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Effects on Strength and Corrosive Characteristics of Hardened Cement Paste Using Rice Husk and Sugarcane Bagasse

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EFFECTS ON STRENGTH AND CORROSIVE CHARACTERISTICS

OF HARDENED CEMENT PASTE USING RICE HUSK AND

SUGARCANE BAGASSE

by

Travis David Garrett, B.A.

A Thesis Presented in Partial Fulfillment
of the Requirements of the Degree
Master of Science

COLLEGE OF ENGINEERING AND SCIENCE
LOUISIANA TECH UNIVERSITY

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Signature Page

ABSTRACT

Cement is one of the most used building materials in the world. The production of ordinary Portland cement contributes to the release of harmful greenhouse gasses. In an effort to reduce these emissions, different materials are being evaluated for their use as partial replacements for ordinary Portland cement. Rice husk and sugarcane bagasse are agricultural waste products and large amounts of these are currently landfilled, making them inexpensive and available. When combusted at high temperatures they form rice husk ash and sugarcane bagasse ash that have pozzolanic characteristics. The high silicon dioxide in these products makes them good options to use as partial replacement for OPC. This study evaluates compressive strength, porosity and corrosion resistance of hardened cement paste containing rice husk ash and sugarcane bagasse ash as partial replacements for ordinary Portland cement.

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CHAPTER 1

INTRODUCTION

1.1 Background

Cement is one of the most used building materials worldwide. It has been an essential part for the development of infrastructure for hundreds of years. The earliest forms of cement consisted of a mixture of calcined lime stone and pozzolanic material such as volcanic ash. The Greeks and Romans have constructed several durable structures with mixtures like this. However, this is not what is known as Ordinary Portland Cement (OPC) today. OPC has four main ingredients and a more complex production process that will be covered in a later section. Because OPC is a very important building material numerous efforts have been made to improve its performance. A few areas of focus include strength development, corrosion resistance, and environmental impact. In this study, pozzolanic materials in the form of biomass ash, specifically rice hush ash (RHA) and sugarcane bagasse ash (SCBA), will be used as partial replacements for OPC to evaluate their ability to enhance the performance of hardened cement paste (HCP).

1.2 Production of Ordinary Portland Cement

To manufacture OPC, raw materials are ground and blended together then heated in a kiln to make Portland cement clinker. There are four principal oxides needed to make Portland cement clinker. They include calcium oxide (CaO), silicon dioxide (SiO_2),

aluminum oxide (Al_2O_3) and iron oxide (Fe_2O_3) (Dodson 1990). These oxides form the

hydraulic compounds shown in Table 1-1.

Table 1-1: Hydraulic compounds in OPC (Dodson 1990)

Chemical Name	Mineral Phase Name	Chemical Formula	Cement chemist's designation
Tricalcium silicate	Alite	$3CaO \cdot SiO_2$	C_3S
Dicalcium Silicate	Belite	$2CaO \cdot SiO_2$	C_2S
Tricalcium Aluminate	Celite	$3CaO \cdot Al_2O_3$	C_3A
Tetracalcium Alumino-ferrite	Iron	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF

The clinker is ground down to the desired fineness, which is the powder that is

OPC. The fineness of the cement is important because it determines the amount of

surface area that is readily available to react with water. This controls the rate of

hydration and rate of strength development in HCP.

1.3   Hydration Process

The main reactions in the cement hydration process are in the silicate phases, alite

and belite. When water reacts with the C_3S and C_2S, it forms Calcium silicate hydrate

(CSH) and Calcium hydroxide (lime). The reactions are shown below.

$$2[3CaO \cdot SiO_2] + 12H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca(OH)_2$$

$$6[2CaO \cdot SiO_2] + 12H_2O \rightarrow 5CaO \cdot 6SiO_2 \cdot 5H_2O + 7Ca(OH)_2$$

CSH is the glue that hardens and gives HCP its rigid structure. The lime by itself does

not contribute to strength characteristics of the cement. However, if a pozzolan, such as

RHA or SCBA, is introduced, it can react with the lime that is a product of the cement hydration and produce additional CSH (Givi, et al. 2010).

1.4   Rice Husk Ash

Rice husk is an abundant agricultural waste product around the world. Each year the United States produces 18 billion pounds of rice. In Louisiana there are approximately 400,000 acres dedicated to growing rice each year, not to mention the 1.2 million acres for growing rice in the neighboring state of Arkansas (Think Rice 2019). When rice is harvested the husk is removed from the grain at a processing center. Rice husks make up approximately 20% of the grain and are not easily composted or useful as animal feed. However, when combusted at high temperatures rice husks will give a 20% yield of RHA. RHA has a high content of amorphous silica that makes it an ideal pozzolan. According to ASTM C618, a pozzolan is a material in which the combination of silicon dioxide, aluminum oxide and iron oxide are not less than 70%. The amorphous SiO_2 content and the porous structure of the RHA depends on the temperature and duration of combustion of the rice husks (Tuan 2011). It can contain as much as 80-85% silica that is highly reactive (Kishore, et al. 2011). Another study showed the content of silica to be between 90-95% (Gursel, et al. 2016). Table 1-2 shows different composition analyses of RHA from other studies.

Table 1-2: Oxide composition of RHA from the literature

	(Shanmugava-divu, et al. 2014)	(Kartini, et al. 2010)	(Hesami, et al. 2014)	(Givi, et al. 2013)
Oxide	Mass percent (%)			
CaO	2.04	na	1.15	1.30
SiO_2	78.40	96.70	86.02	87.86
Al_2O_3	1.04	1.01	0.36	0.68
Fe_2O_3	0.30	0.05	0.16	0.93
MgO	0.80	0.19	0.39	0.35

RHA is porous in nature and has a high surface. Because of its high surface area, cement mixes with RHA require more superplasticizer than other mixes (Zareei, et al. 2017). If a superplasticizer is not being used, then the water demand will increase with RHA addition because the porous structure of RHA allows it to absorb the water (Shanmugavadivu, et al. 2014). The particle size of RHA is also a factor that affects water demand and hydration rates. There have been many different studies reporting different mean sizes for RHA particles. A mean particle size of 7.3 μm was reported by (Tuan 2011). In a different study the mean particle size was 25.83 μm (Kartini, et al. 2010). Sometimes grinding is necessary. One study found that grinding to an average particle size of 10 μm showed some crushing of the cellular structure of RHA, but the effects were minor when compared to the increased reactivity due to smaller particle size (Gursel, et al. 2016).

1.5   Sugarcane Bagasse Ash

Sugarcane is not as widely produced as rice but the bagasse from sugarcane, which is the fibrous residue left over after extracting the juice, when combusted will

produce SCBA. In 2018 sugarcane production in the United States amounted to 34,754

thousand tons, most of which was produced in Florida and Louisiana (Statista 2019).

SCBA qualifies as a pozzolan as defined in ASTM C618, therefore it can be suitable for

use in cement structures. The composition of SCBA as used in other studies is shown in

Table 1-3.

Table 1-3: Oxide composition of SCBA from the literature.

	(Cordeiro, et al. 2012)	(Agredo, et al. n.d.)	(Abdulkadir, et al. 2014)
Oxide	Mass percent (%)		
CaO	2.2	3.8	9.9
SiO2	78.3	72.8	72.9
Al2O3	8.9	6.4	1.1
Fe2O3	3.6	5.5	6.9
MgO	NA	2.3	6.41

The compressive strength of concrete with replacement levels of 10%, 20%, and

30% of OPC with SCBA was found to be less than concrete with only OPC (Abdulkadir,

et al. 2014). The average particle size of SCBA reported in this study was 45 μm.

Another study showed that SCBA with a particle size of 2.7 μm and a replacement level

of 20% had less compressive strength than concrete with only OPC (Cordeiro, et al.

2012). In the same study the chloride ion penetration was recorded. The charge measured

from concrete which SCBA replaced 20% of OPC was 5832 coulombs, compared to

8451 coulombs measured from concrete with only OPC. This can imply that the

permeability of the concrete with SCBA is lower than the concrete with only OPC.

1.6   Pozzolanic Reaction

This reaction occurs when siliceous material, mainly silicon dioxide, reacts with the free calcium hydroxide that is a product of cement hydration. Pozzolan-lime reactions are slow, typically starting a week or more after initial mixing of water and binder.

$$2SiO_2 + 3Ca(OH)_2 \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O$$
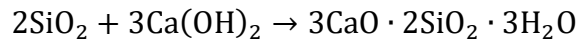
Because of this delayed reaction, cement with pozzolan will be more permeable at early ages and gradually become denser over time. When the pozzolanic reaction occurs, producing more cement gel, the pore size decreases making a denser concrete that is stronger and more durable (Givi, et al. 2010).

1.7   Compressive Strength of Cement and Concrete Structures with RHA

Partial cement replacement by RHA has been shown to enhance the compressive strength of various cement mixes. The optimum amount of RHA to use differs among various studies and ultimately depends on several different factors, such as aggregate used, water to binder ratio and curing time. When using a water to binder ratio of 0.53 for cement mortars and concrete, up to 30% of the cement can be replaced with RHA without negatively affecting compressive strength (Ganesan, et al. 2008). The highest compressive strength recorded in this study for mortar was at 15% replacement with RHA and for concrete at 20% RHA replacement (Ganesan, et al. 2008). Compressive strength of concrete with replacement levels of 4%, 8% and 12% and a water to binder ratio of 0.27 were tested and results showed 8% to have the highest compressive strength, about 17.5MPa compared to 14 MPa with no RHA (Hesami, et al. 2014). Tuan (2011)

studied the effects of RHA on UHPC (ultra high performance concrete), which requires a compressive strength of at least 150MPa. He found 20% replacement to have the higher compressive strength at 91 days while 10% replacement showed higher compressive strength at earlier ages up to 28 days. This was attributed to the RHA absorbing mixing water and delaying cement hydration. Zareei et al. (2017) tested compressive strength of concrete with 25% replacement of OPC with RHA after 7 and 28 days of curing and found an increase of 6.9% and 6.8% in compressive strength, respectively, compared to concrete with only OPC (Zareei, et al. 2017). It was also reported in this study that 28 days of curing was sufficient time for development of strength.

1.8   Corrosion Resistance of Concrete with RHA

Corrosion of steel reinforcement in concrete can jeopardize the integrity of the structure. Corrosion is typically related to the permeability of the cement because that allows damaging agents, such as chloride ions, access to the reinforcement (Gursel, et al. 2016). For this reason, a reliable test to determine permeability is a Rapid Chloride Ion Penetration Test as described in ASTM C-1202. One study conducted this test on concrete containing various percent replacement of OPC with coal fly ash and RHA. They found that cement mixes containing mass percentages of 40%, 40%, and 20% of OPC, fly ash and RHA, respectively, showed over a 50% reduction in chloride ion penetration as mixes with mass percentages of 60% and 40% OPC and fly ash, respectively (Gursel, et al. 2016). In another study, chloride ion penetration was measured in concrete mixes with RHA and SCBA. A replacement percentage of 20% was used for both RHA and SCBA. The charge recorded for rapid chloride ion penetration in concrete with RHA was approximately eight times less than just OPC and about five

times less than concrete with SCBA (Cordeiro, et al. 2012). Corrosion resistance of concrete with a 20% replacement of cement for RHA can be measured by an accelerated electrolytic corrosion test. This test involves submersing the cement specimen in a 6% sodium chloride solution and attaching a copper counter electrode and DC Voltage supply to steel reinforcement in the concrete. After six hours in the solution the reinforcement bar is removed from the cement and cleaned as per ASTM G1. Then each bar is weighed to the accuracy of 0.01 mg to determine the weight loss due to corrosion. The results showed that the weight loss of the reinforcement in the concrete with 20% RHA replacement was 48% less than the reinforcement in concrete without RHA (Shanmugavadivu, et al. 2014).

1.9   Water Absorption and Porosity

The porosity is an important factor to consider when evaluating the durability of cement structures. Several studies have correlated increased strength and reduced corrosion to lower porosity. Hesami (2013) suggests a direct relationship between porosity and permeability and that compressive and tensile strengths are reduced while permeability and porosity are increased. The results from this study show that replacement of cement with RHA is effective at reducing porosity only to a certain amount, 8% -10% depending on the water to binder ratio; after which the porosity increases because the high specific surface area of RHA. However, a different study reported after 28 days of curing that concrete with only OPC was 3 and 7 times more permeable that concrete containing superplasticizer and with replacement of OPC by 20% RHA and 30% RHA, respectively (Kartini, et al. 2010). It was suggested that due to

its finer particles and pozzolanic reaction, the RHA created products to fill the larger

voids in the hydrated cement, thus reducing the average pore radius.

CHAPTER 2

METHODS AND MATERIALS

2.1   Introduction

Cement is one of the most produced building materials in the world and its

production contributes 8-10% of the emissions of greenhouse gasses worldwide

(Christopher, et al. 2017). Concrete is normally used as the foundation for most buildings

so it can be argued that it must be the longest lasting and most structurally sound

material. Because rice husk and sugarcane bagasse are readily available and when

combusted have pozzolanic properties, they should be investigated as a partial

replacement to OPC. If this can be done successfully, the environmental foot print of

OPC production can be reduced and a potentially more sustainable cement can be

implemented into building and construction. The aim of this study is to test varying

amounts of RHA and SCBA as a partial replacement of OPC to see if similar or improved

characteristics can be achieved in HCP. It is important to consider compressive strength,

corrosion of reinforcement embedded in cement and the porosity or pore structure of the

cement when evaluating its performance.

The rice husk makes up about 20% of the mass of a grain of rice and is removed

during harvesting. Because of the high silica content of the rice hull, it is resistant to

composting. It also is not a good enough source of nutrients to be used for animal feed.

However, because the rice husks have a high content of silica, it can generate large

quantities of silicon dioxide when combusted into RHA. Typically, 85-95% of the composition of RHA is silicon dioxide. The form of silicon dioxide in the RHA will react with lime that is a product of cement hydration to produce addition cementitious material. These reactions are called pozzolanic reactions. Studies have shown that using RHA as a partial replacement for OPC can yield stronger concrete

SCBA also contains high percentages of silicon dioxide. It contains around 70 - 80% silicon dioxide and around 5 % aluminum oxide. This qualifies SCBA as an acceptable pozzolan and it can react with lime from cement hydration. The use of SCBA as a partial replacement for OPC has not been as heavily studied as RHA because it contains lower amount of silicon dioxide, making it a weaker candidate for a pozzolan. However, it has been shown to provide sufficient properties when used in concrete. Sugarcane bagasse is an agricultural waste product that can be obtained for cheap, and it can help reduce the amount of OPC produced, thus reducing harmful greenhouse gas emission.

2.2   Materials

For this experiment several materials were required. The primary binder used was Type I/II OPC from Ash Grove. The composition analysis from the mill test report is shown in Table 2-1. RHA and SCBA were used as partial replacements of OPC. The rice husk came from Falcon Rice Mill in Crowley, Louisiana. The sugarcane bagasse came from Lula Westfield in Paincourtville, Louisiana. A Lindberg muffle furnace was used to produce RHA and SCBA. Quarter inch carbon steel rebar was used for reinforcement in cement samples. This rebar was purchased from OnlineMetals.com and designated as Mild Steel 1018 Cold Finish Round. The reinforcement was prepared for embedding in

cement sample by cutting into 5 inch (12.7 cm) sections and polishing with 150 grit sand paper to remove surface debris. Powder free nitrile gloves were worn in all processes to prevent contamination due to skin oils. Plastic cylindrical molds 2 inches (5.08 cm) in diameter and 4 inches (10.16 cm) in height were used for casting specimens. Calcium Hydroxide (95%) from ACROS Organics was used in a curing bath solution. Sodium Chloride from Fisher Scientific was dissolved in mixing water for achieving a sea water concentration and for curing bath to accelerate corrosion. Superplasticizer, MasterSure® Z 60 from BASF was used for retaining workability of mixes. Sulfur capping compound CA-0100 from Test Mark Industries was used for preparing samples for compression testing. The machine used for compression testing was by Test Mark Industries. To test the corrosion potential a copper-copper/sulfate half cell reference electrode (model 2-A) from Tinker & Rasor was used.

Table 2-1: Composition of OPC used in this study. Test method by A.S.T.M C114

CHEMICAL	
Item	Test Result
SiO2(%)	20.54
Al2O3(%)	4.61
Fe2O3(%)	3.32
CaO(%)	63.81
MgO(%)	0.91
SO3(%)	3.17
Na2O(%)	0.16
K2O(%)	0.58
CO2(%)	1.09
Limestone(%)	2.9
CaCO3 in limestone(%)	86.87
Potential Compounds (%)	
C3S	54
C2S	16
C3A	6
C4AF	10
C3S + 4.75C3A	83

2.3 Preparing Rice Husk Ash and Sugarcane Bagasse Ash

Rice husk and sugar cane bagasse were placed into an oven separately at 500 °F

(260 °C) for 5 hours to burn the biomass down to a black ash. The purpose of this is to

reduce the amount of smoke that is produced when the biomass is burning in the furnace.

The black ash is then placed in the muffle furnace at 575 °C for 24 hours to produce

white ash with the carbon removed. These ashes contain high silicon dioxide content.

Although referred to as white ash, the SCBA had an orange tint, due to Fe_2O_3 content of

approximately 4%. RHA and SCBA were used to partially replace OPC. The oxide

composition for RHA and SCBA used in this study are shown in Table 5.

Table 2-2: Oxide composition by of RHA and SCBA used in this study.

	RHA	SCBA
Oxide	Mass percent (%)	
CaO	0.66	6.83
SiO2	94.30	71.36
Al2O3	0.77	11.20
Fe2O3	0.05	3.79
MgO	0.58	1.56

It has been reported that temperatures between 500-700 °C generate the highest content of amorphous silicon dioxide in RHA (Christopher, et al. 2017). RHA produced using the two step method described in this work is 89% amorphous as determined by X-ray diffraction (Kumar, et al. 2018).

2.4 Particle Size Distribution

The particle size distribution was measured for each biomass ash with a "Microtrac" particle size analyzer. This method works by suspending particles from the sample in glycerol then records the particle sizes using a laser light scattering technique. The mean particle sizes for RHA and SCBA were found to be 6.17μm and 6.18 μm, respectively.

2.5 Mixing and Curing

For the non-reinforced samples, the standards set by the American Society for Testing Materials, ASTM C192, were used. Batches of 6 cylindrical specimens two inches (5.08 cm) in diameter and four inches (10.16 cm) in height were prepared. They were prepared using a Kitchen Aid 600™ mixer. The water to binder ratio for this

process was 0.45:1 by mass. The binder includes the combination of cement and biomass ash. Salt water at the concentration of sea water, 35 gNaCl/L, was used as the mixing water to introduce a more corrosive environment for short term corrosion testing and to see if using sea water will yield sufficient compressive strength in HCP. The binder includes a combination of OPC and biomass ash. Each batch contains a different percentage by mass of OPC and RHA or SCBA. Batches of cement paste were prepared with RHA and SCBA as 10%, 20% and 30% replacement of OPC. When necessary small amounts of superplasticizer were added to the mixing water before mixing began to achieve desired workability. A small amount of the mixing water was added to a bottle for rinsing the stirring paddle, then the remaining water added to the mixing bowl. With the mixer set to stir, dry binder was added to water gradually. More specifically, a clean cylindrical mold was used as a scoop for the dry binder, and the scoop was poured over 30 second intervals. After approximately every 6 scoops the mixer was shut down to rinse accumulating binder from the tops of the paddle and bowl. When all the binder was added, a final rinse was performed and the remaining water in the bottle was added to the mixing bowl. The mixture was then stirred for five minutes before pouring. The mix was poured into the cylindrical molds, filling one third at a time and tamping 25 times with a 12 inch (30.48 cm) long by 3/8 inch (0.9525 cm) steel rod as per ASTM C192. The specimens were smoothed off using the rod then capped with the plastic cap included with the molds. After 24 hours the specimens were removed from the molds and placed in a bath of water for curing with a concentration of 2 grams of lime ($Ca(OH)_2$) per liter of water. The samples were stored in plastic bins, submersed in the curing solution and

open to the air at room temperature. At 28 days and at 6 months, samples were removed for compression testing.

For reinforced samples, the same methods reported above were used for preparing samples with reinforcing steel, with the exception that a 5 inch (12.7 cm) piece of 1/4 inch (0.635 cm) carbon steel was inserted into the wet cement in the mold. The steel was suspended though the center axes of the mold 1" off the bottom. Because of time constraints, after 28 days of curing in the lime water the samples were transferred to a bath of salt water at a concentration of 35 g NaCl /L, where they remained except for testing. This environment accelerated corrosion, so that it would be measurable in the time frame of the study. The corrosion potential of the steel was tested at 28 days, 3 months and 6 months.

2.6   Compressive Strength Testing ASTM C39

Before running compression tests on the prepared cement cylinders, the specimens were capped following ASTM C617. This involves heating the sulfur capping compound to 300 °F (149 °C) in a melting pot, then pouring the molten compound into a dish. Each cylindrical cement specimen is lowered vertically into the molten sulfur to harden. Both ends of the specimen are coated this way. This process creates a level surface to evenly distribute pressure across the specimen for compression testing. Compressive strength tests were conducted at 28 days and 6 months after each sample's mixing date. A load was applied at 300 lbs/s, or 95.5 psi/s (658.4 kPa/s), until failure of the specimen occurred. To determine failure a sample break of 85% was used, meaning that if a crack or fracture in the cement cylinder caused the stress on the cylinder to fall below 85% of the load being applied then the machine would stop and display the result.

2.7 Porosity by Water Absorption

After compression testing was completed pieces of the fractured cement were used to test the porosity of the specimens. Pieces 5-10 g were placed into a fresh water bath for 24 hours to ensure saturation. This was simply a precautionary measure as the samples were not removed from the curing solution for more than 6 hours. After this period the pieces were removed, lightly patted with a paper towel to remove the surface moisture, and then massed. The broken pieces were placed in a drying oven at 105 °C for 24 hours to remove all moisture from the pores of the cement. The measurement for water absorption was defined as the percentage of the mass of water the cement piece held when fully saturated compared to the dry mass. The mass was tracked over the next 48 hours to ensure all moisture was removed from the pores.

2.8 Corrosion Potential ASTM C876

At intervals of 28 days, 3 months and 6 months, corrosion potential was measured following ASTM C876. The reinforced samples curing in the saltwater bath were rinsed and placed individually in a container of deionized water with a fill level up to but not over the rim of the cylindrical cement specimen. The rebar exposed out of the top of the cement was polished with 150 grit sand paper and rinsed to remove the layer of oxidation. This process ensured good connectivity with the multimeter. A copper-copper/sulfate half cell electrode and a multimeter were used to read the corrosion potential. The meter was set to DC 20 V for measuring with the ground port connected to the electrode and the positive port connected to the rebar extending out above the water. Placing the porous cap of the electrode into the water adjacent to the cement cylinder, the voltage was recorded to the nearest 0.01V. This voltage is the corrosion potential. It

shows the tendency for corrosion of the rebar through the cement with reference to the copper-copper/sulfate electrode. This test is a good indicator that corrosion activity is occurring in the reinforcement. However, it does not inform the degree or rate of corrosion.

2.9   Superplasticizer

Superplasticizer is used to retain workability in cement paste. It allows particles to slip past each other, enhancing mixing. It also affects the setting time, strength development and corrosion rates of hardened cement structures. One study tested concrete with the addition of 0%, 2%, 4% and 6% by mass of the water of superplasticizer. The findings showed that as the percentage of superplasticizer increased the corrosion resistance increased, with 6% addition of superplasticizer being reported as the optimum percentage. The addition of any amount of superplasticizer gave higher compressive strength than the control with no addition of superplasticizer (Sathanandham, Vijayan and Sathes Kumar, et al. 2015). A different study evaluated four different superplasticizers and found that maximum fluidity across all types was achieved between 1% 1.2% addition of superplasticizer by weight of the cement (Sosa, et al. 2018). To evaluate how superplasticizer effects HCP with biomass ash, HCP samples containing RHA and SCBA with the replacement percentage that gave the highest compressive strength were prepared with the addition of 0%, 0.5%, 0.75%, 1% and 2% superplasticizer by mass of the mix [this includes water and binder]. The percentage of RHA replacement used was 20% and the percentage of SCBA replacement used was 10%. The method of preparation was consistent with that listed in previous sections. Compressive strength tests and porosity tests were conducted 28 days after mixing.

2.10   Results

2.10.1   <u>Compressive Strength</u>

Upon completion of compressive strength testing, improvements are noticeable with the replacement of OPC with both RHA and SCBA. Figure 2-1 shows the data for 28 day compressive strength for different percentages of biomass ash replacing OPC. After 28 days of curing, the compressive strength increases as the percentage of RHA replacement increases. However, as the amount of SCBA increases there is no noticeable trend.
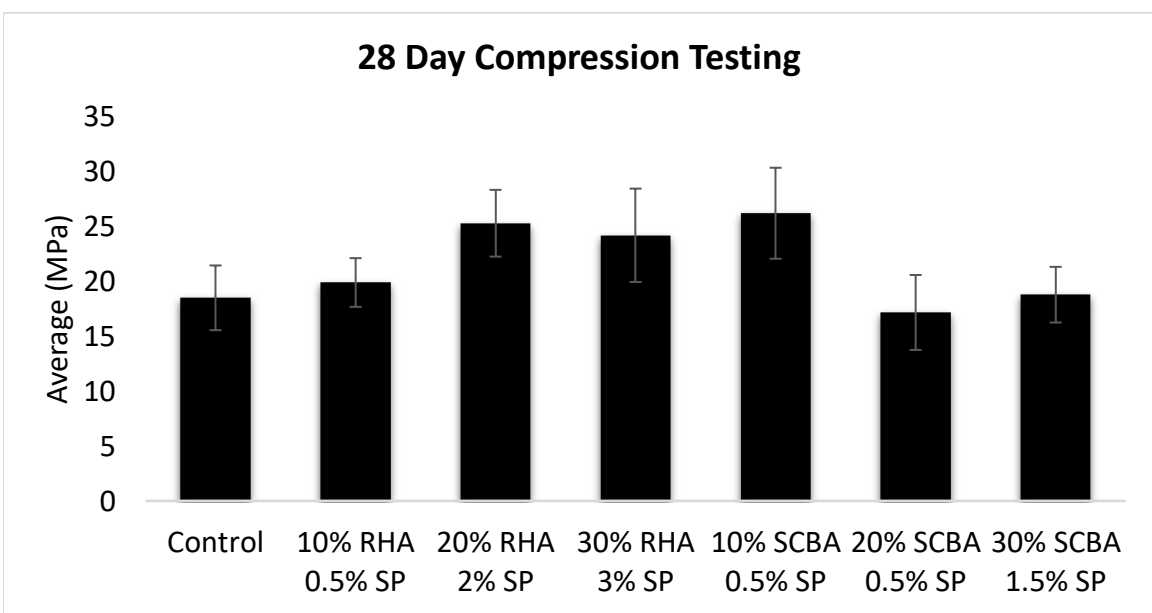

Figure 2-1: Compressive strength 28 days after mixing

An analysis of variance shows that there is days after mixing a significant difference between the control group (0% replacement) and 20% replacement with RHA for 28-day compressive strength. The average compressive strength OPC control and 20% replacement by RHA was 2681 psi (18.5 MPa) and 3665 psi (25.3 MPa), respectively. With 30% replacement by RHA, an average compressive strength of 3506

psi (24.2 MPa) was recorded, but it also required the most superplasticizer to allow the mix to be workable. It can be suggested that this increase in compressive strength be partly attributed to the particle size of the biomass. With an average particle size of 6.17 μm for RHA, it can generate smaller pores and thus a stronger material. Another explanation for this is the pozzolanic reaction that is taking place with calcium hydroxide from the cement hydration and the amorphous silicon dioxide in the biomass. Also, the calcium hydroxide that is in the curing bath solution is available for pozzolanic reaction. This reaction generates additional CSH, which is the glue that holds cement together. However, there is not a noticeable increase in compressive strength as the amount of replacement by SCBA increases. The particle size for SCBA is similar to RHA with an average size of 6.8 μm. SCBA has less silicon dioxide in its composition than RHA, 71% compared to 94%. Silicon dioxide is important for the pozzolanic reaction. This may be the reason that replacement by SCBA does not yield as high a compressive strength as replacement by RHA.

After 6 months of curing there is no significant compressive strength advantage nor disadvantage to using RHA or SCBA as a partial replacement for OPC. Figure 2-2 shows the compressive strength of specimens after 6 months of curing.
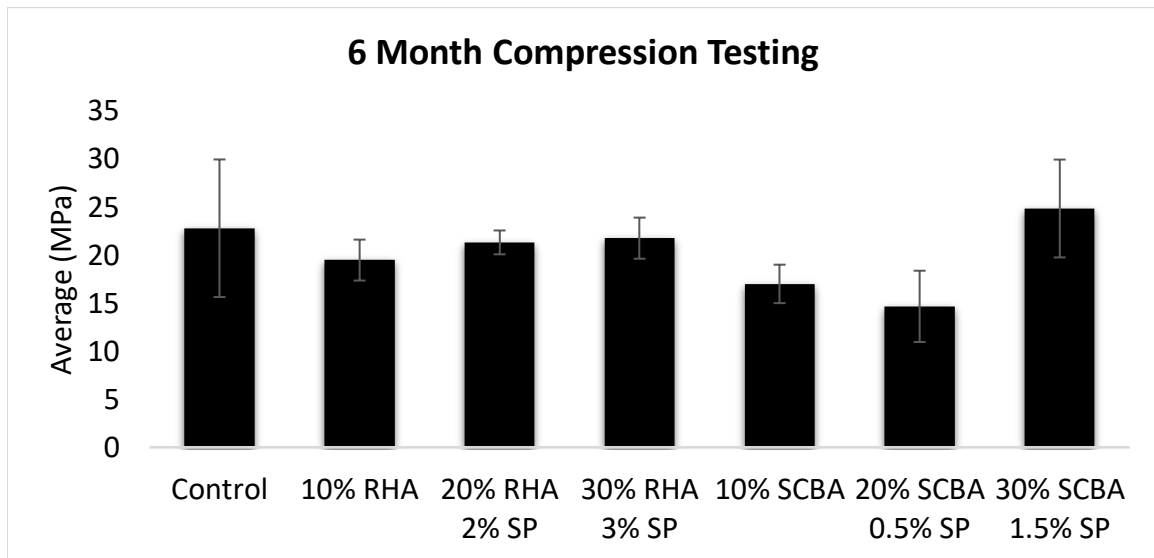
6 Month Compression Testing

Figure 2-2: Compressive strength 6 months after mixing

Compared to results after 28 days, the average compressive strength of samples with only OPC increased after 6 months of curing, while the samples containing biomass decreased. The only exception is HCP samples with 30% SCBA as replacement for OPC.

2.10.2   Porosity by Water Absorption

The mass of water the cement will hold relative to its dry mass is the water absorption. Data for water absorption was collected after compression testing at 28 days

and 6 months. The results, displayed in Figure 2-3 and Figure 2-4, show that as the

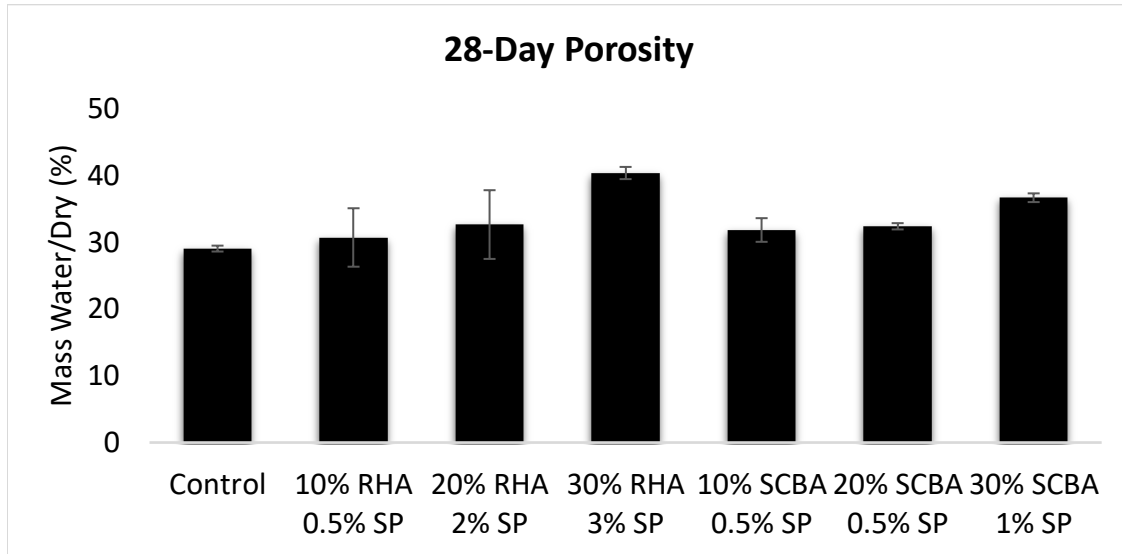percentage of pozzolan increases the water absorption increases.

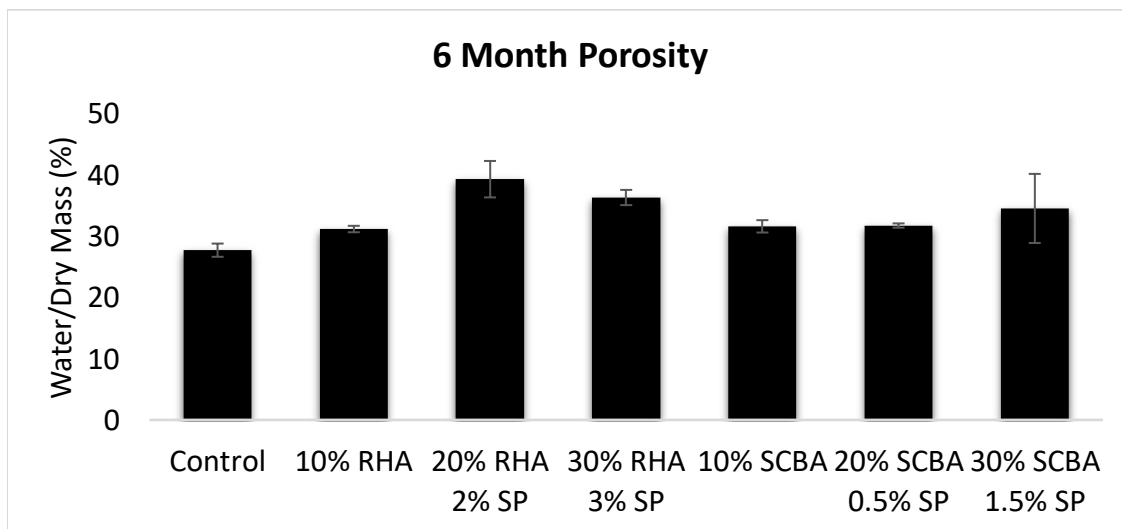Figure 2-3: Porosity by water loss 28 days after mixing.

Figure 2-4: Porosity by water loss 6 months after mixing

The average particle size of RHA is smaller than that of OPC, which could lead

one to infer that the structure would be denser. However, the increase in water absorption

can be attributed to an increase of the collective volume of the pores. One study reported

that with an average particle size of 5 micrometers the water absorption was

approximatly 20% less than the control, but with an average particle size of 95

micrometers the water absorption was greater than OPC (Christopher, et al. 2017). In

another study the saturated water absorption decreased with increasing amount of

replacement by RHA and that it will continue to decrease at later dates (Zareei, et al.

2017).

2.10.3   Water to Cement Ratio

Because the method for preparing molds kept a constant water to binder ratio, the

water to cement ratio increased as more percentages of biomass ash was added. The

compressive strength shows no correlation with water to cement ratio. The relationship

between the porosity and the water cement ratio is shown in Figure 2-5. A positive

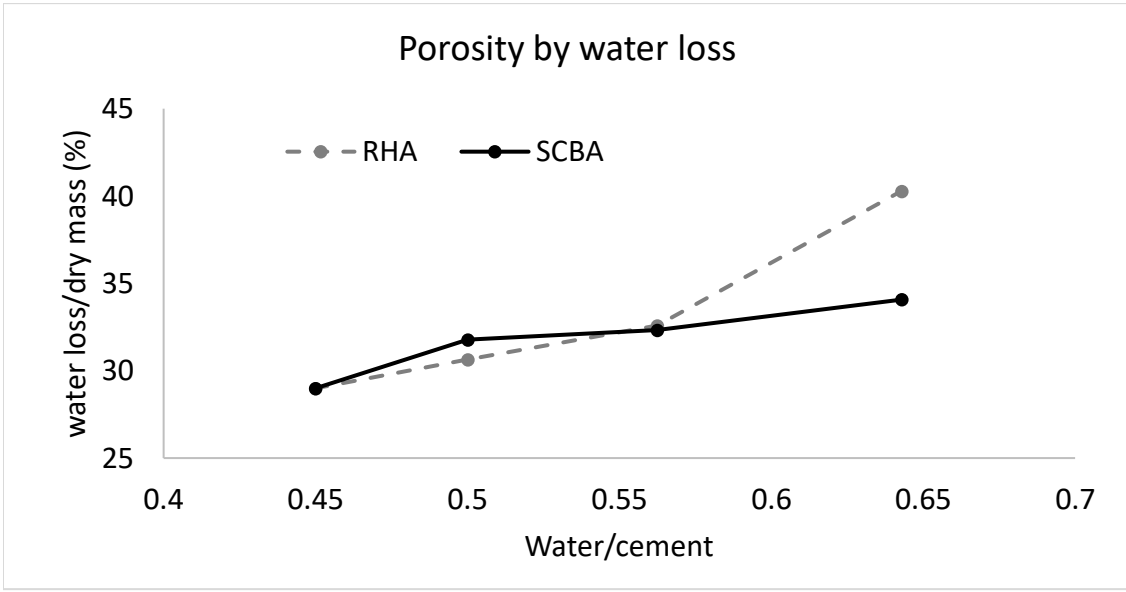correlation is observed between the porosity and the water/cement ratio.

Figure 2-5: Porosity vs. water/cement.

2.10.4 Corrosion Potential

As shown in Figure 2-6, at early stages, more specifically 28 days, the samples with higher percentages of RHA and SCBA gave lower corrosion potential. However, at later times the corrosion potential increases, implying a higher probability of corrosion.
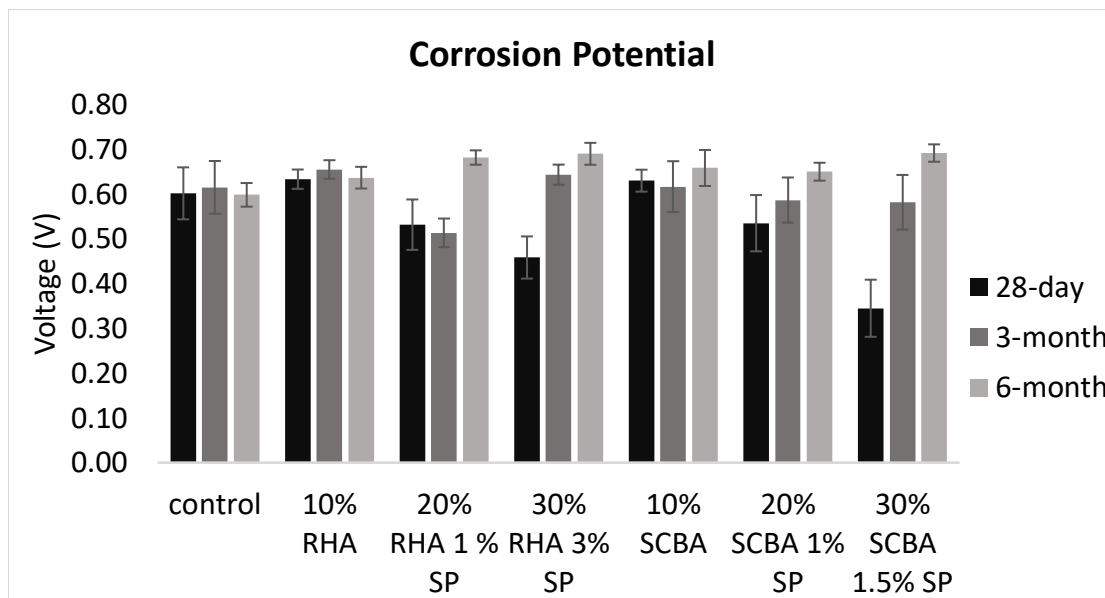
Figure 2-6: Corrosion potential by copper copper/sulfate half cell

The corrosion potential is not directly related to the rate of corrosion, but it is a measure of the probability that corrosion is occurring. The standards according to ASTM C876 on corrosion of steel reinforcement in concrete state that using a copper-copper sulfate half cell and measuring a potential that is more negative than -0.35 V indicates the probability that corrosion is occurring is greater than 90%. At later dates the corrosion potential of specimens with pozzolan are not significantly different from OPC. The effect of rate of hydration and pozzolanic reaction on the sample with pozzolan are most likely contributing to the lower corrosion potential at early times. One study reported increasing setting time with increasing RHA replacement. The main hydration reactions and the pozzolanic reaction are different in that the pozzolanic reaction cannot take place until $Ca(OH)_2$ is released by alite and belite hydration. For this reason, it takes longer for the pozzolanic reaction to occur. Givi et al. (2010) reported that the amount of calcium hydroxide started to decrease after three days and was nearly zero at 90 days. It can be

suggested that the pozzolanic reaction reduces the corrosion rate because of the trend seen with samples of higher RHA content (Givi, et al. 2010).

2.10.5 Varying Amount of Superplasticizer

Not only does the addition of superplasticizer have a noticeable effect on the workability of cement paste, it also improves the compressive strength of the HCP. It is known that too much water in cement mix can jeopardize its strength development, so the addition of a superplasticizer allows for increased workability at lower water to binder ratios. The compressive strengths for 20% RHA replacement for OPC and 10% SCBA replacement for OPC with varying percentage of superplasticizer is shown in Figure 2-7. As the percentage of superplasticizer increases the compressive strength of the HCP tends to increase. The addition of 2% superplasticizer in mix containing 20% RHA yielded a higher workability than would be desired in most construction settings, however, it gave the highest compressive strength among the samples containing RHA. with 0.5% addition of superplasticizer to cement paste containing 10% SCBA showed increased compressive strength when compared to similar cement paste containing no superplasticizer.

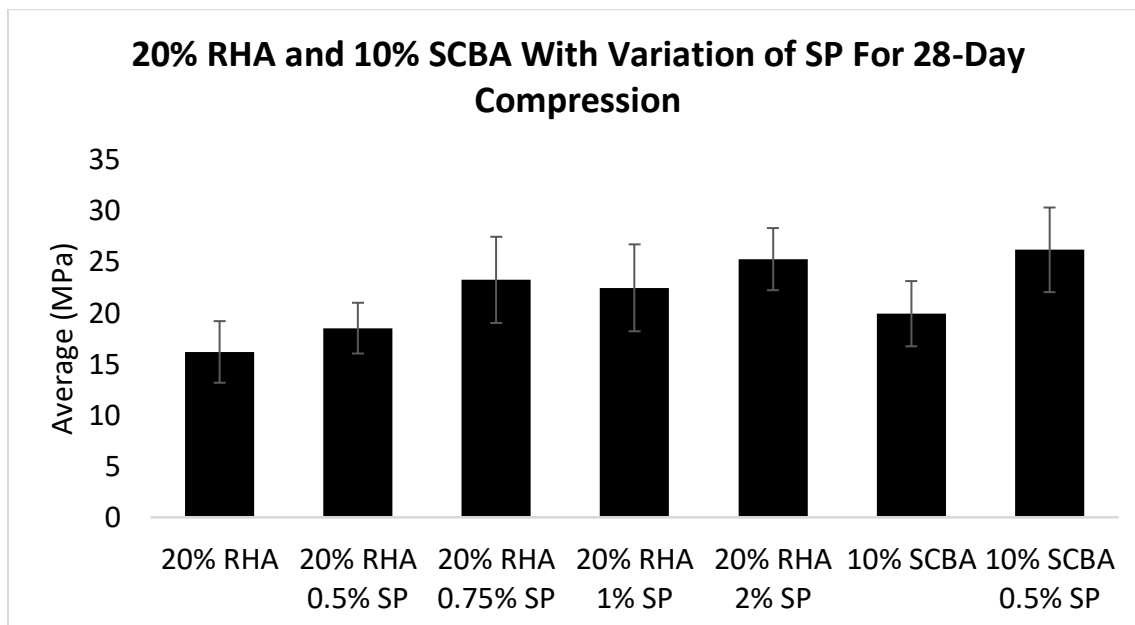**20% RHA and 10% SCBA With Variation of SP For 28-Day Compression**

Figure 2-7: Compression testing of 20% RHA and 10% SCBA with different percentage of superplasticizer 28 days after mixing.

When no superplasticizer was added, the HCP gave the lower compressive strength and the cement paste's workability was lower than what would be desired for pouring. The knowledge that replacing cement with biomass ash may require small amounts of plasticizer will be useful in further research in this area.

Although the compressive strength increases as the percentages of superplasticizer increases, there is no statistically significant difference in porosity between varying percentages of superplasticizer. The results of the porosity is shown in Figure 8. The lowest average porosity was observed in HCP with no superplasticizer added. The lowest standard deviations were observed in HCP with addition of 0.75% SP and 0.5% SP. This may be the optimal range of superplasticizer because of the constistency achieved in the porosity of HCP. The otherside of this argument may be that

the addition of 1% SP is not optimal because it gave the highest average porosity amound
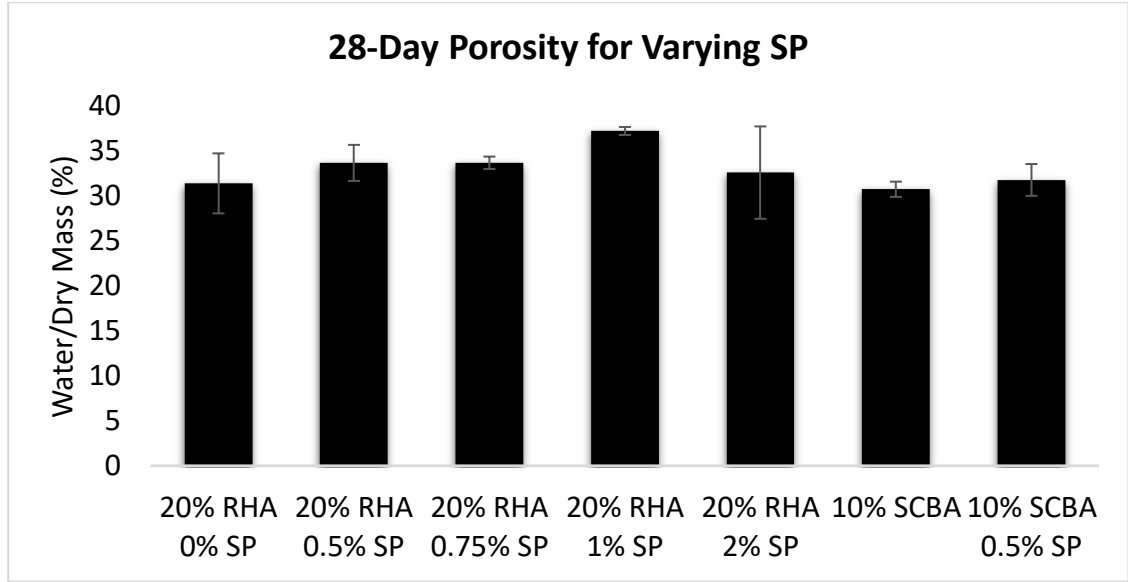
HCP with 20% RHA as replacement for OPC.

Figure 2-8: Porosity by water loss of HCP with 20% RHA and 10% SCBA replacement for OPC 28 days after mixing

CHAPTER 3

CONCLUSION

3.1   Effects of Biomass Ash on HCP

From the results in this study it is observed that at earlier curing ages, 28 days, 20% replacement of OPC with RHA shows the highest compressive strength. The literature discussing the use of RHA in cementitious structures gave increased compressive strength compared to those without RHA. There is no consensus that it benefits only early age compressive strength. However, one study reported by Givi, et al. (2010) shows an increase in the compressive strength of RHA blended concretes as early as 28 days. This agrees with the results in this study. However, after six months of curing in lime solution, specimens containing RHA gave lower compressive strengths than at 28 days, while the compressive strength of specimens with only OPC increased. The difference in compressive strength between HCP with only OPC and HCP with RHA is not statistically significant, therefore, by these methods up to 30% replacement by RHA can be implemented without sacrificing compressive strength of the HCP. This finding agrees with the literature and suggests that the pozzolanic reaction between the silicon dioxide in the RHA and the lime products from cement hydration produces additional CSH that assists in development of compressive strength. The replacement of OPC with SCBA does not show a clear pattern of strength development. After 28 days of curing, 10% replacement by SCBA showed higher compressive strength than the control. The

compressive strength of specimens with SCBA decreased from 28 days to 6 months except for 30% replacement by SCBA.

The water absorption can be used to talk about the porosity of the various samples. The control exhibited the lowest water absorption percentage, leading to the inference that it has the lowest porosity. This does not agree with most sources in the literature especially in terms of particle size. Because the average particle size of both pozzolans used was smaller than the average particle size of the OPC powder, the water absorption would be expected to be lower based on results of other similar studies. However, there are studies that agree with the work reported in the previous chapter. RHA particles are known to have very porous structures, which is why the water demand increases when using RHA in cement mixes. If RHA particles do not react in the cement to fill voids with CSH, they may contribute to and increase overall water absorption, and thus giving a higher porosity to the HCP. Another factor into this is the water to cement ratio. The experiments in this study maintained a constant water to binder ratio, but the water to cement ratio varied. A positive correlation is observed with increasing water to cement ratio and porosity.

Many of studies correlate the rate of corrosion of reinforcement in concrete to the porosity and permeability of the cement. The relationship often reported is that less porous concrete results in lower permeability, and thus it does a better job of protecting the reinforcement from the environment. In this study there is no significant difference in the corrosion potential of HCP with or without use of a pozzolan after 3 months or 6 months of curing. At these stages all samples were in salt water curing solutions. After only 28 days, while all specimens were being cured in a lime water solution, the

specimens with higher percentages of biomass ash gave lower corrosion potential. These findings suggest that, by the standards set in ASTM C876, there is corrosion activity in all HCP sample. RHA and SCBA at higher replacement percentages may delay the initiation of corrosion activity, but further study would need to be conducted to confirm this.

3.2 Recommendations for Further Study

The reason for strength loss of the samples with RHA between 28 days and 6 months should be investigated further. If the HCP contains products that do not contribute to the strength of the structure, such as lime, then they may have an adverse effect on the compressive strength. There is a semi quantitative approach for the hydration of silicate phases and pozzolanic reaction that is discussed by Vance Dodsen, PhD in his book, Cement Admixtures (Dodson 1990). By using this approach, we can calculate that the amount of replacement by RHA to react all the lime from silicate phases in cement hydration is 14.6%. This method rides on unachievable assumptions, such as perfect cement hydration, and 100% of amorphous silica in the pozzolan, but it can be a useful guide to adjusting the ratio of mixes. It may be that non hydrated RHA particles have harmful effects on cement. The same may be said for HCP with SCBA. This could be studied further to minimize the amount of non-cementitious products in cement structures.

The overall compressive strength was evaluated but more study can be done to evaluate elastic and plastic properties. The stress-strain curve of cement paste incorporating biomass ash may be informative and applicable in seismographic situations.

It was confirmed by the corrosion potential tests that corrosion activity was not prevented using biomass ash, but in order to confirm reduced corrosion rates, the corrosion current should be evaluated. Other areas to tests for corrosion activity include chloride ion penetration and sulfate resistance

It requires a relatively high temperature furnace to combust rice husks and sugarcane bagasse to remove most of the carbon content and produce an acceptable pozzolan with high amorphous content. The process of heating rice hull and sugarcane bagasse to produce RHA and SCBA should be studied in order to minimize the amount of energy used. This could further reduce the impact on the environment.

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