Comparison of the Resistance of Belitic Calcium Sulfoaluminate Cement and Portland Cement to Sulfate Attack and Sulfuric Acid

Rilye Dillard

University of Arkansas, Fayetteville

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Comparison of the Resistance of Belitic Calcium Sulfoaluminate Cement and Portland Cement to Sulfate Attack and Sulfuric Acid

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Civil Engineering

by

Rilye Dillard
University of Arkansas
Bachelor of Science in Civil Engineering, 2019

May 2021
University of Arkansas

This thesis is approved for recommendation to the Graduate Council.

_____________________________
Cameron Murray, Ph.D.
Committee Member

_____________________________
Micah Hale, Ph.D.
Committee Member

_____________________________
Richard Deschenes, Ph.D.
Committee Member
ABSTRACT

Microbially induced corrosion (MIC) is a fairly common concrete deterioration mechanism with many negative effects. MIC is a complex chemical and biological process that occurs in sewage systems and is nearly impossible to replicate in a laboratory setting. For this study, sulfate and sulfuric acid attack on concrete were studied to mimic two stages of the MIC process. The ASTM C1012, Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution and a modified ASTM C1012 accelerated method were used to compare the sulfate resistance of belitic calcium sulfoaluminate (BCSA) cement, portland cement (PC), and PC-fly ash blends. The effect of citric acid dosage on sulfate resistance of BCSA cement mixtures was also studied. The standard method was used primarily for comparison to the accelerated method results. Mortar bar expansion and mass change were analyzed to examine the sulfate resistance of varied BCSA mixtures. The most sulfate-resistant mixes contained BCSA cement or a blend of PC and class F fly ash. Citric acid dosage did not seem to affect resistance of BCSA cement to sulfate attack. Resistance of PC, PC-fly ash blends, and BCSA cement to a sulfuric acid solution was also compared. Compressive strength, mass change, and volumetric changes were measured after prolonged immersion in sulfuric acid. Water to cementitious material (w/cm) ratios and curing time for BCSA were also compared to resistance to sulfuric acid attack. The most resistant mix contained a blend of PC and class F fly ash. A higher w/cm was found to be more resistant against sulfuric acid attack when using BCSA, while differing cure times did not clearly indicate sulfuric acid resistance.

Keywords: sodium sulfate solution; ASTM C1012; accelerated C1012 method; belitic calcium sulfoaluminate cement; BCSA; sulfate attack; sulfuric acid
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<td>Microbially induced corrosion</td>
<td></td>
</tr>
<tr>
<td>CSA</td>
<td>Calcium sulfoaluminate cement</td>
<td></td>
</tr>
<tr>
<td>BCSA</td>
<td>Belitic calcium sulfoaluminate cement</td>
<td></td>
</tr>
<tr>
<td>CAC</td>
<td>Calcium aluminate cement</td>
<td></td>
</tr>
<tr>
<td>PC</td>
<td>Portland cement type I</td>
<td></td>
</tr>
<tr>
<td>SRB</td>
<td>Sulfate reducing bacteria</td>
<td></td>
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<tr>
<td>C₃S</td>
<td>Tricalcium silicate, alite</td>
<td></td>
</tr>
<tr>
<td>C₂S</td>
<td>Dicalcium silicate, belite</td>
<td></td>
</tr>
<tr>
<td>C₃A</td>
<td>Tricalcium aluminate</td>
<td></td>
</tr>
<tr>
<td>C₄AF</td>
<td>Tetracalcium aluminoferrite</td>
<td></td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>Calcium hydroxide</td>
<td></td>
</tr>
<tr>
<td>C-S-H</td>
<td>Calcium silicate hydrate</td>
<td></td>
</tr>
<tr>
<td>CaSO₄•2H₂O</td>
<td>Gypsum</td>
<td></td>
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<tr>
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<td>Anhydrite, calcium sulfate</td>
<td></td>
</tr>
<tr>
<td>3CaO•Al₂O₃•3CaSO₄•32H₂O</td>
<td>Ettringite</td>
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<tr>
<td>H₂SO₄</td>
<td>Sulfuric acid</td>
<td></td>
</tr>
<tr>
<td>H₂S</td>
<td>Hydrogen sulfide</td>
<td></td>
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<tr>
<td>SCM</td>
<td>Supplementary cementitious material</td>
<td></td>
</tr>
<tr>
<td>w/cm</td>
<td>Water to cementitious material ratio</td>
<td></td>
</tr>
<tr>
<td>s/cm</td>
<td>Sand to cementitious material ratio</td>
<td></td>
</tr>
<tr>
<td>$C_4A_3\bar{S}$</td>
<td>Ye’elimite</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>Calcium oxide</td>
<td></td>
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</table>
INTRODUCTION

The design life of concrete can be interrupted by several chemical and physical processes. One such process is known as microbially induced corrosion (MIC) [1, 2]. The degradation of concrete due to this mechanism has been problematic for municipal sewage systems for many years [2]. There have been few studies focusing on utilizing alternative cements to prevent MIC [2, 3].

In this study, sulfate and sulfuric acid attack were used to imitate specific phases of MIC. Mortar prisms made with portland cement (PC), belitic calcium sulfoaluminate (BCSA) cement, and PC-fly ash blends were immersed in a sodium sulfate solution. Length and mass changes were examined for each of these prisms to determine the most effective cement system. Next, mortar cubes were submerged in sulfuric acid and the behavior of the cements and blends was observed in this harsh environment. Volume change, mass change, compressive strength change, pH monitoring, and a visual inspection of each specimen were compared at specified intervals.

Sulfate and sulfuric acid attack test methods were chosen to mimic the MIC process. The sulfate attack tests represented the first part of MIC, while sulfuric acid attack represented the final stage of MIC. Sulfate attack introduces sulfates into the concrete which eventually leads to deterioration. Sulfuric acid attack is very similar to MIC in that sulfuric acid is introduced to concrete and eventually leads to dissolving of the cement paste and eventual deterioration and failure of concrete.

Few studies have been done to investigate the resistance of calcium sulfoaluminate (CSA) cements against sulfate attack [4, 5]. No known studies have been done to analyze the resistance of CSA to sulfuric acid attack. BCSA cement is classified as a hydraulic rapid-setting cement [6]. BCSA cement can be thought of as a subset of CSA cements that contains a large percentage
of belite in the clinker. BCSA cement is a more sustainable alternative to PC due the lower CO₂ emissions generated through its production [6, 7]. This is achieved due to the low sintering temperatures and lower carbon content of BCSA [6]. BCSA cement has probably been in use in the United States since the 1970s, but recently it has become of more interest to the research community and to cement producers due to its environmental benefits [8, 9]. BCSA is significantly more expensive than PC. Part of this cost disparity can be explained by the widespread use of PC and economies of scale in its production [7]. Another component of the cost difference is the need for an alumina source in BCSA cement production. BCSA gains its initial strength through the formation of ettringite, which forms quickly, leading to setting times of less than 20 minutes and strengths exceeding 4,000 psi in as little as 2 hours. The formation of ettringite, in this instance, is the main strength producing component in the hydrated cement. Because BCSA contains very little C₃A (tricalcium aluminate) and C₃S (tricalcium silicate, alite), the sulfate resistance is expected to be strong [4]. Apart from having good early age strengths, BCSA cement is low-shrinkage, and has good alkali-silica reaction resistance [10, 6, 11]. The shrinkage resistance of BCSA can extend the expected design life of concrete [6]. A typical BCSA cement composition is listed in Table 1.
Table 1 – Portland and BCSA Cement Typical Compositions (% mass)

<table>
<thead>
<tr>
<th>Component</th>
<th>PC type I</th>
<th>PC type V</th>
<th>BCSA</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃A Tricalcium Aluminate</td>
<td>7</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>C₃S Alite</td>
<td>59</td>
<td>38</td>
<td>-</td>
</tr>
<tr>
<td>C₂S Belite</td>
<td>17</td>
<td>43</td>
<td>45</td>
</tr>
<tr>
<td>C₄AF Ferrite</td>
<td>9</td>
<td>9</td>
<td>2</td>
</tr>
<tr>
<td>C₄A₃S Ye’elimite</td>
<td>-</td>
<td>-</td>
<td>30</td>
</tr>
<tr>
<td>C₅S Calcium sulfate</td>
<td>2</td>
<td>-</td>
<td>15</td>
</tr>
<tr>
<td>Other</td>
<td>6</td>
<td>6</td>
<td>8</td>
</tr>
</tbody>
</table>

Note: Table adapted from [7, 12]

BACKGROUND

MICROBIALLY INDUCED CORROSION

Wastewater infrastructure (pipes, manholes, etc.) is often made with reinforced concrete. Despite its many benefits in this application, concrete can be susceptible to different types of chemical and biological interactions that can reduce its service life. One such mechanism is MIC. Despite being common, there is not much guidance on how to prevent MIC in concrete [13]. MIC can be described through a three-phased process [13]. After placement, PC concrete has a pH of around 12.5 to 14 [14]. In the first phase, known as the ‘carbonation’ phase, sulfate compounds found in the surrounding soil, groundwater, decaying organic matter, seawater, and industrial waste are reduced through anaerobic reactions and by bacteria present around the concrete [13]. During this phase, the pH of the surface concrete is initially lowered to 10 or 11 [13]. The second phase is referred to as the ‘attachment’ phase [15]. Sulfate reducing bacteria (SRB) initiate the production of aqueous H₂S (hydrogen sulfide) [16, 2, 5, 17, 13]. Next, the aqueous H₂S evaporates [2]. This gaseous phase enables the H₂S to penetrate the internal structure of the
concrete which interacts with a layer of biofilm that is present on the concrete [2, 16, 18]. The amount of biofilm that becomes attached to the concrete is dependent upon temperature, surface texture, moisture, and availability of nutrients [13]. In the second phase, the pH of the surface concrete is again lowered to a range of 4 to 6 [15]. The final stage of MIC is the ’deterioration’ phase, when microorganisms containing oxidized sulfur containing compounds oxidize into sulfuric acid [2, 16]. This process further lowers the pH of the surface concrete to 0.5 to 4 [15]. The lower the surface pH becomes, the more acid is produced, which increases the severity of degradation of the concrete [15]. Sulfuric acid is extremely corrosive and leads to inevitable maintenance and repair to manholes and other affected concrete structures [2, 16]. The maintenance and of structures affected by MIC is very expensive. The use of alternative cements could reduce damage caused by the MIC process due to their differing chemical composition from PC. Some alternative cements are expected to have improved sulfate resistance compared to PC [19].

Recreating the entire complex MIC system in a laboratory setting has not yet been accomplished [2, 1, 18, 20]. For this study, two chemical solution exposures were chosen to simulate the primary methods of degradation present in MIC. The first phase of MIC produces damaging sulfate compounds which is a main contributor to both MIC deterioration and sulfate attack. For this reason, test methods primarily used for sulfate attack were included in this study. The last phase of MIC involves the creation of sulfuric acid, so samples in this study were exposed to sulfuric acid solutions. Although sulfuric acid immersion tests cannot replicate the MIC process, these tests can mimic the final stage of MIC [21]. It was expected that a mixture which is resistant to sulfate attack and sulfuric acid exposure should be similarly resistant to damage from MIC. Some test methods have recently been developed to examine MIC in concrete [15]. These
tests are ASTM C1904-20 *Standard Test Methods for Determination of the Effects of Biogenic Acidification on Concrete Antimicrobial Additives and/or Concrete Products*, ASTM 1898-20 *Standard Test Methods for Determining the Chemical Resistance of Concrete Products to Acid Attack*, and ASTM C1894-19 *Standard Guide for Microbially Induced Corrosion of Concrete Products* [15]. These test methods were not used in this study because they were not published until after this research began.

**MICROBIALLY INDUCED CORROSION MITIGATION**

Antimicrobial admixtures have been considered as a preventative measure to the ‘attachment’ phase of MIC [15]. Alkali activated materials have also been studied through sulfuric acid attack, which is a component of the MIC process [22]. Alkali activated materials appear to be more resistant to acid attack than PC, however, this material can still be damaged by sulfuric acid attack [22]. Studies performed by Srubar et al has also shown promising results with alkali activated cements to resist MIC [23].

The effects of MIC on alternative cement systems is still an open research question. The effectiveness of alternative cements in resisting sulfate attack and sulfuric acid exposure has also been mostly untested [24, 25, 26, 27, 5]. Research on the resistance of alternative cements to sulfate attack was performed by Burris et al. Their findings were that calcium aluminate cement (CAC), calcium sulfoaluminate cement (CSA), a blended CAC product, and a chemically activated binder all were more resistant to sulfate attack than PC [28]. CACs do not produce Ca(OH)₂ (calcium hydroxide) which could prevent sulfate attack [28]. CSA cement resists sulfate attack due its chemical makeup containing small amounts of alumina and sulfate [28]. The blended CAC used in their study contained calcium aluminate, CaSO₄ (calcium sulfate, anhydrite), and PC [28]. With higher ratios of CAC to PC, the higher the expected sulfate
resistance [28]. The chemically activated binder showed strong sulfate resistance due to its chemical composition and lack of susceptible sulfate attack chemicals [28]. Supplementary cementitious materials (SCMs), including class F fly ash, have shown promising sulfate attack resistance [25, 29].

There is very little research completed with recommendations on concrete mix designs to resist microbiologically induced corrosion. There is no consensus on concrete mix designs that can resist MIC [30]. Using an antimicrobial admixture, silane quaternary amine, seemed to have increased MIC resistance [31, 2]. Researchers Saha et al found that mixtures containing 30% class F fly ash had improved resistance to sulfuric acid attack, which mimics part of the MIC process [29]. Many other studies also support the replacement of a portion of PC with SCMs at varying percentages including silica fume, ground granulated blast furnace slag, finely ground limestone, nanosilica, ground ferronickel slag, or metakaolin [21, 32, 29, 33, 2]. Researcher Mangat et al also found that SCMs, including fly ash, silica fume, and ground granulated blast furnace slag resisted sulfate attack which could provide good MIC performance [34, 17, 26, 27]. The recommended w/cm range varies from 0.35 to 0.5 when using PC and SCMs [35, 26, 32].

MICROBIALLY INDUCED CORROSION AND SULFATE ATTACK

External sulfate attack has been observed through three main methods [24]. The first involves formation of gypsum and ettringite specifically through sodium sulfate attack [24]. The second is due to a sulfate compound containing salt formed in the evaporative zone of concrete [24]. The last method includes thaumasite formation [24]. The first method described most closely imitates the MIC process [17, 24]. Sodium sulfate attack affects the cement paste portion of mixtures used in concrete structures [36, 24]. The four main compounds found in PC, alite, $\text{C}_2\text{S}$ (dicalcium silicate, belite), tricalcium aluminate, and $\text{C}_4\text{AF}$ (tetracalcium aluminoferrite),
contribute to the formation of ettringite during sulfate attack [37]. \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \) (gypsum) and similar calcium sulfate compounds, including calcium sulfates, are also present in PC [37]. During cement hydration, alite and belite react with water to form calcium hydroxide and C-S-H (calcium silicate hydrate) [37, 29]. Calcium silicate hydrate is the main strength-providing reaction product in PC [37]. Gypsum can also be created through the reaction between calcium hydroxide, formed during cement hydration, and sulfates present in the environment surrounding the concrete, including \( \text{H}_2\text{SO}_4 \) (sulfuric acid) [5, 22]. \( 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O} \) (ettringite) is primarily formed (in PC) through the chemical reaction between tricalcium aluminate, gypsum or other sulfates present in the system, and water [37]. The severity of sulfate attack varies based upon the number of compounds present for these chemical reactions [5]. The formation of gypsum and ettringite when cement paste is exposed to sulfates can lead to expansion, cracking, mass loss and eventual strength loss [17].

Research has shown different cement types and different water to cementitious materials ratios \((w/cm)\) affect the rate at which concrete degrades due to sulfate attack [24, 26, 27]. A higher \(w/cm\) makes concrete more susceptible to sulfate attack due to increased permeability and a weaker pore structure [26]. The tricalcium aluminate content in cement is another important contributing factor to degradation in concrete structures due to sulfate attack [24, 27, 25]. Tricalcium aluminate is one of the main compounds that is responsible for ettringite forming in concrete structures exposed to sulfate [25]. Less tricalcium aluminate in the cement leads to better resistance against sulfate attack [24]. However, even with a cement containing 0% tricalcium aluminate, sulfate attack is still possible [24]. There is also a correlation between the ratio of alite to belite, and sulfate resistance [38]. Higher alite/belite has been shown to reduce sulfate resistance; this has a smaller effect on sulfate resistance than the tricalcium aluminate
content [38]. Current concrete codes and standards limit the amount of acceptable tricalcium aluminanate content and w/cm ratios to counteract sulfate attack [24].

Type I PC contains a high (8-12%) average percentage tricalcium aluminanate [7, 25]. This makes type I PC susceptible to sulfate attack. Type I PC also contains a large amount of alite and some belite [7]. Table 1 shows the composition of PC. These compounds can also indicate how cement is going to withstand sulfate and sulfuric acid attack [38]. The alite/belite ratio for PC type I is about 3.5% [39, 7, 40]. The presence of these compounds and their high concentration will make PC more susceptible to degradation through sulfate and sulfuric acid attack [22]. Therefore, it is expected that the PC mix will perform poorly.

Type V PC is used specifically to protect concrete against sulfate attack. It was originally designed as a low tricalcium aluminanate cement with a larger tetracalcium aluminoferrite content [24]. Type V PC contains on average 0-4% tricalcium aluminanate [14]. The percentage can be compared with the 8 to 12% that is present in type I PC [25]. The cement composition of type V PC is shown in Table 1. The lower tricalcium aluminanate percentage should lead to less ettringite formation in the presence of sulfates. The alite/belite ratio for type V is about 1.5% [14]. This is scarcely lower than the ratio for type I PC. However, some studies have shown that type V cement’s resistance to sulfate attack is not much better than type I PC [5, 41]. The alite/belite ratio also indicates that type V PC may also be susceptible to sulfuric acid attack. PC type V is expected to perform slightly better than PC type I.

SCMs are usually used in addition to PC to increase durability of concrete structures [27]. A small replacement of PC with a SCM can form a more resistant internal structure through decreased pore sizes, which decreases permeability, and a stronger paste-aggregate bond [26, 29]. Sulfate resistance is also increased due to a longer pozzolanic reaction time which leads to a
reduction in calcium hydroxide that is available for sulfate and sulfuric acid reactions to create gypsum and ettringite [26, 29]. The SCMs used in this study were class C and class F fly ash. Some class C fly ashes improve resistance to sulfate attack [26]. Others, however, have led to an increase in expansion and eventual cracking [26]. Research has shown that the minerals that make up class C fly ash are the cause of inconsistent sulfate resistance [26]. Class C fly ash can contain compounds such as tricalcium aluminate, calcium sulfate, and ye’elimite (C₄A₃S̅) which could be the contributing factors to the decrease in sulfate resistance [26]. Tricalcium aluminate and calcium sulfate are introduced in the formation of gypsum and ettringite above. Research has shown that mineralogical and chemical compositions of fly ash strongly indicate sulfate and sulfuric acid resistance [29, 42]. Class C fly ash is described as having a high calcium content compared to class F fly ash due to its higher CaO (calcium oxide) and calcium aluminate contents [25]. For these reasons, mixes containing class C fly ash are expected to perform poorly. BCSA’s chemical composition is quite different from PC. Table 1 shows a comparison of the cement compounds present in BCSA cement and PC. As mentioned previously, for sulfate attack, tricalcium aluminate and alite/belite compounds should be minimized. There is no tricalcium aluminate in BCSA cement clinker, theoretically increasing the sulfate resistance [7]. BCSA contains 0% alite, so the alite/belite ratio reduces to zero [7]. The CSA present in BCSA cement could contribute to a decrease in sulfate resistance [26]. However, this CSA leads to the rapid formation of ettringite at early ages and provides high early strength and fast setting behavior which could provide resistance from external sulfate attack [7, 43].

**MICROBIALLY INDUCED CORROSION AND SULFURIC ACID ATTACK**

Sulfuric acid becomes present in concrete substructures due to acid rain, sewage, and industrial chemical waste [35, 22]. Sulfuric acid can also be created through bacterial sulfide oxidation
created from the release of carbon dioxide from wastewater during MIC [44, 45]. This release of carbon dioxide promotes bacterial growth above the sewer line in the pipes [44, 45]. Sulfuric acid reacts with the cement in concrete substructures which eventually leads to degradation of the concrete [45]. The factors leading to concrete degradation due to exposure to sulfuric acid are the properties of the concrete and the composition of the acidic solution [29]. The strength-providing cement reaction compounds such as C-S-H and calcium hydroxide require an alkaline environment to remain stable. In the presence of sulfuric acid, the pH is lowered, and these cement compounds may deteriorate, primarily the calcium hydroxide. The decalcification of calcium hydroxide is more extreme than with the C-S-H compounds due to its crystalline structure [29]. The presence of calcium silicates and calcium hydroxide promote the growth of gypsum through sulfuric acid attack [22, 44]. The amount of these compounds in the cement determines the extent to which the concrete degrades [29]. Research has shown that the lower calcium hydroxide and C-S-H contents found in cement, the higher the resistance to major degradation in concrete [29]. This suggests that alternative cements, whose strength may come primarily from the formation of other cement compounds, may provide better sulfuric acid resistance.

Cement compositions are expected to influence resistance to sulfuric acid attack [29]. Expected resistance to sulfate attack can give indication on how resistant cement will be to sulfuric acid attack. The presence of tricalcium aluminate, alite, and belite compounds and their high concentration will make PC more susceptible to degradation through sulfate and sulfuric acid attack [22]. Therefore, it is expected that the PC mix will perform poorly. Type V cement contains similar compound compositions to type I PC. This can indicate that type V PC will also perform poorly. Fly ash class C, discussed in the previous section, is described as having a high
calcium content. So, this could decrease sulfuric acid resistance [25]. Class F fly ash has lower calcium content and is expected to have good resistance to sulfuric acid attack [25]. BCSA cement resistance to sulfuric acid attack has not yet been studied. The high concentration of belite could encourage severe degradation through sulfuric acid attack [22].

**MATERIALS AND METHODS**

**MATERIALS**

The mixtures compared in this study contained three cements: type I/II PC, type V PC, and BCSA cement. Class F and class C fly ash were blended with type I/II PC for comparison. Class F and class C fly ash were used at a 30% replacement rate of PC by weight based on other studies relating to sulfate attack and fly ash performance [42, 46]. The class C fly ash was acquired from a Boral Resources plant in Sikeston, MO. The class F fly ash was obtained from a Boral Resources plant in Wilsonville, AL. Type I PC, type V PC, and BCSA cement compositions are shown in Table 1. All mixtures contained an Arkansas River sand quarried in Van Buren, AR. The properties of the sand are detailed in Table 2. Mixture designs are shown in Table 3. A citric acid set retarder admixture was used in all but one mixture containing BCSA. The use of a set retarder such as citric acid is desired in BCSA mixtures to provide adequate working time. The citric acid was prepared as an “admixture” by mixing 5 lb citric acid per gallon of water. Citric acid dosages in Table 3 are given in terms of percent citric acid per cement weight.
### Table 2 – Arkansas River Sand Properties

<table>
<thead>
<tr>
<th>Sieve denomination</th>
<th>Sieve size, mm</th>
<th>Retained, %</th>
<th>Passing, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>% in</td>
<td>9.5</td>
<td>0.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Nº 4</td>
<td>4.76</td>
<td>2.8</td>
<td>97.2</td>
</tr>
<tr>
<td>Nº 8</td>
<td>2.38</td>
<td>8.1</td>
<td>91.9</td>
</tr>
<tr>
<td>Nº 16</td>
<td>1.19</td>
<td>19.5</td>
<td>80.5</td>
</tr>
<tr>
<td>Nº 30</td>
<td>0.6</td>
<td>39.0</td>
<td>61.0</td>
</tr>
<tr>
<td>Nº 50</td>
<td>0.3</td>
<td>83.2</td>
<td>16.8</td>
</tr>
<tr>
<td>Nº 100</td>
<td>0.15</td>
<td>97.9</td>
<td>2.1</td>
</tr>
<tr>
<td>Nº 200</td>
<td>0.075</td>
<td>99.3</td>
<td>0.7</td>
</tr>
<tr>
<td>Pan</td>
<td></td>
<td>99.4</td>
<td>0.6</td>
</tr>
</tbody>
</table>

- Fineness modulus: 2.5
- SSD specific gravity, g/cm³: 2.63
- Absorption, %: 0.55

### Table 3 – Mixture Designs Used in Laboratory Studies

<table>
<thead>
<tr>
<th>Mixture</th>
<th>BCSA Cement</th>
<th>PC, Type I/II</th>
<th>PC, Type V</th>
<th>Class F Fly Ash</th>
<th>Class C Fly Ash</th>
<th>s/cm</th>
<th>w/cm</th>
<th>Citric Acid (% by cement weight)</th>
<th>Test methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCSA-0.485-0.35</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.75</td>
<td>0.485</td>
<td>0.35</td>
<td>†,‡</td>
</tr>
<tr>
<td>BCSA-0.44-0.35</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.75</td>
<td>0.440</td>
<td>0.35</td>
<td>†</td>
</tr>
<tr>
<td>BCSA-0.52-0.35</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.75</td>
<td>0.520</td>
<td>0.35</td>
<td>*;†</td>
</tr>
<tr>
<td>BCSA-0.485-0.35-2.5S/C</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.50</td>
<td>0.485</td>
<td>0.35</td>
<td>†</td>
</tr>
<tr>
<td>BCSA-0.52-0</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.75</td>
<td>0.520</td>
<td>0</td>
<td>†</td>
</tr>
<tr>
<td>BCSA-0.52-0.70</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.75</td>
<td>0.520</td>
<td>0.70</td>
<td>†</td>
</tr>
<tr>
<td>BCSA-0.56-0.35</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.75</td>
<td>0.560</td>
<td>0.35</td>
<td>†;‡</td>
</tr>
<tr>
<td>PC</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.75</td>
<td>0.485</td>
<td>-</td>
<td>*;†;‡</td>
</tr>
<tr>
<td>PC-V</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>2.75</td>
<td>0.485</td>
<td>-</td>
<td>*;†</td>
</tr>
<tr>
<td>PC-FAF</td>
<td>-</td>
<td>0.7</td>
<td>-</td>
<td>0.3</td>
<td>-</td>
<td>2.75</td>
<td>0.485</td>
<td>-</td>
<td>†;‡</td>
</tr>
<tr>
<td>PC-FAC</td>
<td>-</td>
<td>0.7</td>
<td>-</td>
<td>-</td>
<td>0.3</td>
<td>2.75</td>
<td>0.485</td>
<td>-</td>
<td>†</td>
</tr>
</tbody>
</table>

Note: All proportions shown as ratio with total cementitious material except where noted

* Standard ASTM C1012
† Accelerated ASTM C1012
‡ Sulfuric acid test
Despite this, class C fly ash was included in this study due to its ubiquity in the state of Arkansas. The low calcium content in Class F fly ash makes it a better option to address sulfate and sulfuric acid attack [29]. Promising results using Class F fly ash have been found through sulfate attack and sulfuric acid testing [29, 25]. Class F fly ash is expected to resist sulfate and sulfuric acid attacks better than type I PC and class C fly ash with a 30% replacement of PC by weight with fly ash was used in a variety of past studies, so the same replacement rate was used in this research [27, 46, 42]. Past studies have suggested that a higher w/cm may be required for CSA cement mixtures compare to PC [47]. Also, a set retarder (often citric acid) is a requirement for most BCSA cement mixtures to ensure adequate working time.

**MIXTURE DESIGNS**

This study investigated the effects of w/cm and citric acid dosage on the sulfate resistance of BCSA cement mortar. The sulfate resistance of BCSA was also compared with PC and PC-fly ash blends.

Mix designs for the standard ASTM C1012 method, accelerated ASTM C1012 method, and sulfuric acid testing are shown in Table 2. All PC mixtures used the standard w/cm and sand to cementitious materials ratio (s/cm), described in ASTM C1012 (0.485 and 2.75, respectively). BCSA is often thought to require a higher w/cm than PC to ensure adequate hydration, however there is no standard w/cm nor s/cm for sulfate testing of BCSA mixtures [48]. Research shows that concrete performs better against sulfuric acid attack at higher w/cm while lower w/cm are more resistant against sulfate attack [21, 24, 26, 25]. Therefore, several w/cm were tested ranging between 0.485 and 0.56. Two s/cm were tested at 2.75 and 2.5. Citric acid dosing for BCSA mixtures was 0%, 0.35%, and 0.7% by cement weight. These dosages would be expected to
provide 10-15 minutes, 45 minutes, and 1.5 hours before initial set (respectively, in lab conditions) based on past work [49]. The effect of citric acid dosage on sulfate attack resistance was analyzed in this range of dosages. The following mixtures were tested in the standard ASTM C1012 method: PC, PC-V, and BCSA-0.52-0.35 (BCSA mortar with a w/cm of 0.52 and a citric acid dosage of 0.35% by cement weight). These mixes were selected to give a range of sulfate expansions for comparison to the accelerated method. Next, all mixtures were tested using the accelerated sulfate attack method proposed by Aguayo et al [50]. Since the main goal was to rank mixtures based on sulfate resistance the accelerated method was considered a reasonable alternative to the standard C1012 method. Mix designs for sulfuric acid testing were chosen based on preliminary results from the sodium sulfate attack tests. Differing w/cm and curing times for BCSA mixes were analyzed during sulfuric acid testing as well.

METHODS

SODIUM SULFATE STANDARD METHOD (ASTM C1012)

Sulfate testing for cement is typically performed using ASTM C1012, Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution [48]. A major disadvantage of this test method is the time it takes to perform the test – at least 6 months and possibly up to 12 months depending on the exposure condition of interest. In this study, an accelerated sulfate resistance test was used for most samples alongside the standard ASTM C1012 for comparison with a few mixtures. The accelerated test has been shown to provide similar results to ASTM C1012, especially in terms of ranking mixtures by their sulfate resistance [50]. Because the main goal of this study was to rank mixtures in terms of their resistance to sulfate attack, the accelerated method was considered an adequate alternative. For
specimens subjected to the accelerated sulfate test method, samples were prepared as
recommended in ASTM C1012 [48].
Mortar prisms measuring 1 in. by 1 in. by 11¼ in. with a gauge length of 10 in. were used for the
standard sodium sulfate solution test. Mortar cubes measuring 2 in. by 2 in. by 2 in. were cast at
the same time as the mortar prisms. The mortar was mixed according to ASTM C305 and prisms
and cubes cast according to ASTM C157 and ASTM C109, respectively [51, 52, 53]. Once the
prisms were cast, they were put into a partially water-filled container with risers to ensure no
moisture was lost as the prisms set. Figures 1 and 2 show the containers. After 24 hours, the
mortar prisms and cubes were demolded. The mortar cubes were tested after demolding to ensure
a minimum compressive strength of 2,850 psi was reached. All PC prisms were submerged in a
limewater bath until the desired compressive strength was reached while the BCSA cement
prisms were stored in an environmental chamber at roughly 72 F and 50% RH. When the
minimum compressive strength was reached, the container of prisms was then put into an oven at
95˚F to 100˚F for 24 hours. After 24 hours in the oven, the prisms were submerged in a 5%
sodium sulfate solution. The prisms were measured for mass and length change at days 1, 7, 14,
21, 28, 56, 91, 105, 147, 175, 203, 231, and 244 after initial submersion in sodium sulfate.
Length change was measured using a comparator which is shown in Figure 3. Mass change was
measured using a lab scale. At each interval, the sodium sulfate solution was replaced.
Figure 1 – Container for Mortar Prisms with Riser

Figure 2 – Closed Container for Mortar Prisms with Riser
The accelerated test method proposed by Aguayo et al. was also used in this study [50]. This method was developed to provide a more rapid alternative to ASTM C1012 and has been shown to rank the performance of mixtures similarly to the standard method. The same procedures were used to make mortar prisms and mortar cubes for the standard and accelerated method. After the prisms and cubes were mixed and cast, they were put into water filled containers with risers. These containers are shown in Figures 1 and 2. The water-filled container of prisms was then put into the oven at 95°F to 100°F for 24 hours to accelerate the strength gain of the specimens. After 24 hours, the prisms and cubes were demolded and placed in an environmental chamber at 72 °F

Figure 3 – Length Comparator

SODIUM SULFATE ACCELERATED METHOD
under a moist cloth. After demolding, a 2 in. by 2 in. by 2 in. mortar cube was tested to ensure a minimum of 2,850 psi compressive strength. If this compressive strength was not reached, the prisms were put into a limewater bath. The BCSA mixes, however, were left in the environmental chamber instead of the limewater bath. When the mortar cubes reached the desired compressive strength, the prisms were placed back into the water filled containers and were returned to the oven at 95°F to 100°F. The prisms were left in the oven for 2 weeks to cure. After 14 days, the prisms were put into a vacuum impregnation chamber. The impregnation chamber is pictured in Figure 4. The chamber was put under vacuum at 13.3 psi to remove pore solution from the pores of the mortar. After 4 hours under vacuum, the impregnation chamber was filled with 0.5% sodium sulfate solution and put under pressure at 15 psi to fill all pores completely with the sulfate solution. After 20 hours, the prisms were removed from the impregnation chamber. Initial mass and length measurements were taken of each prism before placing them in a 0.5% sodium sulfate solution. On days 1, 2, 3, 6, 9, 12, 17, 22, 27, 34, 41, 48, 62, 76, 90, 104, 118, 174, 202, 230, and 244 after being placed in solution, mass and length change were measured and the sodium sulfate solution was replaced. Length and mass were measured using a comparator (Figure 3) and scale, respectively.
SULFURIC ACID TESTS

The sulfuric acid test method employed for this thesis was based on past work by House et al and Mahmoud et al [21, 33]. Mortar cubes measuring 2 in. by 2 in. by 2 in. were prepared according to ASTM C305 and placed and consolidated according to ASTM C109 [51, 53]. After the mortar cubes were cast, they were put into an environmental chamber for either 7 or 28 days. The PC, PC-FAF, one BCSA-0.56-0.35 batch, and one BCSA-0.485-0.35 batch were cured for 28 days. Another batch of BCSA-0.56-0.35 and CSA-0.485-0.35 were put into the environmental chamber to cure for only 7 days. The purpose of the different curing times was to determine the
effect (if any) of early exposure to sulfuric acid on BCSA cement concrete. After their specified curing times, the cubes were split into three sets. One set was left in the environmental chamber at 72 F and 50% RH. Another set was submerged into water. The last set was immersed in a 1% sulfuric acid solution. This 1% solution was mixed using tap water and 10N solution of sulfuric acid. Every 2 days, the pH of the sulfuric acid was measured using a pH meter. The pH was maintained at 1-2. If the pH exceeded 2, the pH was adjusted until it reached 1. The pH of the sulfuric acid solution was measured, and the solution was replaced at every testing interval. The purpose of the different cube exposures was to provide a way to determine if changes in mass and volume could be attributed simply to the pore spaces in the samples filling with water or if they could be attributed to physical changes from exposure to sulfuric acid.

At days 1, 7, 14, 28, 56, 84, and 112, volume, mass, and compressive strength measurements were taken for samples stored in all conditions. Three cubes from each condition were the designated test subjects for volume and mass change. For the compressive strength tests, three of the other cubes from that exposure condition were crushed at each interval. At each testing interval, the cubes submerged in acid were removed from their containers. The three designated cubes for volume and mass were brushed with stiff-bristle plastic brush lightly 4 times across each face of the cube and rinsed with water to remove any loose material. The rest of the cubes were not brushed to monitor the physical appearance of the cubes subjected to sulfuric acid attack. After the cubes were rinsed, they were set on a towel for 30 minutes to dry. The cubes submerged in water were removed from their containers and set aside onto a towel to dry for 30 minutes before testing. After the cubes dried, mass, volume, and compressive strength measurements were taken. At each testing interval, water and sulfuric acid were replaced.
Volume was measured by taking three measurements at the top, middle, and bottom of each cube face with digital calipers and taking the average of the face dimensions to determine a volume.

RESULTS

SODIUM SULFATE STANDARD METHOD

LENGTH CHANGE RESULTS

Percent strain measured in the standard ASTM C1012 method is shown in Figure 5. Each datapoint represents the average of three prism measurements. The data collected from the standard method showed similar results with the data collected through the accelerated method (shown in the next section). The standard method prisms recorded higher expansions than the accelerated method due to the use of a higher concentration sodium sulfate solution. An increase in strain over the measurement period indicates expansion of the prisms, all prisms expanded over the measurement period. The BCSA-0.52-0.35 samples had lower measured expansion for the entire measurement period than the PC and PC-V mixtures. The BCSA-0.52-0.35 samples had expansions lower than 0.05% after 244 days. BCSA-0.52-0.35 showed an expansion of 0.038% at day 244, while PC and PC-V showed 0.16% and 0.53% expansion, respectively. The Type V cement samples (PC-V) showed about 131.3% more strain than the type I/II PC used in the study (PC). This was not unexpected, since past work has shown some type V cements perform worse when exposed to sulfate solution than type I/II cement [41, 5]. ACI defines four sulfate exposure categories as S0, S1, S2, and S3 based upon the amount of water-soluble sulfate present in the water or soil the structure will be exposed to [24]. Based on Figure 5, the BCSA-0.52-0.35 mixture was the only mixture that remained below 0.05% expansion at 6 months and based on the trend it would likely be suitable for exposure class S3 [24]. This indicates very good sulfate resistance in the BCSA cement mortar.
Figure 5 – ASTM C1012 Average Percent Strain

**MASS CHANGE RESULTS**

Figure 6 shows the mass change of the same mortar prisms from the standard sulfate test method. The BCSA gained the least amount of mass. This is thought to demonstrate a stronger sulfate resistance, since an increase in mass could indicate formation of new reaction products from the sulfate solution [50]. Mass change, however, has been proven to be less reliable than strain measurements [21]. Taken as a whole, the ASTM C1012 results appear to show that BCSA cement expands less than PC in the presence of sulfate solution. The results of ASTM C1012 also showed good agreement with the accelerated method, described in the next section.
SODIUM SULFATE ACCELERATED METHOD

LENGTH CHANGE RESULTS

The accelerated method results are shown in Figures 7-9. Each data point represents the average of measurements on three prisms for each mixture tested with the accelerated method. The graphs show measurements out to 244 days, when the testing was ended. As shown in Figure 7, BCSA mixtures had noticeably different performance compared to PC samples. This figure also shows that at day 35 of submersion, the accelerated method showed very similar results to day 244 of submersion in terms of the relative performance of each mixture. The BCSA cement mixtures had an average expansion of 0.036% at 244 days compared to 0.073% for PC, 0.063% for PC-V, 0.054% for PC-FAC, and 0.047% for PC-FAF. The class F fly ash and PC mixture (PC-FAF) performed the best out of the non-BCSA cement mixtures. Class F fly ash has proven effective at mitigating sulfate attack in past research [25, 29]. The blend of PC and class C fly ash (PC-FAC) performed almost as well. The most sulfate resistant BCSA mix was BCSA-0.56-
0.35 with a maximum expansion of 0.031%. However, the seven BCSA mixes showed only a 0.006% difference between the least and most expansive of the BCSA mixes. With this difference in mind, the effect of w/cm or citric acid dose on sulfate resistance appears to be weak for the ranges tested here compared to differences with other cement systems. Nonetheless, BCSA cement outperformed all other PC mixes based upon expansion comparisons.

**Figure 7 – Accelerated Method Average Percent Strain**

**MASS CHANGE RESULTS**

Mass was also measured on all the prisms exposed to sulfate solutions. The mass change is shown in Figure 8. These results were harder to interpret than the strain results. Mass was expected to increase over the measurement period [50]. Past work has suggested that this increase in mass could be due to filling the emptied pores of the prisms with the sulfate solution which could accelerate ettringite formation within the prisms [50]. The prisms did not experience any significant mass loss by the surface sloughing off. Therefore, figures only show an increase in mass, which could be explained by formation of ettringite and gypsum [50]. The most resistant mix in terms of both mass and strain results seems to be BCSA-0.56-0.35, the mix with the highest w/cm. Previous research showed more resistance to sulfate attack with lower w/cm,
however, using BCSA cement with higher w/cm showed more resistance [25, 26, 24]. However, PC and PC-V seemed to perform better than some BCSA mixes. The class F fly ash mix also seemed to gain more mass than the PC and PC-V mixes. Increase in mass was interpreted as growth of ettringite and gypsum. Again, mass change should not be used as the main metric to determine sulfate resistance because it does not indicate structural integrity [21]. However, for the accelerated method, all mixes stayed below the established expansion limit.

![Figure 8 – Accelerated Method Average Mass Change](image)

**SULFATE RESISTANCE OF BCSA MIXTURES COMPARED TO CITRIC ACID DOSAGE**

Different citric acid doses were used in some of the BCSA mixes in the accelerated method to observe the effect, if any, of citric acid dosage on sulfate resistance. At a 0.52 w/cm, citric acid dosages of 0%, 0.35% and 0.7% by weight of cement were compared. The strain results are shown in Figure 9. Looking at strains only, there does not appear to be a relationship between citric acid dosage and sulfate resistance.
Figure 9 – Accelerated Method BCSA and Citric Acid Average Percent Strain

SULFURIC ACID TESTS

SULFURIC ACID VOLUME CHANGE

The data collected from submerging mortar cubes in 1% sulfuric acid is shown in Figures 10-17. Each data point in all these figures represents an average of three cubes. Length measurements were taken vertically and horizontally at the top, middle, and bottom of each face of the cube with calipers. These values were averaged and then multiplied together to determine the average volume of the cube at each age.

Volume measurements were used as an indication of sulfuric acid resistance. The results for these measurements are shown in Figure 10. It was difficult to discern a trend for some of the volumetrics for the measurement period observed (112 days). Some cubes had differential deterioration on a given face. This could have contributed to inconsistencies between measurements in the results shown in Figure 10. Over the 112-day measurement period, cubes BCSA-0.485-0.35-7D, BCSA-0.485-0.35-28D, PC, and PC-FAF increased in volume. Expansion
of the cubes over the measurement period could be due to formation of gypsum in the samples as sulfuric acid converts available calcium hydroxide or other reaction products. Expansion and increase of volume of the cubes could occur until the outer layers of the cubes slough off. This could lead to an eventual volume decrease. The remaining two sets of cubes contracted over the measurement period, these were samples BCSA-0.485-0.35-28D and BCSA-0.56-0.35-7D. The contraction of these cubes can be interpreted as continual loss of cement paste and sand over time from the surface of the cubes. The most significant volume decrease occurred with the BCSA-0.56-0.35-7D cubes. These cubes had decreased in volume by 1.3% by day 112. The most significant expansion was demonstrated in the PC cubes. The PC cubes increased in volume by 1.5%. The most unchanged volumes were shown with the BCSA-0.56-0.35-28D and BCSA-0.485-0.35-28D cubes, with an increase in volume by 0.4% and a decrease in volume by 0.4%, respectively. Volumetric changes should not be the sole deciding factor in whether a cement is sulfuric acid resistant. Volumetric change cannot directly indicate sulfuric acid resistance, as it does not imply structural integrity.
To better understand the changes in volume of the cubes stored in sulfuric acid, cubes made from the same mixtures were cured in a water bath for 112 days or left in an environmental chamber at 50% humidity for 112 days. The purpose of this was control for any changes in volume from uptake of the water into the cubes or typical hydration of cement in the presence of water. The dry cured cube volume measurements (as a percent of initial volume) were subtracted from the water cured volume measurements (as a percent of initial volume). This was theoretically the volume change that could be attributed to uptake of moisture and additional hydration from being placed in a solution of water. This new volume value was then subtracted from the volume measurement taken from the cubes submerged in the sulfuric acid solution. This should leave only volume changes attributable to sulfuric acid exposure. These adjustments are shown in Figure 11. The PC cubes showed the largest change in volume. Even with these adjustments, the cubes with the smallest volume change were the CSA-0.56-0.35-28D cubes. These cubes
increased in volume by only 0.19%. Again, it is unclear whether these volume changes indicate acid resistance.

**Figure 11 – Adjusted Sulfuric Acid Volumetric Change**

The \( w/cm \) was compared to sulfuric acid resistance for the BCSA mixes. Figure 11 shows the results for the batches with varying \( w/cm \). The two \( w/cm \)'s chosen were 0.485 and 0.56. Using the results in Figure 11, the average change in volume for the 0.485 and 0.56 \( w/cm \) were 0.77\% and -0.34\%, respectively. There was a small increase in volume for the 0.56 \( w/cm \) and a small decrease in volume with the 0.485 \( w/cm \). This shows a small difference in \( w/cm \) effecting volumetric changes for the \( w/cm \) tested.

The effect of time prior to sulfuric acid exposure was analyzed with the BCSA cubes by exposing some cubes to the solution at 7 days and some at 28 days. The 7-day cure time (CSA-0.485-0.35-7D and CSA-0.56-0.35-7D) batches increased in volume by an average of 1.32\%. The cubes cured for 28 days (CSA-0.485-0.35-28D and CSA-0.56-0.35-28D) had an average decrease in volume of 0.89\% by the end of the measurement period. This shows a small
difference in volumetric change based on cure time. The longer the cure time, the smaller the decline in volume, but this effect was relatively small between 7 days and 28 days.

**SULFURIC ACID MASS CHANGE**

Mass change was measured at each interval for all cubes in each environment (sulfuric acid solution, in water, in 50% humidity). Mass change, in these cases, was misleading as it does not clearly indicate an effect of the acid on the cubes. This has been observed in past work on sulfuric acid exposure [29]. The overall mass change in cubes submerged in sulfuric acid can be seen in Figure 12. Initial mass gain can be seen in the PC, PC-FAF, and BCSA-0.485-0.35-7D cubes. The initial gain in mass could be attributed to the water or acid filling the pores in the mortar cubes. The cubes that had the smallest change in mass were the PC cubes. This could be attributed to resistance to sulfuric acid attack or formation of gypsum and ettringite that replaced the mass lost through the degradation of the cement paste. The cubes with the largest loss of mass were the BCSA-0.485-0.35-7D cubes. These cubes lost 4.7% of their mass by day 112. This is a much more significant mass loss than all other cube types which can be attributed to loss of cement paste and eventual loss of bound sand particles due to the sulfuric acid attack.
Figure 12 – Average mass change of cubes stored in sulfuric acid solution

Figure 13 shows the percent mass loss of cubes in sulfuric acid with the difference between water cured cubes and dry cubes subtracted out. This was done to remove any mass change of cubes due to additional hydration of the cement or filling of the pore space with solution. Therefore, whatever mass change remaining could be solely attributed to volume changes from sulfuric acid causing breakdown of reaction products in the cube. The largest loss of mass was still shown as BCSA-0.485-0.35-7D and the smallest difference in mass still shown as the PC batch. The cement pastes for all BCSA mixes deteriorated very quickly with submersion in the sulfuric acid. This could indicate a low resistance to sulfuric acid attack compared to PC or blends of PC and fly ash. Comparing within BCSA cement samples, more curing time before submersion in sulfuric acid led to less mass change (6.01% loss for 7-day cure versus 4.23% for 28-day cure) and higher w/cm seemed to lead to less mass change (5.82% loss for 0.485 w/cm versus 4.42% for 0.56 w/cm).
Compressive strength of the cubes was expected to give a stronger indication of resistance to acid attack than mass change based on past work on acid attack [29]. This is due to the process called ‘softening’. This process softens the outer layers of the mortar cubes which decreases compressive strength [29]. The formation of gypsum across the face of the cubes encourages this ‘softening’ process [22]. Figure 14 shows the compressive strength decrease from the initial strength at the time the cubes were submerged in sulfuric acid. The largest decreases in compressive strength occurred with the BCSA cement mixes. When averaged, the compressive strength of all BCSA mixes decreased about 39.5% from their initial strength. This is a significant decrease in compressive strength, especially when compared to PC and the class F fly ash mixes. The PC batch had a lower decrease in compressive strength of 4.6%. For the PC-FAF mix, however, there was an overall increase in compressive strength of 21.6 from day 1 in sulfuric acid to day 112. Based solely on compressive strength, the strongest resistance against
sulfuric acid attack can be seen in the PC-FAF mix. The best performing BCSA mixture was the mix with the highest w/cm (0.56) placed in sulfuric acid after only 7 days of cure time. This mixture had about 13.7% more compressive strength loss compared to the PC cubes at 112 days.

Figure 14 – Sulfuric Acid Compressive Strength

Figure 15 shows the 112-day compressive strengths of water cured samples compared to samples stored in sulfuric acid solution. The largest absolute difference in compressive strength between water cured samples and samples exposed to sulfuric acid was in BCSA-0.485-0.35-28D. This was a 106.2% difference. The smallest change in compressive strength was for the PC-FAF mix with a 37.8% decrease at day 112. Looking at both Figures 14 and 15, a mixture of class F fly ash and PC appears to provide the best resistance to acid attack of the mixtures tested. The PC and PC-FAF showed similar results to previous research [29]. Looking at the BCSA mixtures only, a counterintuitive relationship emerged: a higher w/cm and shorter curing time appeared to give the best performance. The average difference between compressive strengths determined from cubes submerged in water versus cubes submerged in sulfuric acid was 97.6% and 63.6%.
for w/cm of 0.485 and 0.56, respectively. The calculated difference for the 0.485 w/cm was almost 1.5 times larger than for a w/cm of 0.56. The difference indicates improved sulfuric acid resistance. The lower the difference, the higher the resistance. Therefore, based on compressive strength differences, higher w/cm were more resistant when comparing BCSA samples. This contradicts previous research on PC and blended PC and fly ash mixes [25, 26, 35, 29].

![Graph showing sulfuric acid compressive strength comparisons]

**Figure 15 – Sulfuric Acid Compressive Strength Comparisons**

**PHYSICAL APPEARANCE OF CUBES AND PH OF SOLUTION**

Figure 16 shows the changes in pH over time. The pH of the sulfuric acid solution was measured every 2 days to allow for the solution to be replenished and brought back to 1.0. During the first several weeks the cubes were immersed, the pH in most sample containers rose for each cube mixture. However, as weeks passed, pH changed differently for each cube type. The cement types that were initially more resistant to pH change were the PC-FAF, BCSA-0.56-0.35-7D, and BCSA-0.485-0.35-28D cubes. As time passed, the pH of the solution around PC-FAF cubes did not change greatly while the solution surrounding PC cubes showed an initial pH change.
followed by less change over time. The acidic solution most to pH change as time passed for the BCSA cubes were the BCSA-0.56-0.35-28D cubes. This could indicate that a higher w/cm and longer cure time may aid in resisting sulfuric acid for BCSA cement. When the solution pH does remains unchanged, this means that the ions in the solution are not reacting with the concrete, indicating resistance to sulfuric acid attack [18].

The cubes were visually inspected at each testing interval. Figure 17 shows cubes after demolding (left), after 112 days in sulfuric acid solution (center), and after compressive strength testing at 112 days with phenolphthalein indicator solution applied to the surface (right). The BCSA cubes seemed to lose the most surface paste over time. The cubes used for compressive strength showed white substances on the surface of the cubes. These white substances were more noticeable on the PC and PC-FAF cubes than any of the BCSA cubes. Based on previous research, this white substance was thought to be gypsum formed from the reaction between calcium hydroxide in the cement paste and the sulfuric acid [33, 44, 29, 22]. Phenolphthalein

**Figure 16 – pH Change per Day**

The cubes were visually inspected at each testing interval. Figure 17 shows cubes after demolding (left), after 112 days in sulfuric acid solution (center), and after compressive strength testing at 112 days with phenolphthalein indicator solution applied to the surface (right). The BCSA cubes seemed to lose the most surface paste over time. The cubes used for compressive strength showed white substances on the surface of the cubes. These white substances were more noticeable on the PC and PC-FAF cubes than any of the BCSA cubes. Based on previous research, this white substance was thought to be gypsum formed from the reaction between calcium hydroxide in the cement paste and the sulfuric acid [33, 44, 29, 22]. Phenolphthalein
indicator solution was used to determine acid penetration into cubes after the cube interior was exposed from compressive strength testing. The phenolphthalein indicator solution will turn more basic components of the cubes pink, while showing no change to more acidic surfaces. Calipers were used to determine the depth at which the sulfuric acid penetrated the cubes. Results for acid penetration depth are reported in Table 4. These results showed that PC type I concrete had less acid penetration than the other cement types. All other cement types showed the acid penetrated the cubes about twice as deep compared to PC type I cubes. Average BCSA penetration depths were higher than both PC and PC-FAF cubes.
Figure 17 – Sulfuric Acid Immersed Cubes Before Submersion in Sulfuric Acid (Left) after 112 Days in Sulfuric Acid (Center) and After Compressive Strength Test with Phenolphthalein Indicator on Surface
Table 4 – Sulfuric Acid Penetration Depths

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Depth (in.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>0.050</td>
</tr>
<tr>
<td>PC-FAF</td>
<td>0.091</td>
</tr>
<tr>
<td>BCSA-0.485-0.35-7D</td>
<td>0.095</td>
</tr>
<tr>
<td>BCSA-0.485-0.35-28D</td>
<td>0.100</td>
</tr>
<tr>
<td>BCSA-0.56-0.35-7D</td>
<td>0.099</td>
</tr>
<tr>
<td>BCSA-0.56-0.35-28D</td>
<td>0.095</td>
</tr>
</tbody>
</table>

CONCLUSIONS

The following conclusions are broken up based on conclusions from each stage of the testing reported in this thesis. The results collected from the sulfate and sulfuric acid testing showed that the most effective mixture in resisting both sulfate attack and sulfuric acid exposure was the blend of class F fly ash and PC. This aligns with previous research on sulfate and sulfuric acid attack that has been performed [25, 29]. PC type I/II and type V showed less resistance to sulfate attack. Type I PC showed signs of damage due to sulfuric acid attack. BCSA mixtures tested in this study had the best resistance to sulfate attack but were not any better at resisting sulfuric acid exposure than PC mixtures tested.

Resistance to sulfate attack:

- Comparing the length change of prisms in the standard and accelerated sulfate resistance test methods, BCSA was found to be the most resistant. According to the accelerated method, the second least expansive prisms contained blended PC and class F fly ash.
- Comparing the mass change observed using the standard and accelerated sulfate resistance methods, BCSA showed the least amount of mass gained. This smaller change in mass from day 1 to day 244 indicated good sulfate resistance. The blended class F fly ash and PC were the second most resistant to sulfate attack.
- Citric acid dosage seemed to have minimal effects on with the sulfate resistance of BCSA cement mixtures for the dosages tested.
Varying $w/cm$ were tested for BCSA cement mixtures to compare to sulfate resistance.

The effect of $w/cm$ on sulfate resistance was minimal, but a higher $w/cm$ may have led to better resistance.

Resistance to sulfuric acid:

- The most resistant mix to sulfuric acid attack was the blended PC and class F fly ash mix. PC-FAF showed a small (0.7%) increase in volume from day 1 to day 112 which should be correlated to good durability. Mass change for PC-FAF showed 1.1% decrease in mass. This mix showed an increase in compressive strength over the measurement period while all other mixes showed a decrease in compressive strength. Compressive strength retention was considered the most important factor when ranking sulfuric acid resistance.

- The effect of $w/cm$ on sulfuric acid resistance was compared for BCSA cement specimens only. BCSA cubes showed better mass, compressive strength, and pH change with higher $w/cm$. Little difference was shown in the volumetric measurements.

- The effect of curing time prior to exposure to sulfuric acid was also compared for BCSA cement mixtures. A longer curing time prior to exposure to sulfuric acid (28-day versus 7-day) resulted in smaller mass and volume changes in the BCSA cubes, and the pH of the sulfuric acid solution tended to change less for cubes that were cured for 28-days. When comparing compressive strength, however, cubes cured for 7 days performed better, with higher compressive strengths after 112 days in sulfuric acid. The comparison of BCSA mixture characteristics on sulfuric acid resistance was a small component of this study and this question requires further work.

The PC mixture with a 30% replacement with class F fly ash had the most favorable results when considering both phases of MIC studied in this project. For sulfate attack, the class F fly ash mix
expanded 0.047% while it increased in mass by 1.09%. During the sulfuric acid testing, the class F fly ash mix increased in volume by 0.43%, decreased in mass by 2%, and increased its compressive strength by 21.6%. MIC cannot be prevented; however, a class F fly ash mixture could prolong the service life of manholes compared to PC only mixtures. Based on past work summarized in the background of this thesis in combination with the findings in this report, it is recommended to use SCMs (especially class F fly ash) to replace a percentage of PC to increase resistance against MIC.

**RECOMMENDED FUTURE WORK**

Through the findings of this research, further investigations into sulfate attack and its effects on $w/cm$ and BCSA and should be analyzed. The higher the $w/cm$ for this cement type, the better BCSA performed. There should be research to determine the acceptable range of $w/cm$ when using BCSA cement.

There should be further research into alternative cement types and their resistance against MIC. Previous studies have shown increased resistance against sulfate attack. The new testing methods for MIC could provide a better understanding of alternative cement types, including CAC. These new testing methods are ASTM C1904-20 *Standard Test Methods for Determination of the Effects of Biogenic Acidification on Concrete Antimicrobial Additives and/or Concrete Products*, ASTM 1898-20 *Standard Test Methods for Determining the Chemical Resistance of Concrete Products to Acid Attack*, and ASTM C1894-19 *Standard Guide for Microbially Induced Corrosion of Concrete Products* [15].
REFERENCES


