poor [6], which mandates a definite increase in FDR applications. The average percent increase of the total OPC used in FDR projects in SC for the past 5 years from 2014 to 2018 was 30% compared to 2013 construction season, as shown in Figure 9-1 [Jesse Thompson, pavement engineer at SCDOT, personal communication, March 2019]. However, with increasing demand for OPC in other construction sectors, such as structural applications, its predictable availability for highway applications has become uncertain.

One option that can alleviate the need for cement is to partially replace it with quality supplementary cementitious materials (SCMs) such as class F fly ash, which is a by-product of burning coal in power plants. Large volumes of fly ash (FA) and bottom ash (BA) are stored in temporary storage facilities, known as ash ponds. In the US, About 130 million tons of coal ash were produced in 2014, of which only 46 million tons had beneficial uses [7].

There are certain requirements that need to be met in order for fly ash to be suitable for use as an SCM with OPC in structural concrete applications. ASTM C618 [8] specifies the requirements needed for this purpose. However, large amount of the coal ash produced from burning coals at power plants does not meet at least one of these requirements, such as loss of ignition (LOI). As a result, most of the ashes have been disposed of in storage ponds awaiting future environmentally-sound applications.

These ash ponds have harmed the environment on several occasions. Dan River coal ash spill is one example [9]. Additionally, there has been some evidences that unlined pond ashes have polluted shallow ground water with traces of harmful elements [10]. Most recently, Hurricane Florence floodwater threatened to spill toxic waste from an ash storage pond into Cape Fear river in Wilmington, NC [11].

Figure 9-1 OPC consumption in FDR projects in SC.

Therefore, this study investigated the feasibility of using fly ashes from selected ash ponds in the Carolinas as SCMs to partially replace OPC in FDR projects. Thus far, SCDOT has not employed any SCMs in the FDR operations, and has been interested in considering options that can supplement the limited OPC quantities available in the state. The use of the ponded ash or part of it as a cement replacement would alleviate the environmental impacts in two ways; firstly by reducing the OPC consumption, and secondly by reducing the amount of ash that has long been stored in the ash ponds.

**Experimental Work**

**Materials**

**Ash**

Four different ashes from four different Duke Energy Power Plants were used in this study. Throughout this paper, they are referred to by: A, B, C, and D FAs.
These ashes were sampled in their original form, i.e. as they had been stored in storage ponds. Only the fly ash (FA) portion, i.e. passing No. 200 (75-µm) U.S.A. standard sieve, was considered in evaluating the use of these ashes as SCM for FDR in this project.

**Reclaimed Asphalt Pavement (RAP) and Base Soil**

A blend of base soil and RAP was brought from a SCDOT road rehabilitation project that was being performed by King Asphalt Inc. at (1409 to 1523 N Old Pendleton Rd, Easley, SC 29642). The samples were taken from different spots along the road right after the passing of the reclaimer machine. In order to separate RAP and base soil, a No. 4 (4.75 mm) standard sieve was used. Following separation, particle size distribution for the two fractions was conducted and the results are described in the results section.

**Cement**

Ordinary Portland cement (OPC) Type I/II from Argos USA, produced at Hartsville, SC was used in this study. The chemical composition of the cement is provided in Table 9-1.

Table 9-1 Chemical composition of the cement.

<table>
<thead>
<tr>
<th>Compound Content (%)</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.93</td>
<td>4.77</td>
<td>3.13</td>
<td>62.27</td>
<td>2.71</td>
<td>0.06</td>
<td>0.48</td>
<td></td>
</tr>
</tbody>
</table>

**Sand**

Siliceous natural river sand from a local source was used in this study to prepare mortar specimens for evaluating pozzolanic reactivity of fly ashes. The specific gravity of the sand was 2.63 and fineness modulus of 2.6.
**Test Methods**

To fulfill the objectives of this investigation, the work has been carried out in three main phases:

**Phase I – Characterization of Ash and Base Material Properties**

Physical and chemical characterization of FA from the four different sources were performed. X-ray fluorescence (XRF) and X-ray diffraction (XRD)—were carried out to determine the bulk oxide content and mineralogy of the FAs. Additionally, scanning electron microscopy (SEM) was performed to examine the microstructural properties of the FAs. Lastly, loss on ignition (LOI) was determined for the FAs to quantify the unburned carbon.

**Phase II – Determination of Pozzolanic Reactivity of FAs**

In Phase II, the interaction of each FA with OPC was studied by testing each FA’s pozzolanic reactivity. The tested replacement levels of FA were 20% and 40% by mass of cement. Strength activity index (SAI%) according to ASTM C311 [12] was measured. In addition, setting time according to ASTM C191 [13] was conducted to determine the delay caused by the inclusion of FA in the cement paste.

**Phase III – Evaluation of Performance of Blends of Base Materials and Cementitious Materials**

This phase investigated whether the blend of cement and FA can be used as a stabilizing agent for base soil and RAP mixture. To this end, cylinders of cement-modified recycled base (CMRB) were made of different mix proportions and mixed at optimum moisture content. CMRB cylinders were cured for 28 days and then tested for unconfined compressive strength (UCS). In addition to UCS, durability, and drying shrinkage were examined. Finally, leachate tests were carried out to study any environmental impact.
In this phase, the following test methods were performed:

- Optimum moisture content for the cement-treated base material (AASHTO T99) [14];
- UCS for CMRB cylinders according to (SCT-26 [15] and SCT-142 [16]);
- Durability of CMRB (AASHTO T 135 [17]);
- Shrinkage of CMRB;
- Environmental leachate test, toxicity characteristic leaching procedure (TCLP).

**Mix Proportion**

According to SCDOT Specification (SCT-26) [15], three different sets of specimens were prepared for testing, consisting of 3%, 6%, and 9% cement by mass of the total base soil and RAP mixture weight. Additional specimens with blends of cement and FA with base materials were prepared, wherein the cement was replaced by fly ash at 20% and 40% by mass of cement at each tested cement content.

**Materials Preparation**

**Blend of RAP and Base Soil**

Before any testing using these materials, they were oven-dried at 110°C for 24 hours. Then, they were sieved to pass ¾” standard sieve. The retained portion was crushed to pass the ¾” sieve and added to the rest of the materials. No RAP or aggregate larger than ¾” was used in the mixture, as per the SCT 26 specification [15].

In order to maintain uniformity, a large sample splitter was used to reduce the size of this blend to the needed quantities for each test. Each batch of this blend was used on the same day it was oven-dried after allowing it to cool to room temperature.
The Binder (Cement and FA)

Before using any amount of FA, it was oven-dried and sieved to pass a No. 200 standard sieve. After preparing the needed quantities of both OPC and FA, they were dry mixed together in a metal bowl using a spatula until they uniformly blended and then added to RAP and base soil.

Mixing Procedures

Once all required quantities were ready, the binder (cement with or without FA) was introduced to the blend of RAP and base soil in a large flat metal tray. Afterwards, the whole blend was mixed very well by hand until consistent mixture color was obtained. Finally, the required amount of water was added by pouring it in the middle of the mixture.

The matrix was left for a few minutes so the mixing water could be absorbed by the materials. Following, all constituents were mixed first by a trowel until the full distribution of mixing water was acquired, then finished by hands. According to SCT-26 [15], the matrix was allowed to stand for 5 to 10 minutes in order to help in moisture dispersion.

Optimum Moisture Content (OMC%):

Conferring to SCT-26, this test should be performed on the blend that has the medium cement content, which is 6% from the total mass of RAP and base soil. The OMC obtained using this proportion should be used for all other binder ratios (i.e. 3% and 9%).

The test was carried out for two mix proportions; the first included 6% OPC content as binder, and the second had 40% OPC replacement by FA. C FA was selected to check the effect of using FA on the OMC percentage because, as will be shown later, it had the highest LOI and therefore the highest water demand that could affect the OMC percentage.
**Preparation and Curing of the UCS Test Samples**

SCT-26 requires two specimens for each tested mixture. The specimens were prepared using a 4-inch (100 mm) diameter proctor mold and 5.5 lbs. (2.495 Kg) rammer. Each specimen was made by compacting three equal layers using 25 blows of proctor rammer. Following the compaction of each specimen, it was extruded using a manual sample extruder.

All specimens were covered and cured in a 100% humidity room at 23°C for a period of 28 days before testing. On the night the test was due, specimens were soaked overnight according to SCT-26 [15]. Although SCT-26 requires testing CMRB specimens at 7 days of age, it was decided to test them at 28 days allowing more time for FA-cement interaction and hydration.

Values as low as 200 psi (1.38 MPa) for UCS are acceptable as long as the durability test requirements are successfully achieved [18]. Based on this, the minimum acceptable UCS value considered in this study is 200 psi (1.38 MPa) when the durability test yields good performance (as discussed later).

**UCS Test Procedure**

The loading rate, as per SCT-26, consists of 500 lb./minute for the first 100 lbs., then raised to 1000 lb./minute up to 6000 lbs., then the loading rate should be lowered down to 500 lb./minute until failure. Two specimens were tested for each mixture using these procedures.

**Durability of CMRB**

The durability test has long been used as the main criterion for designing CMRB. However, many agencies have correlated this test with other properties such as UCS or gradation of the base soil. Subsequently, most agencies now specify a minimum 7-day UCS
level to be achieved by CMRB specimens [18]. As long as this minimum UCS is achieved, durability requirements are met. However, the durability test was performed to evaluate the effect of using FA with cement as a stabilizing agent on durability.

AASHTO T135 – method B was followed here since the maximum size of the used materials was ¾ in. (19 mm). The procedure involves subjecting the tested samples to 12 cycles of wetting and drying after they are cured for 7 days in a moist room. Each cycle consists of 5 hour soaking in water followed by 42 hours of drying in an oven at 71°C. Conferring to AASHTO T135 [17], two specimens should be prepared; the first one to monitor volume change due to the wetting and drying cycles and the second one to test the weight loss that results from a 3-lb pressure brushing exerted by a wire brush after each cycle. The final weight loss is used as an indicator for durability.

**Shrinkage of CMRB**

Shrinkage is a change in volume caused by several factors, such as temperature gradients, drying, and cement hydration. Shrinkage results in cracks in the bases that can reflect through the pavement surface, triggering serious durability problems. Drying shrinkage represents the highest fraction of the total shrinkage and it is the leading cause of cracks [19]. High moisture content (above OMC), high clay content, poor compaction, and high amounts of stabilizing cement are factors that boost shrinkage in CMRB [19]. Water ingress through the reflected cracks in the pavement surface has major deteriorating effects that could cause complete failure of the road.

Lowering cement content, increasing pavement thickness, and decreasing the minimum 7-day UCS are the main mitigation measures taken by most of the design agencies [19]. Nevertheless, lowering cement content would pose a durability problem. Hence, optimizing cement content is important and checking for shrinkage is as important
as checking for strength. Therefore, the purpose of executing this test was to investigate
the effect of the FA dosages in the blend of OPC+FA on drying shrinkage of CMRB.

There is no standard method for testing shrinkage of CMRB. It was decided to
follow the same standards and testing methods for testing length change of concrete.
ASTM C157 [20] and ASTM C490 [21] were both followed in this test. Some test
requirements had to be adjusted to suit the use of CMRB materials instead of concrete for
which the standards were designed.

Prismatic specimens with the dimension of 3 in. by 3 in. by 11¼ in. (75 mm by 75
mm by 285 mm) compacted to the same level of density as the CMRB cylinders were
prepared. The 5.5 lbs. (2.495 Kg) proctor rammer was used to compact all the prisms
except at the ends (The areas around the stud gauges), where compaction was done
carefully with a 2 lbs. (907.2 g) hammer and a hard plastic mortar tamper. Two test
specimens were prepared for each mixture. The tested mixtures had 40% FA dosages, and
a pure cement mixture was made as a reference.

*Environmental Leachate Test*

The leaching characteristics of the blended material were evaluated using standard
test method of Toxicity characteristic leaching procedure (TCLP). This test was performed
by the Civil and Environmental Engineering Department at University of North Carolina
at Charlotte (UNCC). Only a summary of the test results is presented here.

The samples that were chosen to conduct this test were taken from the CMRB
specimens after the UCS test was accomplished. The crushed CMRB specimens were kept
in sealed bags until they were transported to UNCC. Five samples were selected to do the
leachate test, the control sample (with 6% cement), and samples with 40% replacement
by FA (A, B, C, and D FAs). Specimens with the highest tested replacement ratio were chosen because they represent the worst case in terms of leaching characteristics.

**Results and Discussion**

**Results of Phase I**

**Physical Properties of FAs**

The specific gravity ranged from 2.19 to 2.26 for the four FAs. The moisture content for A FA was very low (0.3%) because it was collected directly from the power plant, whereas the moisture contents of the other ashes were high and ranged from 20% to 28% because they were collected from the ponds where they had been stored.

Based on laser diffraction test results (Figure 9-2), the FA portion of the bulk ash produced at the four investigated Duke Energy power plants was large (ranged from 70% to 86%), based on particles size of 75 micron, indicating the possible utilization of large amount of the ponded ashes in future pavement rehabilitation projects. Among the tested FAs, D FA had the finest particles, according to the average particle diameter by mass (D$_{50}$) shown in Table 9-2, followed by B and A FAs. Whereas the size of C FA particles was much larger. This suggested better pozzolanic reactivity for D FA and similar performance for B and A FAs. These findings were supported by SEM images as will be shown.

Table 9-2 Average particles diameter by mass for the tested fly ashes.

<table>
<thead>
<tr>
<th>FA Source</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>D$_{50}$ (micron)</td>
<td>27.39</td>
<td>24.85</td>
<td>44.32</td>
<td>22.60</td>
</tr>
</tbody>
</table>
Chemical Composition of FAs

XRF results are listed in (Table 9-3). As shown, the sum of the oxides (SiO$_2$ + Al$_2$O$_3$ + Fe$_2$O$_3$) indicates that the minimum requirement of ASTM C618 for both classes of FAs (C, F) was met. However, when examining the LOI values presented in the same table, only A, B, and D FAs met the requirement of the footnote of class F FA that permits the use of FAs with LOI values up to 12% when acceptable performance or laboratory test results are available [8]. Calcium Oxide percentage, on the other hand, was small for all FAs, which indicated low self-cementing properties. This suggested the incapability of using a high percentage of cement replacement with any of the tested FAs.

The alkali content (Na$_2$O$_{eq}$) was small (less than 2%) in all FAs. Additionally, as per ASTM C618, the maximum percentage of Sulfur trioxide (SO$_3$) for both class C and class F FAs is 5%, which was met by all the tested FAs.

In order to assess the crystalline phases of FAs, XRD was performed and results are shown in (Figure 9-3). Once all crystalline phases were identified, the amount of
amorphous was estimated. The amorphous structure accelerates the pozzolanic reactivity. The amorphous percentage was good for A and B FAs (averaged 64% and 53%, respectively); whereas D FA was 45%. C FA, however, had the highest amorphous at 69%, but its LOI was also the highest at 20.54%.

Table 9-3 Chemical composition for the selected FAs.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Unit</th>
<th>A FA</th>
<th>B FA</th>
<th>C FA</th>
<th>D FA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; (A)</td>
<td>%</td>
<td>27.98</td>
<td>25.33</td>
<td>24.93</td>
<td>27.45</td>
</tr>
<tr>
<td>CaO</td>
<td>%</td>
<td>1.51</td>
<td>4.94</td>
<td>3.51</td>
<td>0.91</td>
</tr>
<tr>
<td>CrO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>%</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>FeO&lt;sub&gt;3&lt;/sub&gt; (F)</td>
<td>%</td>
<td>8.17</td>
<td>8.12</td>
<td>13.86</td>
<td>6.71</td>
</tr>
<tr>
<td>K&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>%</td>
<td>2.34</td>
<td>2.33</td>
<td>1.87</td>
<td>2.11</td>
</tr>
<tr>
<td>MgO</td>
<td>%</td>
<td>1.12</td>
<td>1.21</td>
<td>1.36</td>
<td>0.98</td>
</tr>
<tr>
<td>MnO</td>
<td>%</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>%</td>
<td>0.10</td>
<td>0.15</td>
<td>0.15</td>
<td>&lt; 0.06031</td>
</tr>
<tr>
<td>P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>%</td>
<td>0.25</td>
<td>0.19</td>
<td>0.27</td>
<td>0.30</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt; (S)</td>
<td>%</td>
<td>56.87</td>
<td>53.82</td>
<td>48.33</td>
<td>59.33</td>
</tr>
<tr>
<td>SO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>%</td>
<td>0.35</td>
<td>2.66</td>
<td>4.52</td>
<td>0.88</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>%</td>
<td>1.26</td>
<td>1.20</td>
<td>1.15</td>
<td>1.26</td>
</tr>
<tr>
<td>LOI</td>
<td>%</td>
<td>7.46</td>
<td>6.03</td>
<td>20.54</td>
<td>8.82</td>
</tr>
<tr>
<td>S+A+F</td>
<td>%</td>
<td>93.02</td>
<td>87.28</td>
<td>87.12</td>
<td>93.50</td>
</tr>
</tbody>
</table>
Figure 9-3 XRD results of a) A b) B c) C d) D fly ashes.

Examining the SEM images shown in (Figure 9-4), the majority of the particles are uniformly spherical. Some of the spheres show pores on the surface; these pores increase the surface area leading to a better chemical reactivity. Unburned carbon fragments (shown as dark irregularly shaped particles) are present in all ashes (specifically C ash), which supports the high LOI% value shown in (Table 9-3).

Characterization of Base Soil and RAP

A well-graded soil with minimal amounts of clay and silt requires less cement content to produce a strong and durable recycled base layer. Whereas clayey soil or gap-graded soil requires more cement content to achieve the required strength and durability.
The sieve analysis indicated that the test sample consisted of approximately 35% coarser than No. 4 sieve (gravel size RAP particles), around 60% between No. 4 and No. 200 sieves (sand size particles), and about 5% finer than No. 200 sieve (silt and clay particles).

The classification of base soil according to AASHTO M145 [22] is A-1-b. The usual constituents of this type of soil are stone fragments, gravel and sand with non-plastic or marginally plastic fines. This type of soil is excellent for subgrade materials. According to PCA guidelines [23], the minimum requirement for gradation of the bulk pulverized materials for the portion passing No. 4 sieve was 55%, which was in compliance with the tested bulk materials. Also, RAP ratio was 35% of the tested blend of RAP and base soil.
Results of Phase II

Phase II results are shown in (Table 9-4). Based on the SAI values, all FAs meet the minimum SAI specified by ASTM C618, which is 75%. Therefore, it can be concluded that all FAs had pozzolanic reactivity with A and B FAs being more reactive than D and C FAs.

The percentage increase of initial setting time, compared with control mixture, was highest for 40% A FA mixture, while it was lowest for 20% D FA mixture. As for the final
setting time, the percentage increase compared to the control was highest for 40% A and 40% B and lowest for 20% A and 20% C.

Table 9-4 SAI%, and setting time tests results.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>SAI, %</th>
<th>Setting time, minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At 7 days</td>
<td>At 28 days</td>
</tr>
<tr>
<td>Control (pure Cement)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>20% A</td>
<td>106</td>
<td>110</td>
</tr>
<tr>
<td>40% A</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>20% B</td>
<td>105</td>
<td>102</td>
</tr>
<tr>
<td>40% B</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>20% C</td>
<td>97</td>
<td>96</td>
</tr>
<tr>
<td>40% C</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>20% D</td>
<td>92</td>
<td>98</td>
</tr>
<tr>
<td>40% D</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Results of Phase III

The OMC% for the mixture with 6% cement content was 9.8%, while it was 10% for the cement/C FA blend (C FA was selected due to its higher LOI). The maximum dry density was 120 pcf (1922.2 Kg/m³) for both tested mixtures. So even with the maximum tested percent replacement, no significant FA effect on the OMC% of stabilized recycled base materials. Therefore, a moisture content of 10% was used for all mixtures.

Examining the UCS results shown in (Table 9-5), mixtures with 3% binder ratio did not yield good strength. At higher binder ratio, however, and with 20% replacement, the strength of control mixture was nearly reached in the mixtures that contain B FA and D FAs. In terms of strength loss compared to control mixtures, B FA-containing mixtures had shown the least strength loss.

The better performance of B and D FAs can be credited to the low LOI value, the fineness of the particles, and the amorphous structure, all of which facilitated the
pozzolanic activity. The SAI results also support the higher UCS of B FA containing mixtures since its value was the highest among other mixtures.

Table 9-5 UCS results for all mixtures, psi (MPa) (1 psi = 0.0069 MPa)

<table>
<thead>
<tr>
<th>Binder (OPC+FA) content in the mix, %</th>
<th>Cement replacement level in the binder, %</th>
<th>Fly ash source</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A</td>
</tr>
<tr>
<td>3%</td>
<td>0</td>
<td>190 (1.3)</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>140 (1.00)</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>100 (0.69)</td>
</tr>
<tr>
<td>6%</td>
<td>0</td>
<td>245 (1.69)</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>225 (1.55)</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>150 (1.03)</td>
</tr>
<tr>
<td>9%</td>
<td>0</td>
<td>450 (3.10)</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>375 (2.59)</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>305 (2.10)</td>
</tr>
</tbody>
</table>

Practically, UCS results are plotted in terms of cement content of 3, 6, and 9% as illustrated in the control curve in Figure 9-5, then; the desired strength can be used to estimate the required cement content [15]. When inspecting the UCS values for the FA containing mixtures, as shown in Figure 9-5 and Figure 9-6, it can be noticed that UCS of control mixtures (pure cement stabilization) were achieved using less cement in the FA blended mixtures. This would reduce the volume of cement consumed every year in road rehabilitation projects along with consuming a considerable amount of FA; which would greatly alleviate environmental complications.

In order to further investigate this advantage, a mixture having 12% binder was prepared using 40% cement replacement ratio with A FA. This means that the cement content of this mixture is only 60% of the binder which equals to 7.2% cement content. The specimen was also cured for 28 days then tested for UCS. The result of UCS obtained was 570 psi (3.93 MPa), which was even higher than the 9% control sample’s strength of 450 psi (3.10 MPa).
Looking at Figure 9-5 and Figure 9-6, they clearly indicate a better performance of B FA among the other FAs. Additionally, it can be inferred that when using FA to replace cement (at either 20% or 40% replacement), about 4.5% cement content was the minimum
to yield higher UCS than if cement alone had been used for stabilization (the average point where all curves in both figures intersect).

The tested mixtures for durability were selected to have 6% binder ratio with 40% cement replacement by each FA, In addition to the control mixture with 6% OPC. Results for weight loss from the wire brushing were about the same for all of mixtures (around 8%). There was no significant volume change in the specimens after 12 cycles of wetting and drying. For acceptable performance of CMRB in terms of durability, maximum weight loss limits were established based on soil classification [18]. For A-1 soil, the limit is 14%, which is higher than all weight losses for the tested mixtures. Since the only replacement ratio tested here is 40% from a total of 6% binder, higher binder ratios are anticipated to yield good performance too in this test because of the small values of weight loss observed here.

For the shrinkage test, comparator readings for length change were taken until no significant length changes were observed. All the results were plotted in terms of age of specimens and are shown in Figure 9-7. The results clearly show that the shrinkage was greatly reduced when cement was used for stabilization (control mixture), as it was reduced from 1535 µƐ for soil-only sample at 21 days to 785 µƐ. The FA containing mixtures samples had slightly higher shrinkage than cement stabilized samples. Samples with B and A FAs had shrinkage that was closer to the shrinkage of control samples (875 µƐ, and 895 µƐ respectively).
Results from TCLP tests showed that the measured concentrations of the tested elements, (Ag, As, B, Ba, Cd, Cr, Pb, Se), from both Methods ((US EPA Methods 1311 and 1313 pH natural)), are less than the Resource Conservation and Recovery Act (RCRA) regulatory concentration limits and the hazardous waste screening criteria. Therefore, these fly ashes are considered safe from environmental pollution perspective.

Conclusions

Based on the results of the different phases of this study, the following conclusions are drawn:

All fly ashes evaluated in this study, had shown pozzolanic reactivity. The SAI values at 7 and 28 days were higher than the minimum of ASTM C618 for all FAs tested. The presence of FAs in the cementitious paste did prolong the setting time.

As for the CMRB results, the inclusion of FA into the cement stabilized base soil caused a reduction in UCS. The higher the replacement ratio, the higher the strength drop. A strength drop of up to 51.3% was observed (in 40% D FA mixture). B FA mixtures
demonstrated the lowest strength reduction among the other FA mixtures. The observed trend was the strength loss decreased as binder ratio increased for both replacement ratios (20% and 40%).

Consequently, it can be inferred that by increasing the binder ratio and the cement replacement ratio, higher values of UCS can be reached at less cement content than if cement was used alone. This would help consume larger quantities of FAs reducing the environmental impacts the storage ponds have along with reducing the cement consumption rate.

In terms of long-term performance, all the tested samples passed the wetting and drying durability test based on the recommendation of the PCA [18]. Moreover, The FA containing mixtures samples had slightly higher shrinkage than cement stabilized samples. Samples with B and A FAs had shrinkage that was closer to the shrinkage of control samples (875 µƐ, and 895 µƐ respectively compared to 785 µƐ for control at 21 days).

**Recommendations**

Further testing is required for full characterization of all ashes used in this study. Only the FA portion used as SCM to replace cement in this study. It might be beneficial to test the potential of using the whole ash with cement to stabilize the blend of RAP and base soil. Furthermore, the only improvement that was applied to ash before using it was sieving it on No. 200 standard sieve and using the passing portion. It is recommended to apply other means of improvement such as grinding or burning to get rid of the high value of LOI%.

The binder (cement with/without FA) was applied dry to the mixture of RAP and base soil. Some studies have shown properties improvement if the blend is introduced as
slurry [18]. This is also beneficial in the field in order to reduce the airborne dust produced when mixing the dry cement with base soil.

Different soil type should be investigated in order to study the effect of soil type on the properties of CMRB specimens. Also, the effect of amount of RAP should be studied.

Finally, this lab investigation should be followed by in-situ study in order to obtain more realistic performance of different types of base soils and RAP.

Acknowledgments

We, the authors acknowledge Tim Smart and Tony Mathis from Duke Energy Corporation which provided funding to accomplish this work. We also acknowledge Eric Carrol, and Jay Thompson from SCDOT for their help throughout the work. Similarly, we acknowledge John Sanders from the National Brick Research Center at Clemson University for his help conducting some of the tests.
References


Chapter 10

LABORATORY INVESTIGATION OF SUSTAINABLE CEMENT ALTERNATIVES FOR USE IN FULL DEPTH RECLAMATION OF ASPHALT PAVEMENTS

Abstract

Cement has been used to stabilize base soils and to rehabilitate existing pavements in a Full-Depth Reclamation (FDR) process. The FDR is a quick means of repairing worn-out asphalt pavements. The reclaimed asphalt pavement (RAP) is mixed with the underlying base soil, and subsequently, the whole blend is stabilized with cement and water. Compaction produces a strong base for placing a new layer of asphalt. However, cement manufacturing process is responsible for a relatively significant portion of manmade CO2 emissions. Also, the amount of cement that is allocated for FDR projects does not meet the demand in some states like South Carolina (SC). Besides, Industrial waste disposal has become one of the most difficult problems nowadays. Ash ponds are an example of disposal areas where all the off-spec fly ashes produced from burning coal at power plants are disposed of at. Manufacturing of glass fibers is another example that produces a lot of waste which is dumped in landfills due to extreme difficulty in recycling. Therefore, this study investigates the suitability of partial or full replacement of cement in FDR by fly ash, ground glass fibers (GGF), and slag. To this end, the suggested industrial byproducts are utilized either as pozzolans to partially replace the cement, or as precursors for geopolymer-based stabilization. Unconfined compressive strength, flexural strength, elastic modulus, and durability of the stabilized FDR samples were inspected. The laboratory results showed the possibility of using the suggested industrial wastes in FDR stabilized mixtures.
Introduction

Full Depth Reclamation (FDR) is a quick method to rehabilitate existing pavements by mixing the pulverized asphalt and base materials with cement and water. Compacting the resulting blend at optimum moisture content provides a stable base upon which a new layer of asphalt pavement can be constructed. This technique has been employed since the 1980s, and it has been extensively performed by many transportation agencies due to its vast advantages. These advantages include cost-effectiveness, the use of 100% recycled materials, capability of rehabilitating severely-damaged pavements, being carried out completely in-situ with minimal traffic interruption, restricting the reflected cracks on the pavement surface, and boosting the structural performance of the new pavement layers [1]–[4].

As for the binders used with the FDR process, cement is the most frequently used stabilizer. Other binders include Class C fly ash, hydrated lime, asphalt emulsion, and foamed asphalt, have been used in FDR [1]. Class C fly ash is not abundantly available in the study area. The use of lime and asphalt-based stabilizers results in lower initial strength and more susceptibility to moisture than cement-based stabilization [4]. In addition, the use of cement is suitable for a wider range of soil types than any other stabilizer [4]. This makes cement as the suitable material for various applications in most of the DOTs,

Over the last decade, South Carolina Department of Transportation (SCDOT) has successfully used cement in pavement rehabilitation projects using FDR. As a result of this on-going success, SCDOT is progressively ramping up the use of FDR in its pavement rehabilitation operations. In 2012, North Carolina (NC) and South Carolina (SC) were ranked second and fourth, respectively, in the amount of state-maintained mileage of roads [5]. In SC, the pavement condition of over 50% of state-maintained roadways is
rated as poor and very poor, which mandates a definite increase in FDR applications. There was a 200% increase in cement consumption in several FDR projects in SC between 2013 and 2016 [6]. However, with increasing demand for cement in other construction sectors, such as structural concrete, its predictable availability for highway applications has become uncertain.

One option that can alleviate the need for cement is to partially replace it with a quality supplementary cementitious material (SCM) such as ground glass fibers (GGF). In the production process of the glass fiber, its quality is carefully checked and examined for flaws. A significant amount of glass fiber that does not meet satisfactory physical qualities is rejected as off-spec glass fiber and removed from the production line as industrial waste. This waste is sometimes ground to reduce the volume, and thus, the cost of transportation [7]. Due to the difficulty of recycling glass fibers [7], all of the off-spec glass fibers are landfilled. The glass fibers industry is growing in the Carolinas [8], and thus the generated waste glass fiber. There have been a few studies that explored the use of ground glass fibers (GGF) as an SCM in OPC concrete or as a precursor for geopolymer concrete [9]–[12]. In places where this material is abundant, it could be a good alternative to replace cement partially or fully in many applications. Therefore, it was suggested, in this work, to explore the use of this material in stabilizing the FDR layer.

Another Industrial waste that could be used to replace cement is the ponded fly ash. Large volumes of ash are stored in temporary storage facilities, known as ash ponds. These ash ponds have harmful impacts on the environment, such as the occurrence of ash spills. Additionally, there have been indications that unlined pond ashes have polluted shallow groundwater with traces of harmful elements [13]. Therefore, it is essential to find applications where these ponded ashes could be used. In the US, about 130 million tons of
coal ash were produced in 2014, of which only 46 million tons had beneficial uses [14]. This lower percentage of beneficially used fly ash is due to its quality and properties. ASTM C618 stipulates the chemical and physical requirements needed for the fly ash to be suitable for cement replacement. However; large amounts of the coal ash produced from burning coal at power plants does not meet at least one of these requirements, and as a result, most of the ashes have been disposed of in the storage ponds awaiting future environmentally-sound applications.

Another option that has gained large popularity and fully replaced the use of cement in some applications is the use of alkali-activated materials or geopolymers. Although many studies have investigated different SCMs for utilization as a partial or full replacement of OPC in FDR, a few have studied the geopolymer-based full depth base-soil stabilization [15]–[17]. For example, Adhikari et al. [16] employed class F fly ash-based geopolymer to stabilize a blend of soil and reclaimed asphalt pavement (RAP). A combination of NaOH (sodium hydroxide) and Na$_2$SiO$_3$ (sodium silicate) solution was used as the activator. Reference mixtures of 5% and 10% OPC-based stabilization were used. The fly ash, soil, and RAP were all mixed dry, following the alkali solution was added and thoroughly mixed. Samples were heat cured for 48 hours at 60 °C, then they were demolded 24 hours after removal from oven and tested for unconfined compressive strength (UCS). They concluded that the use of geopolymer to stabilize the base materials is effective, and good strength and durability could be achieved.

Although the use of geopolymer for base soil and RAP stabilization was successful in some studies, none of them considered the practicality of using such technology in the field. For example, the use of heat curing for 24 or 48 hours is impractical. Also, it is difficult to handle the corrosive liquid used for activating the geopolymer. Therefore, this
study aims to investigate the performance of geopolymer stabilized bases in practical ways as possible. Ambient curing for geopolymer stabilized samples and the wet mixing of geopolymer pastes with the base materials were utilized in the current study.

To sum up, this study investigated the feasibility of using GGF either individually or blended with ponded fly ash or slag as SCM to replace cement partially or fully in FDR process. This could provide options that can supplement the limited cement quantities available in the states. The use of the selected industrial byproducts would also alleviate the environmental impacts in two ways; firstly, by reducing the cement consumption, and secondly by reducing the amount of industrial waste that has detrimental impacts on the environment.

Experimental Program

Materials

Binding agents

Cement

Type II ordinary Portland cement (OPC) meeting ASTM C150 [18] supplied by ARGOS was used in this study. The chemical composition is provided in Table 10-1.

Ponded Fly Ash

The ponded fly ash was brought from an ash pond in North Carolina. The ash was dried out in oven at 110 °C for 24 hours, then sieved on No. 200 standard sieve (75 micron). Only the passing portion was used in this study and it represented more than 80% by mass of the total ash. The fly ash was characterized for its chemical, petrographical, and physical properties. Chemical composition is presented in Table 10-1, while particle size distribution and SEM image of fly ash are shown in Figure 10-1.
Ground Glass Fibers

The ground glass fibers were obtained from PPG industries. The waste of glass fibers was ground to fine powder yielding an average particle size of 4 micron. This material has been shown to work well as pozzolan as well as a precursor for geopolymer production [9], [10], [12]. The chemical composition and physical properties are shown in Table 10-1.

Slag

The slag used in this study was from Lafarge-Holcim US of grade 150. The slag, in this investigation was only used in binary blends with GGF to help improve the strength development of the geopolymer at ambient temperature without the need for heat curing. Table 10-1 shows the chemical composition and physical properties of slag.

Reagents

Sodium Hydroxide Solution

Sodium hydroxide pellets with 99% minimum assay were acquired from Fisher Chemicals and they were used to prepare the 8N NaOH solution that was used to activate the geopolymer mixtures. The solution was prepared a day before any geopolymer-based MRB samples were made.
Figure 10-1 SEM image for the ponded fly ash, (a) after sieving, (b) in the original state.

Table 10-1 Chemical composition and physical properties of the materials used in this study.

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific Gravity</th>
<th>LOI</th>
<th>Average PS, µ</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>SO₃</th>
<th>Alkali eq.</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>3.15</td>
<td>2.6%</td>
<td>–</td>
<td>19.93</td>
<td>4.77</td>
<td>3.13</td>
<td>62.27</td>
<td>2.70</td>
<td>0.06</td>
<td>0.48</td>
<td>2.95</td>
<td>0.38</td>
</tr>
<tr>
<td>PFA</td>
<td>2.50</td>
<td>1.6%</td>
<td>20.1</td>
<td>52.79</td>
<td>25.01</td>
<td>09.28</td>
<td>06.02</td>
<td>1.05</td>
<td>0.56</td>
<td>2.58</td>
<td>0.99</td>
<td>52.79</td>
</tr>
<tr>
<td>GGF</td>
<td>2.60</td>
<td>1.0%</td>
<td>4.0</td>
<td>47.72</td>
<td>10.36</td>
<td>0.34</td>
<td>19.62</td>
<td>2.27</td>
<td>0.67</td>
<td>0.10</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

**Bound Materials**

Base Soil and Reclaimed Asphalt Pavement (RAP)

The base soil and RAP were obtained from a rehabilitation project that was performed by King Asphalt for SCDOT in Walhalla, SC. The samples were taken just after the passing of the reclaimer right before the process of laying cement started. The two portions were separated by sieving on No. 4 standard sieve. The tested mixtures had 35% RAP and 65% base soil which was easily controlled after separating the two portions apart. The base soil was granular, non-plastic soil, clean of organic matters. The RAP was sieved into three different sizes and the particles used for the MRB samples consisted of: 30% of passing 19.0-mm and retained on 12.5-mm, 30% passing 12.5-mm and retained on 9.5-mm, and 40% passing 9.5-mm and retained on 4.75-mm. This gradation was chosen to
represent the original RAP content from the mentioned job site. The blend of soil and RAP is classified as A-1-b according to AASHTO M-145.

![Particle size distribution of base soil + RAP](image)

**Figure 10-2 Particle size distribution of base soil + RAP**

**Tested Properties and Test Methods**

**Moisture–Density Relationships**

The purpose of this test is to determine the optimum moisture content (OMC) required to result in a maximum density of the blended materials. This test was conducted using selected mixtures at each binder ratio. The selected mixtures were Control from the cement-based stabilized group and G&S from the geopolymer stabilized group. Also, since the ponded fly ash used turned out to have a relatively high LOI value which could affect the OMC value, one mix that contained cement and PFA was tested for OMC.
Unconfined Compressive Strength

This test was performed in accordance with SCT-26, which requires two specimens for each tested mixture. The specimens were prepared using a 4-inch (100 mm) diameter proctor mold and 5.5 lbs. (2.495 Kg) rammer. Each specimen was made by compacting three equal layers using 25 blows of proctor rammer. Following the compaction of each specimen, it was extruded using a manual sample extruder. All specimens were covered and cured in a 100% humidity room at 23°C until tested. On the night the test was due, specimens were soaked overnight according to SCT-26. The CMRB specimens were tested at 7 and 28 days.

Several studies and transportation agencies have recommended minimum values for UCS. Low strengths may not be enough to support the traffic loads, while the high strength requires higher binder, and this leads to drying shrinkage cracks that could reflect on the pavement surface. Today, most agencies use unconfined compressive strength as the main or even the sole criterion based on which the optimum cement content is selected. Unfortunately, unlike the requirements for cement content based on durability criteria, the strength-based criteria for selection of cement content evolved in an incoherent manner across the country and as a result a variety of strength requirements
are specified across the country with a low of 200 psi in Louisiana to 500-750 psi in Texas to 800 psi in Arizona [19]. Also, in Europe, the minimum USC ranged from 305 psi to 725 psi for different countries [20]. Therefore, in this study, a range from 300 psi to 800 psi is to be used as the target UCS.

Modulus of Elasticity (E)

Two CMRB 4in. by 8in. cylinder specimens were prepared for this test. The procedure of this test followed ASTM C469. After testing the CMRB specimens for 28-day UCS, the 40% ultimate load was identified. The specimens were preloaded twice up to 40% of its ultimate load before the official test is performed. The value of E was taken as the slope of a line between a strain of 0.05 and 40% of the ultimate load.

Figure 10-4 Elastic modulus test setup.

Drying Shrinkage

Shrinkage is a change in volume caused by several factors, such as temperature gradients, drying, and cement hydration. Shrinkage results in cracks in the bases that can reflect through the pavement surface, triggering serious durability problems. Drying shrinkage represents the highest fraction of the total shrinkage and it is the leading cause
of cracks in CMRB [21]. High moisture content (above OMC), high clay content, poor compaction, and high amounts of stabilizing cement are factors that boost shrinkage in CMRB [21]. Water ingress through the reflected cracks in the pavement surface has major deteriorating effects that could cause complete failure of the road. Lowering cement content, increasing pavement thickness, and decreasing the minimum 7-day UCS are the main mitigation measures taken by most of the design agencies [21]. Nevertheless, lowering cement content would pose a durability problem. Hence, optimizing cement content is important and checking for shrinkage is as important as checking for strength.

There is no standard method for testing shrinkage of soil-cement. It was decided to follow the same standards and testing methods for testing length change of concrete. ASTM C157 and ASTM C490 were both followed in this test. Some test requirements had to be adjusted to suit the use of CMRB materials instead of concrete for which the standards were designed.

Wetting/Drying Durability Test (W/D Test) AASHTO T135 Method B

Durability test using the criteria of wetting and drying cycles was established in the 1930s when soil-cement started to see more developments. In this test, two Specimens were prepared. Following preparation, they should be cured for seven days in a curing room. After that, specimens are subject to what consists of one cycle of wetting and drying, which is submerging the specimens for 5 hours followed by placing them in a 71°C oven for 42 hours. The test should include 12 cycles. At the end of each cycle, wire brushing is applied to all of the surface area of the specimens twice to remove any loosened materials. The pressure applied by the wire scratch brush should be about 3-lbs. Weight loss is monitored at each cycle and the final weight loss is used to indicate durability. AASHTO
T135 – method B was followed here since the maximum size of the used materials was 19 mm (3/4”).

The first specimen (labeled No. 1 specimen) in the durability test is used to monitor volume change after each wetting and drying cycle. Volume of specimens was calculated by taking the average diameter and average height by digital caliper measurements taken at the same points each time. The wire brushing is applied on the second specimen (labelled No. 2 specimen). The 3-lb pressure applied while brushing was achieved by placing a 3-lb object on top of the wire scratch brush. At the end of all cycles, specimens were put in an 110° C oven for 24 hours and the final oven-dry masses were obtained. These masses were corrected for the amount of water of hydration retained in specimens which -according to AASHTO T135- is estimated to be 1.5% for A-1 soil.
Freeze/Thaw Durability Test (F/Z Test) ASTM D560 Test Method B

In this test, after compacting and extruding the two samples from a 4-in. diameter standard proctor mold, initial measurements for the mass and volume are taken. Then, all samples are cured for seven days in a standard curing room. Next, the samples are subjected to 12 cycles of freezing and thawing. Each cycle consists of freezing at \(-23 \pm 2^\circ\) for 24 hours, followed by thawing at the standard moist room for another 24 hours. Measurements of volume and mass are taken after each half cycle. At the end of each cycle, a brushing using wire brush is performed on one of the samples. The weight loss and volume changes are to be calculated at each cycle. Not among the ASTM D560 requirements, the UCS values are usually measured after completion of all F-T cycles and compared to the original UCS.
Tube Suction Test

For evaluating the moisture susceptibility of the stabilized base materials, the Tube Suction Test (TST) was conducted. The surface dielectric values of the samples are measured in this test, which represent the amount of free water present in the samples. The higher the dielectric value for a sample, the higher the water in the capillary pores. Higher dielectric values samples may not show good resistance for freezing and thawing cycles. This test was developed by the Texas Transportation Institute and the Finnish National Road Administration [22]. The measured Dielectric values have been correlated with the performance of CMRB in durability against W-D and F-T cycles [23], [24]. This method could be a quicker alternative and less costly option for testing the durability of CMRB. The test was conducted in accordance with Tex-144-E [25], except the sample size. It suggested the use of 6in. cylinders by 8in. length, but the test in this study was performed using the same sample sizes as the UCS and Durability samples, i.e., 4in. diameter by 4.58 in. length as the size of standard proctor mold.

In this test, three samples are compacted and extruded, two of these three are used for the TST test and the third is tested for UCS on the same day it was compacted. When
the two specimens are extruded, a dry porous stone is placed on the top and bottom separated from the surface of the specimen by a filter paper. After that, the two samples with their porous stones are placed in an oven at 140 ±9°F (60 ±5°C) for 48 ±2 hr. Next, the specimens are taken out of the oven and left to cool down for at least 2 hours. Then five initial readings for the dielectric values are taken distributed uniformly over the top surface of the specimen (four readings were taken in this study as the size of the samples was smaller). The whole set is wrapped with a latex membrane to ensure no loss in moisture occurs over the period of the test. The samples are then placed in a flat tray and water is filled to a level where a ¼ in. above the bottom porous stone is covered with water. This level of water should be maintained until the end of the test. The dielectric measurements are taken daily at about the same time for 10 days. Then the samples are tested for UCS to evaluate the retained strength, and then moisture content is measured from the whole broken samples. The final dielectric values are taken as the average of last three days of the test.

In this study, this test was only performed for the mixtures having 6% of binder for both the cement-based groups and the geopolymer-based group. The test setup is shown in Figure 10-7.
Mixture Proportion

The two binding systems that were tested in this investigation were cement-based and geopolymer-based binders. In the cementitious system, the cement was replaced by 0% (for control mixtures) and 40% with GGF and ponded fly ash (PFA). While in the geopolymer system, binders of GGF, GGF+PFA, GGF+slag were used to produce the binding geopolymer pastes. For all systems, ratios of binding agent of 6%, 9%, and 12% were all investigated. Figure 10-7 shows the different tested mixtures and a general layout for the experimental work done in this study.
Figure 10-9 Experimental program layout.

Table 10-2 Mixtures proportion and test methods.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cementitious</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6% Control</td>
<td>Cementitious</td>
<td>6%</td>
<td>0</td>
<td>0</td>
<td>√</td>
<td></td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>6% G &amp; F</td>
<td>Geopolymer</td>
<td>5.4</td>
<td>0</td>
<td>3.6</td>
<td>0</td>
<td>×</td>
<td>√</td>
<td>√</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>6% G &amp; S</td>
<td>Geopolymer</td>
<td>0.9</td>
<td>0</td>
<td>0</td>
<td>×</td>
<td>√</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>6% F</td>
<td>Geopolymer</td>
<td>4.5</td>
<td>4.5</td>
<td>0</td>
<td>×</td>
<td>√</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>6% Control</td>
<td>Cementitious</td>
<td>6%</td>
<td>0</td>
<td>0</td>
<td>√</td>
<td></td>
<td>√</td>
<td>√</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>6% G &amp; F</td>
<td>Geopolymer</td>
<td>7.2</td>
<td>0</td>
<td>4.8</td>
<td>0</td>
<td>×</td>
<td>√</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>6% G &amp; S</td>
<td>Geopolymer</td>
<td>0.6</td>
<td>0</td>
<td>6</td>
<td>0</td>
<td>×</td>
<td>√</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>6% F</td>
<td>Geopolymer</td>
<td>6.0</td>
<td>0</td>
<td>6</td>
<td>0</td>
<td>×</td>
<td>√</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
</tbody>
</table>

الأسماء:  GGF: Glass Fibers, F: Ponded Fly Ash, S: Slag
√: Performed
×: Not Performed
Results and Discussion

Moisture–Density Relationships

The moisture density relationship was tested following ASTM D558 and the results are plotted in Figure 10-10. The optimum moisture content (OMC) ranged from 8.5% to 9.5% with average of 9% as shown in the plot. Therefore, the 9% moisture were chosen to be used with all the mixtures. The moisture-density relationships for the geopolymer mixtures were conducted using the 8N NaOH solution and the results did not differ much from the cementitious mixtures at the same binder content.

![Figure 10-10 Moisture-density relationship. The dotted lines are the range of OMC for all tested mixtures.](image)

Change of Moisture Content (%MC) VS UCS

It is well recognized that the moisture content of CMRB plays an important role in achieving the maximum density. While the use of optimum moisture content in preparation of test specimens is justified in lab evaluation, achieving precisely the optimum moisture content in the field can be difficult, and in some cases the moisture
content may exceed the optimum moisture content. Particularly, in cement-modified recycled base moisture is not only needed to achieve the maximum density but also for hydration of Portland cement. In order to study the impact of moisture content on the properties of CMRB, samples with about 2% above or below the OMC is cast while conducting the OMC test.

When the optimum moisture content (OMC) was measured, CMRB samples were cast at each step of change of moisture. These samples were then tested for UCS to study the effect of deviating the moisture content from the optimum value. The results of this investigation are shown in Figure 10-11. As expected, the peaks of maximum density and the UCS relative to the moisture content are coincided as the better packing and denser structure of the stabilized soil increased the UCS. Nevertheless, analyzing the data to calculate the strength loss per unit loss of %MC revealed, as shown in Table 10-3, that the geopolymer-based stabilized mixtures had lesser variability in UCS compared with the cementitious stabilized mixtures when the moisture content differs from optimum.
The cement-based stabilized samples are more sensitive to moisture variability from optimum. The reason might be because geopolymerization reaction is not hydration reaction in nature like cement. The alkaline level in the solution will be the same even with the varying solution content, and that is what needed to initiate the geopolymerization reaction.
reactions. However, had the activator been added in dry condition, such as powder NaOH to the blend of base soil and RAP (as was observed in some studies), then water had been added to reach level of OMC, the variation here would be noticeable. Because the change of amount of water may render lower alkalinity in the pore solution, which would slow the geopolymer reaction mechanism. High alkalinity is required to dissolve the aluminosilicate network, especially with fly ash.

**Unconfined Compressive Strength (UCS)**

All the results from all mixtures are presented in Figure 10-12. There is a box provided in the same figure to denote the range of acceptable UCS. As expected, the strength increases with the increase of the binder dosage level. Also, the continuous increase in UCS between 7 and 28 days. It can be noted that the geopolymer-based stabilization group has higher ratio of 28-day to 7-day UCS. This indicates that the geopolymer reaction at ambient temperature is slower than the cement hydration. All of the DOTs use the 7-day UCS to determine the required cement content instead of 28-day UCS. If the geopolymer-based method is to be promoted for use in FDR, this study recommend checking both 7 and 28-day UCS as it might be highly stronger than the required, which could cause shrinkage cracks to reflect on the pavement surface followed by moisture ingress and deterioration.
For the geopolymer-based mixtures, the G&S group had the highest UCS followed by G group and G&F group. Both the 6% G&F and 9% G&F failed to obtain the minimum UCS at 7 days, but the 28-day UCS was higher than the lower limit for both. For all the geopolymer-based stabilized samples, the 28-day UCS was higher than the 7-day UCS by at least 42% and the % increase in geopolymer stabilized samples were higher than the cement stabilized samples. Comparing G&S geopolymer group with the Control group, the UCS was lower at 7 days for all binder ratios, while it was higher at 28 days. It should be noted that no heat curing was utilized to accelerate the strength development for the geopolymer, instead, it was cured at ambient temperature. Therefore, it could be inferred that the geopolymerization reactions had a slower early-age rate than the cement hydration, but they continue at a faster rate in later age at ambient temperature curing.
Two specimens were tested for each mixture at each age. The overall average and median differences of all the tested UCS specimens were 9.71 and 11.29, respectively. The average and median differences for the cement-based stabilized samples were a little lower than the geopolymer-based stabilized samples. This could most likely be attributed to better dispersion of the cementitious paste and for the faster rate of cement hydration at early age forming hydration products before even the base soil materials were mixed. Unlike the geopolymer paste reactions which are slower at early age at ambient curing temperature. Note that ASTM D1633 stipulates no specific value for average and median differences but it does mention the values of 8.1% and 6.1% taken from a related study.

**Flexural Strength**

The results of testing CMRB prisms for flexural strength are shown in Figure 10-13, and a correlation with UCS and natural resonance frequency in both flexural and torsional modes is also presented in the same figure. The ratio of modulus of rupture ($F_r$) to UCS at 7 and 28 days ranged from 25% to 35% and from 12% to 25%, respectively. According to Thompson, 1986 [26] the flexural strength to UCS of CTAB ranges from 20% to 25%, this applied here only to the cement-based stabilized mixtures in respect to their 28-day UCS as well as the 6% G&S from the geopolymer-based stabilized mixtures. The correlation of $F_r$ with UCS at 7 and 28 days revealed that the two properties are highly correlated at 7 days than 28 days of sample age. additionally, the natural resonance frequency taken for the flexural CMRB prisms correlated very well with the results of $F_r$. 
In concrete, the relationship between the modulus of rupture and the square root of the compressive strength is equal to 7.5. Evaluating the results gained from this study for the CMRB mixtures, it can be concluded that this relationship comes close to 7.5 at higher UCS. At 7 days, and for the Control and the 6% G&S mixtures, which had the highest UCS, this number was 7.3. Then it follows the reduction in UCS to be 6.5, 5.8, and 3.8 for 6%40%PFA, 6%40%G and 6% G, respectively. It should be noted that these numbers are reduced when examining the same relationship at 28-day UCS.

**Drying Shrinkage**

The results of drying shrinkage test are shown in Figure 10-12. The control mixtures group had the lowest drying shrinkage among the tested mixtures. The higher the binder content the less the drying shrinkage. This concept also valid in the two
geopolymer tested mixtures (6% G&S and 9% G&S). Comparing the 40% replacement of GGF and PFA, the 6%40%G had a significantly higher shrinkage than the 6%40%F. the higher fineness of GGF than PFA might have been the reason that caused the higher shrinkage. The shrinkage rate of the two tested geopolymer-based stabilized mixtures was higher than the cement-based stabilized mixture. The reason would possibly be that the geopolymerization reactions are not hydration reaction, but actually they released amounts of water, unlike the cement hydration. If the amount of water released is higher than the formation rate of geopolymer products to fill in the created voids, shrinkage may occur leading to cracks.

![Figure 10-14 Drying shrinkage results.](image)

**Wetting/Drying Durability Test (W/D Test)**

The results of the W/D test are presented in Figure 10-15. As it can be seen, the 6% Control mixture experienced the least weight loss because of the W/D cycles and the metal
wire brushing after each cycle. In contrast, the 6%40%G had the highest weight loss. It should be noted that the three geopolymer-based mixtures had weight losses averaged between the control and the 6%40%G. while performing this test, the drying at 71 °C for 42 hours seemed to further improve the strength of the geopolymer-based stabilized samples, which could yield a false positive results of W/D cycles durability. The freezing and thawing (F/T) test would be a better indicative of the performance of such mixtures. The final mass losses were 4.14%, 6.48%, 5.1%, 4.46%, and 5.19% for 6%Control, 6%40%G, 6% GGFG, 6% G&F, and 6% G&S, respectively.

![Weight Loss% for W/D Durability Test](image)

Figure 10-15 W/D durability test results.

Results for weight loss from the wire brushing ranged from 4% to 8.5% as shown in the figure. There were no significant volume changes in the specimens after 12 cycles of wetting and drying. For acceptable performance of CMRB in terms of durability, maximum weight loss limits were established based on soil classification [19]. For A-1 soil, the limit is 14%, which is higher than all weight losses for the tested mixtures. Since the
only binder ratio tested here was 6%, higher binder ratios are anticipated to yield good performance too in this test because of the small values of weight loss observed here.

**Freeze/Thaw Durability Test (F/Z Test)**

The performance of the tested mixtures in resisting deterioration by freezing and thawing is shown in Figure 10-16. The 6%Control and the 6% G&S performance performed the best followed by 6%40%G and 6% G. As for the 6% G&F mixture failed the test having had significant mass loss (more than 14% as per PCA guidelines [27]). In fact, the No. 1 specimen that was made to monitor volume change was failed and broken at the F/T cycle no. 11, as shown in Figure 10-17.

![Percent Mass Loss at Each F/T Cycle](image)

Figure 10-16 F/T test results.
Figure 10-17 F/T specimens: the left picture was taken at the beginning of the test, and the right picture was for (6% G&F) specimens after 11 cycles of F/T.

**Tube Suction Test**

The final measurements of the dielectric values (DV) from this test are shown in Table 10-4. The 6%Control had the lowest value followed by the 6%G&S and 6%40%G. The maximum value was recorded for the geopolymer-based sample of 6%G. The increase in DV value has been associated with a decrease in the retained UCS after the period of capillary suction [28], [29]. Additionally, the DV values have been reported to correlate well with the W/D test results of residual UCS and mass loss [30]. Figure 10-18 shows correlation between the mass losses obtained in W/D and F/T durability tests. The tested mixtures were separated to the two groups of cement-based CMRB and geopolymer-based CMRB. The determination factor R² indicates very good correlation with the mass losses of cement-based group in both the F/T and W/D tests. Also, the positive correlation between the two tests show in increase in mass loss with increase in DVs, which makes sense. However, the geopolymer-based group results of both durability tests did not show good correlations with the DV values. The geopolymer binders behave differently than cement binders in terms of exposure to cycles of wetting and drying. It is thought that these cyclic conditioning of the geopolymer stabilized CMRB would increase the strength,
and thus, less mass loss would be recorded. Nevertheless, it seems that the geopolymer stabilized CMRB has substantially lower resistance to F/T cycles. In this case, this study suggests the use of F/T durability tests over the W/D test for geopolymer-based stabilized CMRB.

Table 10-4 the Final dielectric values from the tube suction test results

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>6%Control</td>
<td>5.175</td>
</tr>
<tr>
<td>6%40%PFA</td>
<td>6.643</td>
</tr>
<tr>
<td>6%40%G</td>
<td>5.913</td>
</tr>
<tr>
<td>6% G</td>
<td>6.825</td>
</tr>
<tr>
<td>6% G&amp;F</td>
<td>6.575</td>
</tr>
<tr>
<td>6% G&amp;S</td>
<td>5.738</td>
</tr>
</tbody>
</table>

Figure 10-18 Correlation between dielectric values and W/D and F/T test results

**Compressive Strength from Portions Broken in Flexure**

After one year of storage at room temperature, broken portions from the prisms that were used to test flexural strength and drying shrinkage were used to test UCS again
in accordance with ASTM D1634, the modified cube method. The results of this test are shown in Table 10-5, and the percent increase compared to the 7-day UCS is also shown in the same table. As it can be seen, the strength gain is still continuing for the geopolymer-based stabilized samples. The % increase was higher for all the geopolymer-based mixtures (highlighted in orange) than the cement-based ones (highlighted in green).

Table 10-5 Results of UCS taken from broken prism samples

<table>
<thead>
<tr>
<th>Label</th>
<th>Avg. UCS, psi</th>
<th>7-day UCS</th>
<th>% increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>6%Control</td>
<td>960.00</td>
<td>505.00</td>
<td>90.10</td>
</tr>
<tr>
<td>9%Control</td>
<td>1420.00</td>
<td>665.00</td>
<td>113.53</td>
</tr>
<tr>
<td>12%Control</td>
<td>1360.00</td>
<td>705.00</td>
<td>92.91</td>
</tr>
<tr>
<td>6%40%F</td>
<td>670.00</td>
<td>325.00</td>
<td>106.15</td>
</tr>
<tr>
<td>6%40%G</td>
<td>850.00</td>
<td>395.00</td>
<td>115.19</td>
</tr>
<tr>
<td>9%40%G</td>
<td>910.00</td>
<td>555.00</td>
<td>63.96</td>
</tr>
<tr>
<td>12%40%G</td>
<td>1615.00</td>
<td>760.00</td>
<td>112.50</td>
</tr>
<tr>
<td>6% G</td>
<td>1000.00</td>
<td>270.00</td>
<td>270.37</td>
</tr>
<tr>
<td>6% G&amp;F</td>
<td>730.00</td>
<td>215.00</td>
<td>239.53</td>
</tr>
<tr>
<td>6% G&amp;S</td>
<td>1240.00</td>
<td>565.00</td>
<td>119.47</td>
</tr>
<tr>
<td>9% G&amp;S</td>
<td>1925.00</td>
<td>630.00</td>
<td>205.56</td>
</tr>
</tbody>
</table>

It was mentioned earlier that having a high UCS is not desirable for CMRB. As it can be seen, some of the CMRB mixtures have passed 1000 psi in UCS and this is well above any transportation agency maximum values. Although there is a high chance that having a high strength after one year of service is not problematic, but this study suggests running some extra durability tests especially drying shrinkage, W/D and F/T tests to ensure that the improvements in the performance on the long term are still maintained.

Conclusions

Full depth Reclamation (FDR) is increasingly becoming the standard rehabilitation strategy for asphalt pavements for most of the transportation agencies,
which is accompanied with a vast increase of cement. This study explored different alternatives for the use of cement in FDR. Two binding systems were tested: the cementitious binding system and the geopolymer-based binding system. Ground glass fibers, ponded fly ash, and slag were used in these systems. The following conclusions can be drawn from the current study:

1- There was no significant difference in the amount of water and alkali solution needed to raise the moisture content to the optimum level. All the tested mixtures for OMC ranged from 8.5% and 9.5%.

2- The geopolymer-based stabilized mixtures had lesser variability in UCS compared with the cementitious stabilized mixtures when the moisture content deviates from optimum.

3- The possibility of replacing 40% of cement by GGF and PFA in CMRB as the resulting 7-day UCS was in the minimum range established in this study.

4- Geopolymer stabilized CMRB samples experienced higher drying shrinkage than the cement-based mixtures. The probable attribute to this as suggested was that the reaction mechanism in geopolymer is not like cement based on hydration, rather the geopolymer reactions release some water that may leach out causing more drying. This suggestion needs further investigation.

5- The criteria of selecting an optimal mix design based on the UCS for the geopolymer-based stabilized mixtures is not enough. It should also include testing the durability both W/D and F/T test, especially the F/T test. Both stabilization systems were capable of resisting the W/D cycles and the mass losses were less than 8%. The geopolymer-based stabilized samples experienced significantly less mass loss compared to the cement-based stabilized CMRB samples. However, in
F/T test, the geopolymer-based CMRB had weak resistance to deterioration caused by freezing and thawing cycles.

6- The tube suction test results represented in the dielectric values have correlated very well with W/D and F/T test results for the cement-stabilized CMRB group, but the correlation with the geopolymer-based CMRB was weak. This study suggests that the problem is not in the TST itself, but the need to adjust the durability tests for the geopolymer-based stabilization.

Finally, this study encourages the use of several industrial wastes such as the off-spec glass fibers and the ponded fly ash to replace the use of cement in FDR either partially or fully. This promotes sustainability on all the levels for environmental, social and economic perspectives.
References


Chapter 11

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

This study intended for optimizing the use of different classes of fly ash and enhancing their performance in Portland cement concrete and geopolymer concrete. These classes of fly ash included both standard fly ashes that meet specification requirements and off-spec fly ashes that do not meet at least one of the specification requirements. The proposed solution that was investigated in this study was blending fly ash with ground glass fibers (GGF). Using this combination, certain performance deficiencies in portland cement concrete and geopolymer concrete were targeted for each of the following fly ashes: class C fly ash (CFA), class F fly ash (FFA), and off-spec fly ashes (OSFA). The following conclusions were drawn from this study:

For CFA, as outlined in the work included in chapter 4 and 5, the ternary blend of GGF and CFA had shortened the setting time at the investigated high dosage level (at cement replacement of 40%). The long setting time is considered a performance deficiency associated with CFA at high levels. The high dosages of CFA are inevitable because they are needed to address durability related problems such as alkali-silica reaction (ASR) or sulfate attack. The ternary blends of GGF+CFA have improved the fresh properties of both mortar and concrete and enhanced the early-age strength at the evaluated cement replacement level. Similar enhancements were observed for FFA+GGF ternary mixtures in terms of early-age strength and flowability or mortar. The ternary CFA+GGA also experienced a reduced drying shrinkage compared to the binary CFA mixture. At the same time, the ternary blend significantly helped boost the performance of mitigating ASR and resisting sulfate attack and chloride ion penetration. The combinations of 10% GGF with
30% CFA and 20% GGF with 20% CFA by mass of the binder appear to be the optimal blending levels to improve performance in terms of SAI, drying shrinkage, resistance to ASR and sulfate attack. Comparing the performance of binary mixtures, The GGF-containing mixtures had higher early compressive strength even at high replacement ratio of 40% for both mortar and concrete.

The resistance of in-spec fly ashes (CFA & FFA) in binary in ternary blends with GGF to chloride ion penetration was investigated and the results were discussed in chapter 6. It was included that the GGF-containing mixtures had a substantially better resistance to chloride ion penetration than the fly ash-based mixtures. In assessing the chloride penetration of concrete, both tested methods which were the Rapid Chloride Penetration Test (RCPT) and the Rapid Migration Test (RMT) have shown comparable results. The RCPT and RMT results were highly correlated with the measured surface resistivity of concrete.

The excellent performance of the ternary blend was attributed to the exceptional pozzolanic reactivity of GGF, the small particle size, and high surface area. All these properties of GGF has contributed to densifying the mortar and concrete structure, reducing permeability, and enhancing porosity. The findings from the TGA, the percent absorption, sorptivity, surface resistivity, and the chloride migration coefficient corroborate the performance observed.

For the off-spec fly ashes, all the selected ashes from the ash ponds had a high LOI. The LOI ranged from 6% to 20% for the four characterized fly ashes. Full characterization results can be found in chapter 3 of this dissertation. In terms of particle size distribution, only the particles finer than 75 microns were used in this study and they represented more than 75% of the as-received ponded ash. This enhancement of the particle size not only
important for pozzolanic activity but it is also significant to slightly reduce the LOI of the ash. The LOI is usually presented in the coarser particles of fly ash. Two of the characterized fly ashes were selected for investigation of performance in cement and geopolymer mortar and concrete.

Chapter 7 represents the work of high LOI fly ash (RFA) blended with GGF as supplementary cementitious material (SCM) in cement mortar and concrete. In addition, the RFA+GGF was briefly explored as precursors for geopolymer mortar, but despite the noticed enhancement no significant compressive strength was observed. However, both fresh properties represented in flow of mortar and slump of concrete and the hardened properties represented in SAI and compressive strength of concrete are all improved in the ternary cement+RFA+GGF blended mixtures. The combination of high LOI fly ash and GGF improved the performance of ASR mitigation even at a low dosage of GGF. The mixture 10R10G which had only 20% replacement of cement by the combined blend of RFA and GGF was able to fully mitigate ASR in MCPT test. The main performance deficiency associate with the high LOI is that it affects the air content of concrete. However, and based on the foam index test, the combined blend of 10R10G required less AEA to achieve the same air content in concrete than the binary RFA. This would help increase the resistance to freezing and thawing cycles and at the same time, it did not significantly affect the compressive strength since smaller amounts of AEA was added to obtain the target air content.

The other selected ponded fly ash (CSFA) was the one with the lowest LOI among all the ponded ashes and it was investigated as a precursor for geopolymer mortar and concrete. To ensure sustainability, the blends of GGF and CSFA were activated by using NaOH solution only, as the use of sodium silicate is the main contributor to the
geopolymer total carbon footprint. The pure fly ash mixture did not yield any significant compressive strength even when heat-cured at 60 °C for 24 hrs. in addition, the use of sodium silicate solution along with NaOH solution to activate the pure CSFA rendered a very sticky mortar that was difficult to be handled and cast. However, when the fly ash is blended with GGF significant improvement in the compressive strength was observed. The use of GGF to replace the necessity of using sodium silicate solution with fly ash geopolymer mixtures has been proved successful. At 60 °C curing for 24 hours, a percent increase in strength from 44% to 220% were achieved for 10% to 50% replacement ratios.

Chapter 9 details the results of the feasibility study of using all the four characterized ponded fly ashes as a cement replacement in cement modified recycled bases (CMRB) following the procedures for full depth reclamation (FDR) of asphalt pavement. The study concluded the possibility of using 20% replacement of cement at the tested binder ratios of 3%, 6%, and 9%. It was also concluded that higher unconfined compressive strength (UCS) resulted in CMRB bases with smaller amount of cement when high replacement ratio (40%) was used in CMRB. All the tested mixtures have passed the wetting and drying (W/D) durability test and showed a slightly higher shrinkage than that of the pure cement stabilized CMRB.

The search for cement alternatives to be used in FDR was further investigated in the work presented in chapter 10. Another purpose of this investigation was to compare the current practice followed in FDR by cement with FDR using geopolymer-based stabilization using 8N NaOH alkali solution. There was no much difference between the optimum moisture ratio (OMC) obtained for both systems of stabilization at the tested binder ratios of 6%, 9%, and 12%. Also, the geopolymer-based stabilized mixtures had lesser variability in UCS compared with the cementitious stabilized mixtures when the
moisture content deviates from optimum. Geopolymer stabilized CMRB samples experienced higher drying shrinkage than the cement-based mixtures. The probable attribute to this as suggested was that the reaction mechanism in geopolymer is different than cement which is based on hydration. Rather, the geopolymer reactions release some water that may leach out causing more drying. The geopolymer-based stabilized samples experienced significantly less mass loss compared to the cement-based stabilized CMRB samples. However, in F/T test, the geopolymer-based CMRB had weak resistance to deterioration caused by freezing and thawing cycles. Therefore, it was suggested that when designing geopolymer-based stabilized pavement materials the sole dependence on UCS should not be the followed practice. W/D and F/T test must be conducted to confirm the performance of geopolymer-based stabilized bases.

Finally, this study helps reduce the environmental burdens of the ash that has long stored in ash ponds and promotes its use in concrete to reduce the cement and the associated carbon emissions. The use of GGF along with fly ash is an excellent option to alleviate the declining supplies of fly ash and to enhance the durability performance of fly ash-containing concrete mixtures.

**Recommendations**

The use of GGF to partially replace CFA at high replacement levels (as much as 50% in the SCM blend, with an overall replacement level of cement at 40%) appears to be a viable option to account for the dwindling supplies of fly ash and to boost the performance of CFA in mitigating ASR and sulfate attack. Although the beneficial effects of GGF in mitigating ASR and sulfate attack are proven in this study, additional research is needed to determine the precise mechanism involved. It is recommended to further
investigate the microstructure of concrete to confirm the enhancement in reducing permeability, improving porosity, and densifying the structure of concrete.

A similar study is recommended for blends of class F fly ash and GGF in mitigating ASR and resisting sulfate attack. Although it is well known that class F fly ash performance in mitigating ASR is very good, the blend of FFA and GGF may offer a good option to aid the shortage of FFA in some regions.

The inclusion of GGF into the off-spec fly ash binary mixtures could alleviate the environmental implications of ash ponds and offer a new avenue where all the stored fly ashes can be utilized. However, further environmental study needs to be conducted to investigate the effect of the presence of heavy metals and hazardous elements in the ash on the concrete and the possibility of leaching them out to the surrounding environment.

The off-spec fly ash tested in this study were all proven to successfully partially replace cement in FDR projects. It is recommended, however, to study different way by which the off-spec fly ash can be utilized in FDR. For example, the possibility of mixing the ash in its original form with base soil and RAP before the addition of cement. The presence of fly ash in the blend would certainly enhance the overall performance of the stabilized layer and may reduce the amount of cement needed to reach the required UCS.

All the results obtained in the FDR-related studies were in a laboratory setting and they need to be further explored in field. Also, the compliance of geopolymer-based stabilized base materials with all the current practices followed in FDR with cement needs to be further investigated.
Chapter 12

APPENDICES
Appendix A


The results of leaching tests (US EPA Methods 1311 and 1313 pH natural) conducted on the five soil stabilization samples prepared at Clemson University are summarized in the table below. The mix blends include 9% binder content composed of either 0% coal fly ash/100% cement in the control sample or 40% coal fly ash/60% cement in the Roxboro, Marshall, Cliffside, and Riverbend samples. Full descriptions of the test methods and results are presented in the subsequent pages of the report.

In conclusion, the concentrations of the elements leached from all five mixes, for both Method 1311 and Method 1313 at pH Natural, are less than the RCRA regulatory concentration limits and the hazardous waste screening criteria (table above).

<table>
<thead>
<tr>
<th>Element</th>
<th>Range of leached values from all CFA/PC samples (Leached values from control samples)</th>
<th>Regulatory Limits for elements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TCLP Method 1311</td>
<td>Method 1313 pH Natural</td>
</tr>
<tr>
<td></td>
<td>Average Concentration (mg/L)</td>
<td>Average Mass (mg/Kg)</td>
</tr>
<tr>
<td>Ag</td>
<td>0.00 (0.00)</td>
<td>0.00 (0.00)</td>
</tr>
<tr>
<td>As</td>
<td>0.005 – 0.010 (0.003)</td>
<td>0.10 – 0.20 (0.05)</td>
</tr>
<tr>
<td>B</td>
<td>0.081 – 0.303 (0.039)</td>
<td>1.61 – 6.06 (0.77)</td>
</tr>
<tr>
<td>Ba</td>
<td>0.021 – 0.032 (0.016)</td>
<td>0.40 – 0.63 (0.32)</td>
</tr>
<tr>
<td>Cd</td>
<td>0.00 (0.00)</td>
<td>0.00 (0.00)</td>
</tr>
<tr>
<td>Cr</td>
<td>0.249 – 0.286 (0.311)</td>
<td>4.98 – 5.73 (6.22)</td>
</tr>
<tr>
<td>Pb</td>
<td>0.008 – 0.010 (0.008)</td>
<td>0.15 – 0.20 (0.15)</td>
</tr>
<tr>
<td>Se</td>
<td>0.019 – 0.036 (0.020)</td>
<td>0.38 – 0.72 (0.40)</td>
</tr>
</tbody>
</table>