Exploring Strengthening Mechanisms for Class C and Class F Fly Ash in Load Bearing Floor Tile Applications

by

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Table of Contents

1. ABSTRACT ................................................................................................................................................. 4

2. INTRODUCTION AND THEORY .............................................................................................................. 5
   2.1 COAL COMBUSTION PRODUCTS (CCPs) ................................................................................................. 5
   2.2 FLY ASH TILES ........................................................................................................................................ 5
   2.3 FLY ASH .................................................................................................................................................. 7
   2.4 RECYCLING FLY ASH ............................................................................................................................. 9
   2.5 CURING CHEMISTRY ............................................................................................................................... 9
   2.6 CALCIUM OXIDE ..................................................................................................................................... 11
   2.7 CALCIUM CHLORIDE ............................................................................................................................. 12
   2.8 SODIUM SILICATE .................................................................................................................................. 12
   2.9 AIR ENTRAINMENT AGENT .................................................................................................................... 13

3 EXPERIMENTAL DESIGN ............................................................................................................................. 13
   3.1 FABRICATION METHOD .......................................................................................................................... 13
   3.2 FLY ASH ADDITIVES ............................................................................................................................... 14
   3.3 CHARACTERIZATION METHODS ............................................................................................................ 15
       3.3.1 Compressive Strength Testing ........................................................................................................ 15
       3.3.2 Flexural Strength Testing .............................................................................................................. 16
       3.3.3 Impact Testing Setup ..................................................................................................................... 16
       3.3.4 Water Absorption Testing ............................................................................................................ 17
       3.3.5 Freeze-Thaw Cycle Testing ......................................................................................................... 18

4 RESULTS AND DISCUSSION ........................................................................................................................ 18
   4.1 INITIAL COMPOSITION SELECTION ..................................................................................................... 18
       4.1.1 Compressive Strength .................................................................................................................... 20
       4.1.2 CaO additive .................................................................................................................................... 21
       4.1.3 CaCl₂ additive ............................................................................................................................... 22
       4.1.4 Varying Curing Time ..................................................................................................................... 23
       4.1.5 Trace elemental analysis ............................................................................................................... 25
       4.1.6 Air Detrainer .................................................................................................................................. 27
       4.1.7 Air Entrainer .................................................................................................................................. 27
   4.2 FLEXURAL STRENGTH ............................................................................................................................ 28
   4.3 FREEZE-ThAW CYCLING ......................................................................................................................... 29
   4.4 WATER ABSORPTION ............................................................................................................................. 30
   4.5 DENSITY .................................................................................................................................................. 31
   4.6 IMPACT TESTING .................................................................................................................................. 32

5 CONCLUSION .................................................................................................................................................. 33

6 FUTURE WORK ............................................................................................................................................... 35

7 ACKNOWLEDGEMENTS ............................................................................................................................... 35

8 WORKS CITED .................................................................................................................................................. 36
List of Figures

Figure 1: Coal Combustion Products Generation and Use .............................................................. 5
Figure 2: SEM Image of Class F Fly Ash ..................................................................................... 8
Figure 3: Powder Elemental Analysis of Class F Fly Ash ............................................................. 8
Figure 4: Schematic of C-S-H Fibril Formation ......................................................................... 10
Figure 5: SEM Image of Reacted Class F without Fibril Formation .......................................... 11
Figure 6: SEM Image of Reacted Class C Fly Ash with C-S-H Fibril Formation ...................... 11
Figure 7: Flexural Strength Testing Experimental Setup on Instron ........................................ 16
Figure 8: Impact Resistance Testing Setup ................................................................................ 17
Figure 9: Visible cracking after 60 days ...................................................................................... 19
Figure 10: Class C and Class F samples unable to withstand water immersion ...................... 19
Figure 11: Compressive Strengths of different water to fly ash compositions ........................ 21
Figure 12: Effect of CAO addition on compressive strength .................................................... 22
Figure 13: Effect of CaCl2 addition on compressive strength ................................................... 23
Figure 14: Effect of curing time on strength of Class C samples ............................................. 24
Figure 15: Effect of curing time on strength of Class F samples ............................................. 25
Figure 16: XRD elemental analysis of curing water ................................................................... 26
Figure 17: Effect of Air Detrainer on Compressive Strength .................................................... 27
Figure 18: Effect of air detrainer on compressive strength ....................................................... 28
Figure 19: Effect of freeze-thaw cycling on compressive strength ......................................... 30
Figure 20: Water absorption is decreased by a sodium silicate immersion .............................. 31
Figure 21: Indentation in Class F sample after impact .............................................................. 32
Figure 22: Indentation in Class C sample after impact .............................................................. 33

List of Tables

Table 1: ASTM Standards for Ceramic Tiles ............................................................................. 6
Table 2: Fly Ash Elemental Composition ................................................................................... 7
Table 3: Element Analysis of Curing Water ............................................................................... 26
Table 4: Flexural Strength Values ............................................................................................. 29
Table 5: Density of Fly Ash Tiles ............................................................................................... 31
Table 6: Optimal Final Conditions .......................................................................................... 34
Table 7: Properties of final composition of tiles .................................................................... 34
1. Abstract

Approximately 62.8 trillion kJ are consumed annually worldwide in the manufacturing process of traditional clay tiles. With this in mind, the goal of this project was to develop an eco-friendly alternative to clay tiles that maintain the ASTM building code standards. Through experimentation, a fly ash tile was produced that consumes 99% less energy in the manufacturing process than commercial clay tiles. The final product is a fly ash tile composed of two classes of fly ash, water, and several additives to strengthen the material. Standard ASTM tests were conducted. This fly ash tile is an energy efficient clay-tile alternative that excels in many mechanical properties.
2. Introduction and Theory

2.1 Coal Combustion Products (CCPs)

According to the U.S. Environmental Protection Agency, Coal Combustion Products are byproducts generated from the process of burning coal. Fly ash, boiler slag, and desulfurization gypsum are common CCPs and are used in many different fields. Despite the usefulness of many of these byproducts, under 40% of the products are recycled (Figure 1). There is therefore tremendous potential in utilizing these materials.

![Figure 1: Coal Combustion Products Generation and Use](image)

2.2 Fly Ash Tiles

Currently, there is a ready market for fly ash tiles, as 18.5 billion square feet of ceramic tiles are sold annually in the United States. However, the manufacturing process of clay
tiles generally includes a firing step that requires 62.8 trillion kJ to be consumed annually worldwide\(^3\). Thus, there is an unmet need to reduce the energy consumption during the manufacturing stage. One way to eliminate the firing method is to replace clay with fly ash, thereby taking advantage of the cementitious and pozzolanic properties of the fly ash. These energy conservation benefits, coupled with the recycling of an otherwise waste material, make for an environmentally conscious product. Additionally, there are currently few applications for class F fly ash because of its low calcium oxide content. Thus the goal of this project is to develop a novel method of creating tiles with both classes F and C fly ash that maintain the industry-accepted quality (Table 1) while reducing manufacturing energy consumption by approximately 99%.

### Table 1: ASTM standards for ceramic tiles

<table>
<thead>
<tr>
<th>Property</th>
<th>ASTM Minimum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive Strength(^4)</td>
<td>Standard: 9.7 MPa</td>
</tr>
<tr>
<td>(1.5”H x 1”D)</td>
<td>Heavy: 17.2 MPa</td>
</tr>
<tr>
<td>Flexural Strength(^5)</td>
<td>Floor: 31.65 MPa</td>
</tr>
<tr>
<td>(3”x1.5”x0.3”)</td>
<td>Wall: 11.39 MPa</td>
</tr>
<tr>
<td>Freeze-Thaw Cycling(^6)</td>
<td>Low-grade: 5 cycles</td>
</tr>
<tr>
<td></td>
<td>High-grade: 15 cycles</td>
</tr>
<tr>
<td>Water Absorption(^7)</td>
<td>Vitreous: 7%</td>
</tr>
<tr>
<td>(wt %)</td>
<td>Non-vitreous: 20%</td>
</tr>
</tbody>
</table>

To reach these values, many processes were optimized and additives were introduced. The processes studied here include the optimization of the ratio of water to fly ash, the curing method (humidity chamber and/or water bath), and the curing time. Additives
considered include calcium oxide, calcium chloride, and air entrainment agents to improve strength, sodium silicate to reduce water absorption and increase integrity.

2.3 Fly Ash

Fly ash, a ferroaluminosilicate powder, is a waste product of coal combustion. The American Society for Testing and Materials (ASTM) classifies fly ash based on oxide content; a minimum of 50% silicon-, aluminum-, and iron oxide content is required of class C fly ash, and greater than 70% is needed for class F (Table 2) and are classified according to ASTM C618. The high calcium oxide content in Class C makes it cementitious, causing it to harden when mixed solely with water. Class C fly ash is used mostly in materials where high early strength is important. Class F is pozzolanic, since it has less than 15% calcium oxide, such that calcium oxide must be added to the fly ash for cementitious properties to result.

<table>
<thead>
<tr>
<th>Table 2: Fly Ash Elemental Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Materials</td>
</tr>
<tr>
<td>SiO2</td>
</tr>
<tr>
<td>Al2O3</td>
</tr>
<tr>
<td>Fe2O3</td>
</tr>
<tr>
<td>CaO</td>
</tr>
</tbody>
</table>
Figure 2 is an SEM micrograph of class F fly ash powder. There is a size distribution of particles ranging from 5-100μm.

As can be seen in the elemental analysis in Figure 3, where the purple shade represents calcium, the larger particles in the Class F fly ash have less calcium than the smaller particles, but they include more aluminum and iron, which are both important for the curing process. Additionally, these large particles act as nucleation sites during the C-S-H fibril formation.
2.4 Recycling Fly Ash

Due to the cementitious nature of class C fly ash, it can be recycled as an additive in cement and bricks\textsuperscript{11}. Fly ash that remains in landfills poses an environmental threat; when wind blows the powder, the harmful trace elements (e.g. mercury, arsenic, lead, etc.) may contaminate rivers and lakes, and the small particle size may introduce harmful respiratory effects for people living nearby. In the United States, however, only 38.1\% of the 110.4 million metric tons of fly ash produced annually is recycled\textsuperscript{12}. This fly ash is spread across the continental United States, with class F mainly produced on the east coast and class C on the west coast\textsuperscript{13}.

Using fly ash in place of natural materials can yield benefits to the environment, economy, and product performance improvements by saving source materials, reducing energy consumption, and greenhouse gas emissions.

2.5 Curing Chemistry

Calcium silicate hydrate (C-S-H) is the main product of the hydration of cementitious materials and is primarily responsible for the strength of these samples due to covalent, ionic, and Van der Waals forces within the structure. The configuration ranges from poorly crystalline in some areas to amorphous in other regions. A schematic of C-S-H fibril formation is shown in Figure 4. It forms a nanometer scale fiber matrix that binds the original particles into a cementitious phase, which then sets and hardens into a stronger material.
These flakes or fibrils greatly decreases the permeability of the cement because the C-S-H fibrils fill the spaces in the material. Hydration rates vary depending on the sample, so setting time and hardening rate vary with composition of the material. Calcium content is necessary for the fibril formation, illustrated in the reaction below. Due to low calcium content, the Class F unreacted samples did not exhibit fibril formation (Figure 5), while the Class C samples did (Figure 6). Silicate chains are replaced with hydroxyls which then produce Ca-OH.

\[
\text{Fe}_x\text{Al}_y\text{Si}_z\text{O}_z + \text{Ca(OH)}_2 \rightarrow (\text{CaO})_x(\text{SiO}_2)_y(\text{H}_2\text{O})_z + \text{Fe}_2\text{O} \cdot 2\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} + 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O} + \text{Ca(OH)}_2
\]

where \(\text{Fe}_x\text{Al}_y\text{Si}_z\text{O}_z\) is the fly ash, \(\text{Ca(OH)}_2\) is the lime component, and \((\text{CaO})_x(\text{SiO}_2)_y(\text{H}_2\text{O})_z\) is the calcium silicate hydrate ("C-S-H" binder phase).
2.6 Calcium Oxide

Calcium oxide (CaO) is a white alkaline crystalline solid at room temperature. The chemical reaction of interest involves the addition of water. As the calcium oxide hydrates, the exothermic reaction below results.

\[
\text{CaO + H}_2\text{O} \rightleftharpoons \text{Ca(OH)}_2
\]

As a counter to class C's cementitious properties, in pozzolanic materials (i.e. class F), only small particles in conjunction with water and calcium oxide can form cementitious mixtures. The reaction with calcium above allows the material to set and harden.
2.7 Calcium Chloride

Calcium chloride (CaCl₂) is a salt of calcium and chloride, which is solid at room temperature and provides calcium ions in solution. Literature has indicated that the additional calcium from CaCl₂ acts as a reagent that drives the pozzolanic reaction forward towards the production of C-S-H fibrils¹⁶. Thus, in this project, calcium chloride was added in order to increase the reaction rate of the fly ash and improve the mechanical properties of the tiles.

2.8 Sodium Silicate

Sodium silicate (Na₂SiO₃) is a white powder that is soluble in water and forms a glassy silica gel when heated in the reaction below.

\[ \text{Na}_2\text{CO}_3 + \text{SiO}_2 \rightarrow \text{Na}_2\text{SiO}_3 + \text{CO}_2 \]

Silicates are widely used to activate pozzolans, since the cation activates the siliceous material and the chain polymeric anion contributes to the formation of calcium silicate hydrate¹⁷. For these reasons, it has been included in cements, refractories, and tile processing¹⁸. Moreover, sodium silicate is a good additive for strengthening materials. Immersing tiles in a sodium silicate solution helps to increase durability and water resistance by polymerizing the surface silicates¹⁹.
2.9 Air Entrainment Agent

Air entrainment agents, often used to strengthen concrete bricks, create microscopic bubbles in materials. Without air entrainment agents, excess water evaporates and leaves pores. When these pores are later filled with water, the water in these pores expands, often resulting in cracking. The addition of an air entrainment agent often helps reduce water absorption levels and increases durability of the products. Air bubbles typically range from 10-500 micrometers in diameter and absorb stresses induced from freezing. This process therefore improves freeze-thaw resistant ability.

3 Experimental Design

The motivation behind this study was largely based on an effort to continue a project started last semester in order to develop a useful finished product and develop a more thorough understanding of the chemistry involved. To this end, the initial fabrication method was adopted from that project.

3.1 Fabrication Method

In order to recycle fly ash into tiles for various applications, the important of water concentration in each sample was recognized. Water is a crucial component, as enough water needs to be added in order to ensure the formation of the C-S-H fibrils in both the Class C and Class F samples. However, too much water could increase the distance between the particles, resulting in a higher porosity in the samples and therefore a lower strength.
The correct ratio of fly ash to water would maximize the strength of the sample without compromising other mechanical properties. The varied oxide content between the Class C and Class F fly ash explains different optimal final ratios determined for each class.

In the case of the class F, tiles with ratios of 3:4, 2:3, 1:2, and 1:3 (water:fly ash) were fabricated. Class C tiles were fabricated by varying the ratios between 1:4, 1:5, 1:6 and 1:7 (water:fly ash).

The Class C fly ash and water slurry was mixed using an electric mixer for 3 minutes and then pressed in the mold at 2500 psi for 1 minute. The Class F fly ash and water slurry was mixed using an immersion blender for 15 minutes and then pressed in the mold at 2500 psi for 15 minutes.

Various molds were constructed to accommodate test specifications. After pressing, the samples were dislodged from the molds and cured. Several different curing methods were studied, but the final curing method for the Class C samples was a 24 hour water bath followed by a 28 day humidity cure. The final curing method for Class F samples was a 28 day humidity cure.

3.2 Fly Ash Additives

A selection of additives was incorporated into the fly ash formulations in order to improve the mechanical strength and water resistance of the tiles. Additives that were explored for mechanical strength improvements were calcium oxide, calcium chloride, and air entrainment agent. Calcium oxide content was incorporated into the fly ash in amounts of 5, 10, and 15 wt % for class C(1:4) formulations, and 5, 15, 25 and 30 wt % for class
F(1:2) formulations. More CaO was added to the Class F formulations due to a lower initial calcium content. Calcium chloride was added at 6 wt % to the water required for both class C(1:4) and class F(1:2) tiles, as was determined to be optimal from the literature. Air entrainment agents and air detrainment agents were added at 0.5 wt% to the C(1:4) and F(1:2) samples to increase mechanical performance. This value was also gathered from the literature. After curing, tiles were soaked in 13 wt % sodium silicate solution to provide water resistance.

3.3 Characterization Methods

Fly ash tile samples were characterized via compressive strength testing, flexural strength testing, freeze-thaw cycle resistance, water absorption, and impact testing.

3.3.1 Compressive Strength Testing

Compressive strength testing was the primary mechanical test used to select final compositions of the fly ash tiles and to compare its strength with traditional clay tiles. ASTM C473 was used to determine experimental setup. The compressive strength was testing using an Instron and a 150 kN load cell. Sample geometry for these tests was a 1 inch diameter cylinder of 1.5 inches in height (though the heights varied slightly depending on the sample) in order to ensure a proper aspect ratio.
3.3.2 Flexural Strength Testing

Flexural strength tests were conducted using an Instron and a 1 kN load cell with 1.7 inches distance between supports. These tests were performed on 3 inch by 1.5 inch by approximately 0.4 inch samples (samples varied slightly in thickness due to changes in compression). ASTM C473 was used to determine experimental setup. Samples were placed on top of two rollers spaced two inches apart, with a third roller descending into the sample at a rate of 2 mm per minute, as shown in the Figure 7. The load and extension at which each sample failed were recorded.

![Figure 7: Flexural strength testing experimental setup on Instron](image)

3.3.3 Impact Testing Setup

Impact resistance was measured on an Instron Dynatup Series 9250HV as shown in Figure 8. Samples were placed over a hole with diameter 1.25 inches. A bore with a hemispherical head of 5/8 inch diameter was dropped from above. The carriage weighed 7.007 kg and was dropped from a height of 0.1185 m to hit the sample with 72 in-lb of
energy as dictated by ASTM D5420. If the sample did not shatter, the depth of indentation was measured to quantify the impact resistance of the sample.

![Figure 8: Impact Resistance Testing Setup](image)

### 3.3.4 Water Absorption Testing

A water immersion test is described in ASTM C473. This test consisted of drying the samples using a low temperature oven (110-120°C) followed by a 24-hour room temperature water soak. Changes in weight were recorded. Any increase in weight was assumed to be attributed to water uptake; samples are assumed not to lose any mass during immersion.
3.3.5 Freeze-Thaw Cycle Testing

Freeze-thaw durability is a crucial property to evaluate the suitability of a material in cold weather. Freeze-thaw deterioration occurs when a material is more than 91% saturated. When water freezes, its volume increases. The expansion of volume generates pressures, which act on materials. When this pressure exceeds the tensile strength of the surface later, cracking occurs. (Air entrainment agents were added in order to avoid cracking.)

Freeze-thaw samples were pre-soaked in room temperature water for one hour. Then, each cycle consisted of freezing the tiles for three hours at -15°C and thawing for one hour in room temperature water. A total of 15 cycles were examined.

4 Results and Discussion

4.1 Initial Composition Selection

Though the previous study had selected C(1:4) and F(1:3) as the ideal compositions, the initial composition selection was revisited due to issues that arose from the selected compositions. After 60 days, many of the Class F samples had visible cracking on the surface, as can be seen in Figure 9.
Additionally, the samples did not always yield consistent results. Both the Class F and Class C samples would occasionally disintegrate immediately after being submerged in water in the curing process, as can be seen in Figure 10.

Figure 9: Visible cracking after 60 days

Figure 10: Class C and Class F samples unable to withstand water immersion
4.1.1 Compressive Strength

Since the final product of the previous study did not meet ASTM compressive strength standards, compressive strength was the primary metric to evaluate the mechanical characteristics of these samples.

Compressive strength testing was used to determine the ideal composition of each fly ash prior to including any additives or modifying the experimental design. These samples had the dimensions 1 inch diameter cylinder of at least 1.5 inches in height. These were tested under the conditions deemed optimal by the previous study.

As is consistent with the results of last semester, a value of 8.61 MPa was observed for C(1:4), which was significantly higher than all other class C compositions and was thus chosen as the ideal composition. The F(1:2) sample yielded the highest compressive strength, with a strength of 1.01 MPa. These samples had poor facial integrity and yielded inconsistent results and were therefore not pursued in the last study, but these samples became more consistent after additives and experimental design was optimized. Therefore, the C(1:4) and F(1:2) samples were chosen as the initial compositions on which further improvements were made.

ASTM C34 identifies the compressive strength of wall tiles to be 3.4 MPa and ASTM C212 requires a minimum compressive strength of floor tiles to be 4.8 MPa for 0.75-inch thick tiles. Thus, the Class C samples already exceeded the compressive strength requirements, but the Class F samples were lower than what is required. The class C samples surpassed the latter metric, and their high strength allows them to be classified as a “special duty” floor tile.
From the information in Figure 11, F(1:2) and C(1:4) were selected as the initial composition. The initial high compressive strengths of the Class C samples are due to the formation of C-S-H fibrils due to the higher calcium content. For this reason, a series of steps were taken to add calcium to the Class F samples in order to encourage the formation of these fibrils.

4.1.2 CaO additive

Based on the importance of Ca$^{2+}$ ions in the curing chemistry, calcium oxide was added to the samples in order to improve the mechanical strength of the C(1:4) and F(1:2) samples. The addition of CaO strengthened the Class F samples, but weakened the compressive strength of the class C samples.

In the previous study, most of the 30% CaO Class F tiles did not have the structural integrity to survive the curing process. However, after a significantly longer mixing time
(15 minutes) in order to ensure the CaO was evenly distributed in the samples, the Class F samples were able to withstand humidity curing with 30% CaO addition. This significantly increased the calcium content in the Class F fly ash, which gives the class F cementitious properties by allowing the formation of more C-S-H fibrils, strengthening the samples.

The opposite relationship was observed for class C samples, even after a 15 minute shaking time, as well. The compressive strength decreased significantly with the addition of CaO. Since the class C samples already have the optimal Ca content, any additional Ca weakened these samples as a result of excess binder formation.

For the same reasons, a similar trend was observed with the addition of 6 wt% CaCl₂. The addition of Ca encourages the curing reaction to drive forward, which results in the formation of more C-S-H fibrils. As can be seen in Figure 13, this addition nearly doubled
the strength of the class F samples, but weakened the class C samples by more than 66% with excess binder formation. In the Class F samples, the additional calcium accelerated the setting and strength development of the samples.

![Figure 13: Effect of CaCl2 addition on compressive strength](image)

4.1.4 Varying Curing Time

First, the cure time for the Class C samples was optimized. As was determined in the previous study, a 24 hour water cure time was shown to be optimal for the Class C samples, as can be seen in Figure 14. After this one day water cure, a humidity cure was performed for 28 days. Compressive strength of the Class C samples increased slightly after the 28 day humidity cure. The Class C samples weaken if placed in water longer than 24 hours due to excess binder formation, thereby weakening the material. However, the humidity cure
encourages the C-S-H binder to form at a slower pace, thereby slowly strengthening the material.

![Figure 14: Effect of curing time on strength of Class C samples](image)

The curing method for the Class F samples was then modified. The Class F samples were not able to withstand the water cure, so the curing process began with the humidity cure. The compressive strength of the class F tiles increased by 30% after a 28 day humidity cure, as is seen in Figure 15. The 28 days gave the samples sufficient time to allow for the cementitious reaction to occur.
The compressive strength increased significantly after the 28 day humidity cure due to the hydration process that took place, where the interstitial spaces originally filled with water are replaced by the formation of C-S-H fibrils\textsuperscript{20,21}. The porosity of the samples should be evaluated in order to correctly interpret these results.

4.1.5 Trace elemental analysis

A trace elemental analysis was conducted on the water in the water bath in order to ensure harmful materials were not leaching into the water, as harmful leaching is a great concern with regard to water curing. An XRD analysis (Figure 16) was conducted.
The results are listed in Table 3. This elemental analysis was consistent with the original fly ash composition and it can therefore be determined that there are no harmful elements leached into the water. Mercury leaching is a particular concern found in the literature, but no mercury was accounted for in the water\textsuperscript{22}.

\textbf{Table 3: Element analysis of curing water}

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>46.59</td>
</tr>
<tr>
<td>Sodium</td>
<td>29.44</td>
</tr>
<tr>
<td>Aluminum</td>
<td>16.04</td>
</tr>
<tr>
<td>Potassium</td>
<td>7.10</td>
</tr>
<tr>
<td>Chlorine</td>
<td>0.32</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.26</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.25</td>
</tr>
</tbody>
</table>
4.1.6 Air Detrainer

Air detrainer (Fritz-Pak-Air Minus) was added to both the Class C and Class F samples. The air detrainment agent follows standards of ASTM C260. Air detrainment agents minimizes the air in the material. The addition of the air detrainer weakened the strength of both samples significantly, as is seen in Figure 17. The reduced air contact in turn weakens the samples. The microscopic entrained air bubbles help relieve pressure, which actually strengthen the materials.

![Figure 17: Effect of Air Detrainer on Compressive Strength](image)

4.1.7 Air Entrainer

An air entrainment agent (Fritz-Pak-Air Plus) was therefore added to the samples. These are known to improve freeze-thaw durability by produce micro-closed air bubbles,
which can respond to the forces generated by freeze-thaw cycles without inducing cracking in the samples.

The air entrainer strengthened the Class F samples, but weakened the Class C samples (Figure 18). The Class F samples use the air bubbles to help relieve stresses. However, these additional air bubbles only seem weaken the Class C samples.

![Figure 18: Effect of air detraier on compressive strength](image)

### 4.2 Flexural Strength

Flexural strength was another metric to evaluate the mechanical characteristics of the samples (Eq 1). After the compressive strength was maximized and optimized, the flexural strength calculations were conducted. Flexural strength values are listed in Table 4.

\[
\text{Flexural Strength (MPa)} = \frac{3 \times \text{Max Force (N)} \times \text{Support span (mm)}}{2 \times \text{Width (mm)} \times \text{[Thickness (mm)]}^2} \quad (1)
\]
### Table 4: Flexural Strength Values

<table>
<thead>
<tr>
<th>Composition</th>
<th>Flexural Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(1:2)</td>
<td>6.3</td>
</tr>
<tr>
<td>C(1:4)</td>
<td>10.2</td>
</tr>
</tbody>
</table>

ASTM Standards indicate a wall tile must have a flexural strength of 2.1 MPa and a floor tile must have a flexural strength of 5.8 MPa. Both the class F and class C samples have exceeded this ASTM standard.

### 4.3 Freeze-Thaw Cycling

The freeze-thaw responses of the fly ash tiles were examined through 15 freeze-thaw cycles. ASTM C1026 requires just a sight evaluation of defects after five, ten, and fifteen cycles. In order to quantify the effects of the freeze-thaw cycles evaluate changes in the mechanical properties of the tiles, compressive strength was measured after 3, 6, 9, 12, and 15 cycles. No facial cracking or damage was observed for any composition tested and the tiles maintained their integrity. Additionally, a visual inspection was conducted after 15 days and no cracking had developed. Further, the compressive strength of C(1:4) and F(1:2) tiles had not changed, as can be seen in Figure 19. This high level freeze-thaw durability could be attributed to the air entrainment agent, as the added air bubbles flexibly respond to the forces created during the freeze-thaw process.
4.4 Water Absorption

Water absorption was measured according ASTM C212, which defines the maximum water absorption of tiles for general use to be 7%, though commercial clay tiles have water absorption levels well under that value.

Prior to sodium silicate addition, the tiles exhibited water absorption levels well above 7%. To improve the water absorption, the tiles were immersed in a 13% sodium silicate solution. This encouraged the formation of a glass-like surface of the samples. Water absorption of these coated samples was less than 7% for both classes, as can be seen in Figure 20.

This significant decrease in water absorption levels can be explained by the reaction of sodium silicate with the silicon-oxygen anions in the fly ash. Polymers are formed that begin to coagulate which creates a water-stable silica gel. This fills the pores in the samples, which inhibit the water from being absorbed.
Figure 20: Water absorption is decreased by a sodium silicate immersion

4.5 Density

The density of the tiles was calculated by dividing the mass of the dry cured samples over total volume (Table 5). The Class F tiles are about half as dense as the Class C tiles.

Table 5: Density of fly ash tiles

<table>
<thead>
<tr>
<th>Composition</th>
<th>Average Density (g/cm^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(1:2)</td>
<td>1.07</td>
</tr>
<tr>
<td>C(1:4)</td>
<td>1.99</td>
</tr>
</tbody>
</table>
4.6 Impact Testing

Samples were tested for impact resistance. The depth of indentation after an impact of 72 in-lb of energy was compared between class F and class C tiles. The tiles of these two final formulations did not shatter after impact. The depth of the indentation gives a quantitative measure of the impact resistance. The average depth of indentation was 8.32 mm for the Class F samples (Figure 21) and 6.21 mm for the Class C samples (Figure 22). The lower depth of indentation in the Class C samples can be attributed to more dense C-S-H fibrils.

Figure 21: Indentation in Class F sample after impact
5 Conclusion

Novel methods of recycling both Class C and Class F fly ash were significantly improved. This is incredibly valuable for the Class F fly ash, of which few applications are known.

The properties of the multiple formulations of tiles varied due to the difference in elemental compositions of the two classes of fly ash. The strength and rate of strength gain of fly ash are a result of the different characteristics of the fly ash, including elemental composition and particle size. When taking flexural strength, aesthetics, and reproducibility into account, it was found that a water:fly ash volume ratio of 1:4 for class C and 1:2 for class F were the best formulations. Class C tiles met compressive strength ASTM standards for floor tiles without any additives, but was further strengthened after the curing process. CaO and CaCl₂ were added to the class F samples in order to increase mechanical strength (but only weakened the Class C samples). The addition of air entrainer
increased the mechanical performance of the Class F samples significantly. Additionally, curing methods were optimized for both classes. Both compositions of tiles were soaked in sodium silicate to reduce the water absorption. The final conditions that were deemed optimal for the tiles are given in Table 6. The properties of the final compositions for wall and floor tiles meet or exceed those required by ASTM Standards (Table 7).

**Table 6: Optimal Final Conditions**

<table>
<thead>
<tr>
<th></th>
<th>F (1:2)</th>
<th>C (1:4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO (wt %)</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>CaCl₂ (wt %)</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>Cure Time</td>
<td>28 day (humidity)</td>
<td>1 day (water) + 28 day (humidity)</td>
</tr>
<tr>
<td>Thickness (in)</td>
<td>0.55</td>
<td>0.45</td>
</tr>
</tbody>
</table>

**Table 7: Properties of final composition of tiles**

<table>
<thead>
<tr>
<th></th>
<th>F (1:2)</th>
<th>C (1:4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive Strength (MPa)</td>
<td>5.4</td>
<td>10.1</td>
</tr>
<tr>
<td>Flexural Strength (MPa)</td>
<td>6.3</td>
<td>10.2</td>
</tr>
<tr>
<td>Freeze-Thaw (cycles)</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Water Absorption (%)</td>
<td>5.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Depth of Indentation (mm)</td>
<td>8.3</td>
<td>6.2</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.07</td>
<td>1.99</td>
</tr>
</tbody>
</table>
These tiles exhibited significant improvement in mechanical performance as compared to the previous study. Additionally, the tiles can now meet the ASTM standards with thickness of .55 in for Class F samples and .45 in for Class C samples, allowing them to better compete with traditional clay tiles on the market.

By omitting the firing process that is used in the manufacturing of commercial clay tiles, these fly ash alternatives conserve 12.2 MJ/m² during their production. In conclusion, this study has produced an environmentally friendly and economically feasible alternative to wall and floor ceramic tiles.

6 Future Work

More research could be done regarding non-firing glazing methods to improve the aesthetics of the products. Additionally, there is more work that could be done in order to further strengthen the material. A porosity study could be conducted in order to gain further understanding of the role of the C-S-H fibrils. Nanoparticles, polymer additives, or fibers can be implemented. Studies can be conducted after even longer curing times, as studies have shown that materials continue strengthening even after years.

7 Acknowledgements

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Angie Locknar for their assistance.

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