PERFORMANCE BASED TESTING FOR AIR ENTRAINMENT AND TOTAL HEAT OF RECLAIMED FLY ASH

By

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PERFORMANCE BASED TESTING FOR AIR ENTRAINMENT AND TOTAL HEAT OF RECLAIMED FLY ASH

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Abstract: As coal combustion energy plants are being converted to natural gas, the tons of fly ash produced in the United States has dramatically decreased. The current demand in fly ash supply can be mitigated with the introduction of reclaimed fly ash. The objective of this paper is to develop performance-based testing for traditional, blended, and reclaimed Class F fly ash. Research and test results from laboratories will provide information to compare the change in performance of different fly ash materials at either 20% or 40% replacement in comparison to cement. This work investigated the ability of the foam index test to predict the AEA dosage in concrete mixtures containing fly ash and investigated the use of isothermal calorimetry to provide the availability for rapid testing to compare the impact of the heat of hydration with reclaimed, blended, and traditional Class F ash.

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CHAPTER I

THE NEED FOR PERFORMANCE BASED TESTING FOR RECLAIMED FLY ASH

1.1 INTRODUCTION

The use of concrete as a construction material is highly sought after due to the economic advantages and ability of this composite material to withstand environmental conditions. However, the harmful effects that cement production has on the environment are driving researchers to search for alternatives to lower CO_2 emissions. For each ton of cement produced, 900kg of CO_2 is released into the atmosphere [1]. One method for reducing the content of cement in a concrete mixture is by partially replacing the cement with fly ash. The reuse of fly ash improves the sustainability of a concrete mixture by reducing the percentage of cement in concrete [2].

Fly ash is a useful supplementary cementitious material (SCM) and has been shown to improve both the durability and workability of concrete. Fly ash is a waste material from the coal combustion process that is typically sent to a landfill if another purpose is not identified. In 2019, the coal ash production volume decreased by 23 percent from the previous year according to the American Coal Ash Association [3]. As coal combustion energy plants are being converted to natural gas, the tons of fly ash produced in the United States has dramatically decreased. On the other hand, other types of ash are available in abundance to be used in concrete. However, guidelines need to be developed.

1.1.1 Types of Ashes

There are a variety of types of ash as shown in Table 1-1. The most popular types of ash have been Class C and Class fly ash, which is a material produced from coal-fired power plants. ASTM C618 has multiple requirements for fly ash to be used in a concrete mixture. However, the only solution available by the purchaser for any material that fails to meet specification is by rejection. This research compares the performance of fly ash that would otherwise be rejected to fly ash that meets the specifications of ASTM C618.

Table 1-1 Types of Ash

Type of Ash	Standard	Description of Ash
Class F Fly Ash	ASTM C 618	Contains pozzolanic properties
Class C Fly Ash	ASTM C 618	Contains pozzolanic and cementitious properties
Class N Fly Ash	ASTM C 618	Raw or calcined natural pozzolans
Reclaimed Fly Ash	----	Fly ash removed from a landfill
Blended Fly Ash	----	Combination of traditional and reclaimed fly ash
Bottom Ash	----	Heavier by-product from coal-fired power plants

1.1.2 Fly Ash Classification

Traditional fly ash is fly ash that meets the requirement for ASTM C618. For this study, all traditional fly ash is categorized as either Class C or Class F.

Reclaimed fly ashes are collected from disposal sites that do not meet the requirements of ASTM C 618 [4]. This material is a category from fly ash that is rarely used in current construction practices. The ability to add this fly ash to a concrete mixture prevents this material from otherwise becoming a waste product. Including reclaimed fly ash as an option for concrete mixtures will increase the availability of fly ash.

Blended fly ashes are defined as fly ashes that are a combination of two types of fly ash. For this study, blended fly ash could either be a combination of two traditional fly ashes or traditional fly ash blended with reclaimed fly ash.

1.1.3 Chemical and Physical Characteristics of Ash

The durability advantages in a concrete mixture with fly ash are directly dependent on the quality of the fly ash used. Since the oxide contents in each fly ash have variations, ASTM C618 has specified requirements for each fly ash. One method that ASTM C618 uses to separate fly ash into categories is based on the oxide contents. The main differentiation between Class C and Class F fly ash is the limitations on the calcium oxide content. These categories are either Class C if the calcium oxide is at or above 18% or Class F if the calcium oxide content is less than 18% [4]. This requirement was used to classify both reclaimed and blended fly ash as either Class C or Class F.

Another characteristic of fly ash that can exhibit variation between suppliers is the particle size. If a fly ash particle has a significantly smaller particle size, the hydration reactions can occur more quickly due to the increased surface area [2]. Chapter II and III of this paper will include the analysis of both the oxide content and particle size distribution.

1.1.4 Fly Ash Sources

The fly ash sources are produced from the United States from various states including Oklahoma, Texas, Georgia, North Carolina, and Ohio. The reclaimed fly ash was processed through either sieving or heating methods.

1.2 OBJECTIVE

The objective of this paper is to develop performance-based testing for traditional, blended, and reclaimed fly ash. Research and test results from laboratories will provide information to compare the change in performance of different fly ash materials at either

20% or 40% replacement in comparison to cement. These fly ash materials are subjected to a variety of material testing involving concrete and paste mixtures.

This work will be completed in the following chapters:

- Chapter II: DETERMINING PERFORMANCE OF RECLAIMED FLY ASH IN AIR ENTRAINED CONCRETE
- Chapter III: RATE OF HEAT EVOLUTION FOR RECLAIMED FLY ASH

CHAPTER II

DETERMINING PERFORMANCE OF RECLAIMED FLY ASH IN AIR ENTRAINED CONCRETE

2.1. INTRODUCTION

The durability of concrete is dependent on the ability to withstand environmental effects. One of the major factors deteriorating infrastructure is cracking due to freezing and thawing of concrete. Research has shown that to resist damage from cycles of freezing and thawing, small and well-distributed air-void systems are necessary for concrete [5]. Obtaining a concrete mixture with a desired air void distribution requires the addition of an air-entraining agent (AEA) to the concrete [6]. The damage inflicted on concrete from cycles of freezing and thawing can be mitigated with effective air void spacing. The use of air-entraining agents will encourage the formation of air voids in the concrete mixture as well as prevent these bubbles from coalescing. The desired volume to prevent cracking from freezing and-thawing cycles is approximately 6% of the concrete volume [5].

When designing admixture dosage, it is common practice to make a trial mixture to adjust the design of the concrete mixture. The use of AEAs has proven difficult in characterizing dosage proportions [7]. A primary factor that affects the AEA dosage is the impact of carbon within fly ash to absorb the AEA [8]. The addition of fly ash can cause difficulty in the entrainment of air for a concrete mixture. The residual unburned carbon content in fly ash will adsorb the AEA and create challenges during the mixing process to increase the air content [17].

2.1.1 Aim of this work

This study focuses on how the combination of cement and fly ash impacts air entrainment dosage. The addition of fly ash in concrete can alter the amount of air-entraining required for each mixture to obtain the desired air content. It would be desirable to establish a simple test procedure that can be used to determine the impact of fly ash on the dosage of air entrainment. The Foam Index test is a rapid test method that shows the potential to predict the AEA demand for fly ash [7]. This work aims to extend the use of the foam index test to traditional, blended, and reclaimed fly ash. Also, this work establishes the correlation between the foam index and the AEA dosage required in concrete to obtain a certain air content. This will establish the foam index test as an important quality control tool for traditional, blended, and reclaimed fly ash.

2.2 EXPERIMENTAL METHODS

2.2.1 Laboratory Materials

Each fly ash source was evaluated with the automated scanning electron microscope (ASEM) to determine the proportion of 11 chemical oxides (SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, SO_3, Na_2O, K_2O, TiO_2, P_2O_5, SrO) for each fly ash material. These fly ash sources can be classified as Class F, Class C, blended, and reclaimed ash. The chemical oxides and classification for each source as a percent of the total source are reported in Table 2-1. The loss on ignition (LOI) content of the fly ash is also included in Table 2-1. This was measured per ASTM C311.

Table 2-1: Fly Ash Oxide and LOI Analysis

	LOI		**Oxide %**										
	%	**STD**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**SO_3**	**Na_2O**	**K_2O**	**TiO_2**	**P_2O_5**	**SrO**
C3	0.56	0.03	25.32	19.26	5.22	32.5	7.76	2.6	3.42	0.63	1.08	1.89	0.32
RF1-1	4.59	0.25	53.04	25.31	11.45	3.36	0.52	0.93	0.35	4.39	0.41	0.18	0.03
RF1-2	2.56	0.04	57.57	23.51	10.12	2.82	0.49	0.48	0.21	3.85	0.67	0.19	0.05
RF2	14.73	0.88	57.55	30.47	5.15	1.45	0.26	0.07	0.03	3.43	1.05	0.06	0.49
RF3	2.12	0.06	54.53	30.54	7.33	2.94	0.15	0.13	0.02	3.61	0.63	0.02	0.1
RF4	2.91	0.05	53.5	26.22	9.91	4.62	0.7	0.35	0.08	3.53	0.51	0.14	0.42
RF5	0.58	0.03	57.88	27.51	6.62	2.37	0.24	0.17	0.13	4.08	0.59	0.03	0.38
RF7-1	0.43	0.02	59.12	20.68	5.95	9.07	1.9	0.56	0.25	1.67	0.42	0	0.38
F27	8.72	0.18	52.88	23.86	12.25	5.26	0.39	0.61	0.4	3.36	0.47	0.12	0.39
75% RF4 + 25% C3	1.99	0.03	46.46	24.48	8.74	11.59	2.47	0.91	0.92	2.81	0.65	0.58	0.4
90% RF1-2 + 10% C3	3.22	0.14	54.35	23.09	9.63	5.79	1.22	0.69	0.53	3.53	0.71	0.36	0.08
85% F27 + 15% C3	8.17	0.14	48.75	23.17	11.2	9.35	1.5	0.91	0.85	2.95	0.56	0.39	0.38

All of the laboratory concrete mixtures in this test used one coarse aggregate and one fine aggregate source. The coarse aggregate was a #57 crushed limestone with a nominal maximum size of 25 mm (1”) and the fine aggregate was a natural sand meeting ASTM C 33 [11] for fine aggregate. One ASTM C 150 [14] Type I Portland cement source was used. Wood rosin-based air-entraining admixture (AEA) that meets the requirement for ASTM C260 [16] was used. No other chemical admixtures were used.

The fly ash is labeled using an existing system for fly ash for the laboratory. The letters are used as an identifier for the type of ash followed by an assigned number. Traditional fly ashes are labeled either “C” or “F” and a corresponding number. Blended fly ash and reclaimed fly ash first begin with a “B” or “R” respectively and then are followed with “C” or “F” and a corresponding number.

Nine fly ash sources were used in this study. Seven of these sources are classified as reclaimed fly ash. Each reclaimed ash is categorized as Class F based on the oxide content. The other two fly ash sources are traditional fly ashes. One is class C and the other is Class F. Three of the fly ash sources were combined with the traditional class C fly ash at different proportions to find unique points in the dataset and simulate the possible blending of fly ash.

2.2.2 Concrete Mixing and Testing

One standard concrete mixture was used in this study to help limit the variabilities associated with air content. This mixture design is shown in Table 2-2. The concrete mixture used a 0.45 water to cementitious ratio with 20% replacement from a fly ash source.

Table 2-2: Mixture proportions

w/cm	Cement kg/m^3	Ash kg/m^3	Paste Volume (%)	Coarse kg/m^3	Fine kg/m^3	Water kg/m^3
0.45	290	72	24	1077	713	163

Note: kg/m^3 = 1.685 lb/yd^3

For the laboratory mixtures, aggregates were brought from outside stockpiles into a temperature-controlled room at 72°F (22°C) for at least 24 hours before mixing. The aggregates spun in a mixing drum for at least three minutes. A representative sample for moisture content testing was used to apply a moisture correction to the mixture. At the time of mixing, all aggregates were loaded into the mixer along with approximately two-thirds of the mixing water. This combination was mixed for three minutes to allow the aggregate surface to saturate and ensure the aggregates were evenly distributed. Next, the cement, fly ash, and the remaining water mixed for three minutes. The resulting mixture rested for two minutes while scraping the sides of the mixing drum.

2.2.3 Fresh Concrete Testing

A 70 L concrete mixture was prepared in a drum mixer. After the mixing period, the slump test ASTM C143 [15] was performed as well as two 7 L samples were tested using both gravimetric method ASTM C138 [12] for density and pressure method ASTM C231 [13] for air content. The air content samples were investigated simultaneously by two different operators. The concrete used for the slump test was returned to the mixer where the concrete used for the air content was discarded. This left the total volume of the concrete mixer to be 56 L. Next, the AEA admixture was added, and mixing continued for three minutes. A portion of the concrete was then removed and two gravimetric measurements were taken using ASTM C138 [12]. The removed concrete was then returned to the mixture. An AEA admixture was added to the mixer and the concrete was mixed for three minutes. This process continued until the change in density from the original gravimetric test was approximately 8%. A minimum of three AEA dosages was investigated for each mixture. A final measurement was taken for slump and air content with the pressure method.

The testing procedure for air content requires water to be added to the concrete specimen. Due to this, the volume of concrete removed from the mixture to measure the air content must be discarded. This will result in a decrease in the total volume of the mixture each time a dosage of AEA is added to the concrete mixture. To measure the change in air volume with each addition of AEA dose, the examination of the total air volume in a fresh concrete mixture for this test is a combination of both the gravimetric and pressure method. The combination of these methods opens up the ability for multiple dosages of AEA to be added to a single concrete mixture. The impact of each dosage on the air content can be determined while allowing mixture design properties such as volume, aggregate gradation, and cement and water chemistry to remain constant [5].

2.2.4 Concrete Performance

By using a combination of the air volume measurements from the gravimetric and pressure method, a correlation can be made from the initial density and air content. This correlation was then used to measure the change in air content with each dosage of AEA. Since each measurement taken after the addition of AEA dosage did not change the total volume of the concrete mixture, the dosage could be continually added in increments until the desired air content was achieved.

The difference between the final air content estimated with the gravimetric method and the final air content calculated with the pressure method was less than 0.5% for all concrete mixtures. The difference in air content was distributed throughout the number of dosages to adjust the data points on the line as explained in previous publications [5].

2.2.5 Foam Index Test

The foam index test is used to predict the amount of air-entraining agent needed for a certain cementitious mixture. There are many versions of this test but systematic testing has been done to find a useful vessel volume, material ratios, and fluid content to provide the best correlation to concrete [6-9]. The test consists of a 125 mL container partially filled with 5g of cement, 5g of fly ash, and 25mL of water. The container was sealed with a lid and shaken for twenty seconds. A 2.5% wood rosin AEA solution is added with a dropper in increments of two to five drops at a time and then shaken for ten seconds. The ability of the fly ash to maintain a steady foam on the surface is considered the foam index value and the volume of AEA added is quantitatively used to compare the different mixtures [10]. Figure 2-1 shows a comparison of the expected behavior of the foam stability at the beginning and end of the test.

a) Unstable foam b) Stable foam

Figure 2-1: Comparison of Foam Stability

This study focuses on the combination of cement and reclaimed fly ash. The amount of each oxide present in the reclaimed ash will affect the reaction with the air-entraining agent. This will alter the amount of air-entraining required for each mixture.

The foam index procedure was used to find the foam index for all 12 sources. These values were compared to the amount of AEA dosage required for concrete mixtures. Three foam index tests were measured per fly ash and the average amount of drops required to reach stability is considered the foam index value.

2.3 RESULTS

The increase in percent air by the total volume of the concrete mixture Figure 2-2 shows the results of a typical set of data from concrete mixtures at different AEA demands. Each result represents the average dosage lines of two concrete mixtures with the same fly ash. A trend line was fitted to this data set was found for each concrete mixture. A correlation coefficient R^2 value was measured to determine the accuracy of the data in regression analysis. The dosage performance each fly ash in concrete were consistently above an R^2 value of 0.91. This shows a large positive correlation between the increase in air content with the increase in AEA dosage. All trend line equations for the twelve concrete mixtures in this study are shown in the appendix.

Fly ash with a foam index value below 20 was considered to have a low AEA demand. The required dosage to obtain 6% air in the concrete for a low AEA demand was on average 70 mL per 100 kilograms of cement. Fly ash with a foam index value above 40 was considered to have a high AEA demand. The required dosage to obtain 6% air in the concrete for a low AEA demand was on average 232 mL per 100 kilograms of cement. The trend lines for these tests can be used to predict concrete mixtures with fly ash that has similar AEA demands as the data set shown.

For example, if fly ash shows a low AEA demand from the foam index test, the slope from the first plot on Figure 2-3 can be used to predict the behavior in air content as AEA dosage is added. This provides a more accurate estimation for the AEA required to reach the desired air content. The results of this graph can be implemented on concrete mixtures with traditional, reclaimed, and blended ashes.

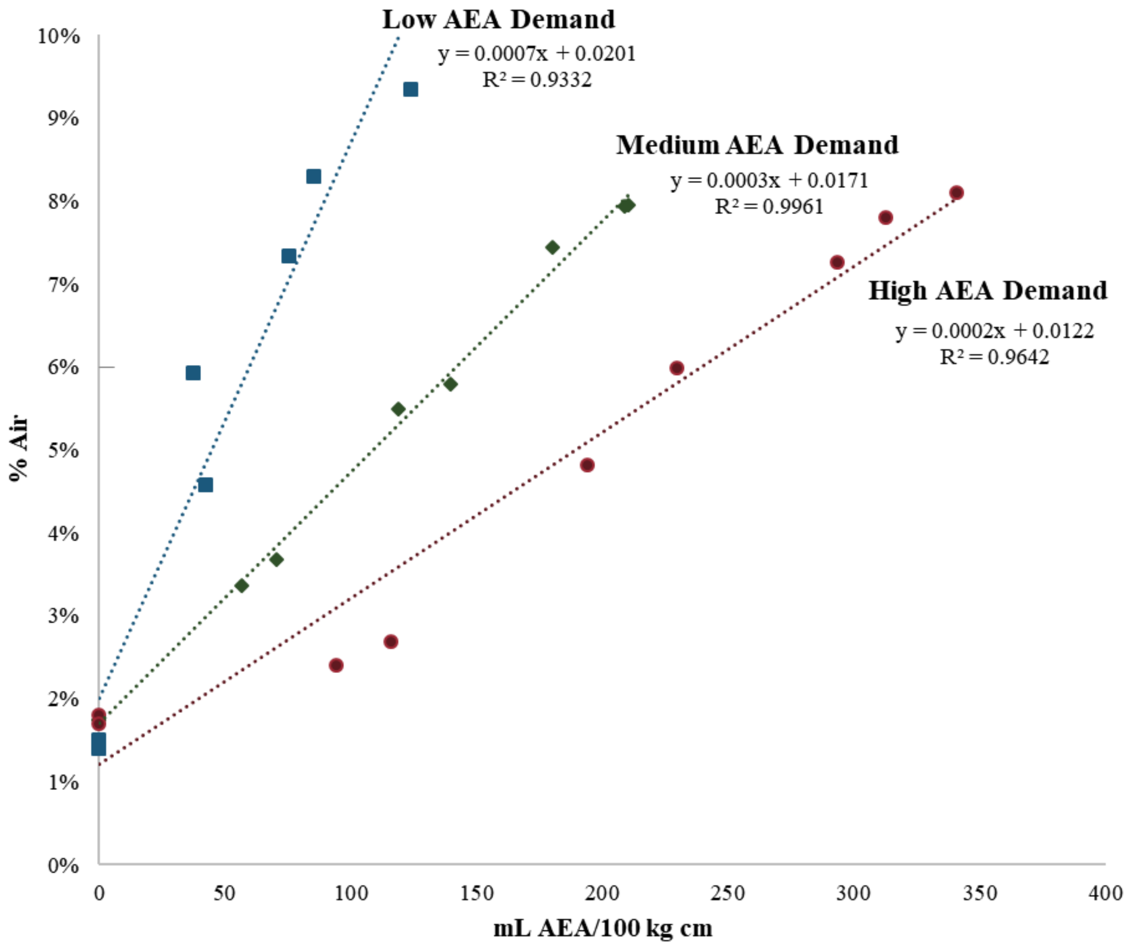

Figure 2-2: Change in air content with the addition of AEA dosage

Figure 2-3 shows the correlation between the LOI results and the drops of AEA required to reach stable foam. The results show that there is no correlation between the LOI test and the AEA demand. A limit of 6% LOI has also been added to the figure to show the typical limit allowed by ASTM C 618. Three fly ash in this study exceed the 6% LOI limit, however, the AEA demand to reach a stable foam does not exceed that of fly ash within the 6% LOI limit. This shows that the LOI limit may not be a useful indicator of performance of the AEA requirement of fly ash. The use of a performance based test will allow a wider ray of materials of fly ash to be used.

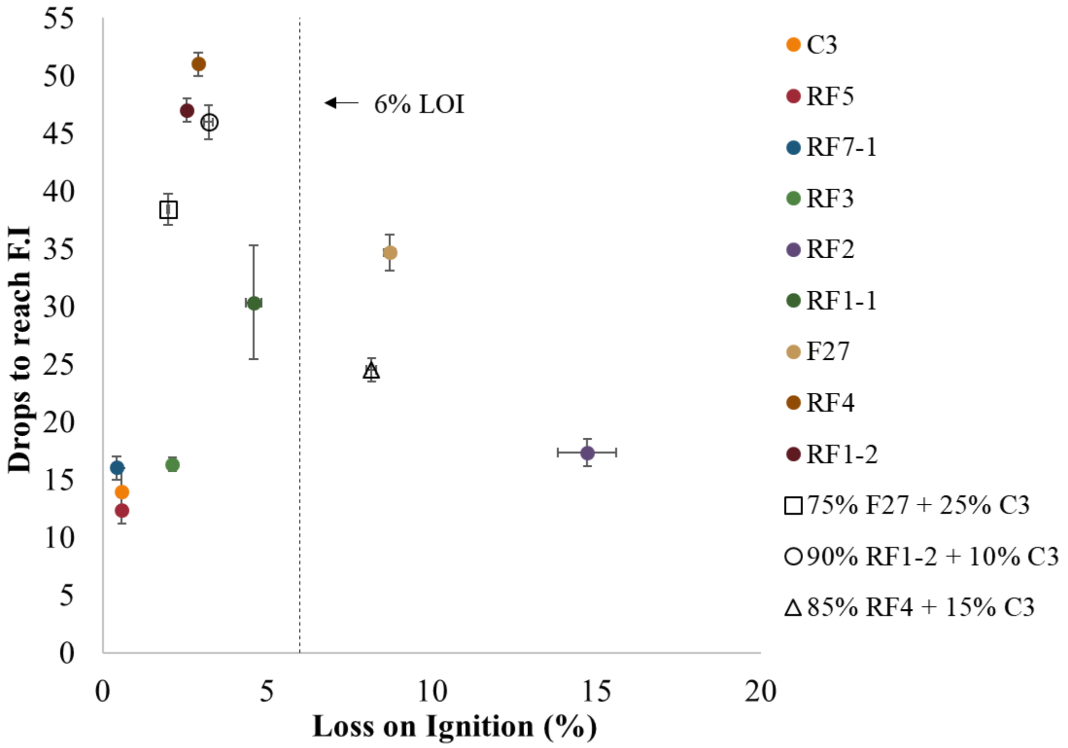

Figure 2-3: Number of drops to reach foam index vs. loss on ignition

Figure 2-4 compares the AEA dosage and the number of drops required to reach the foam index. This chart shows the amount of AEA required for 6% air vs. the number of drops required to reach a stable foam. The value of 6% air content was used since it is a common value in concrete specifications [7]. A trend line from Figure 2-3 is provided. Since the trend line for all of the points in Figure 2-3 shows a R^2 value greater than 0.90, the data shows a large positive correlation between the AEA dosage for concrete mixtures with different fly ash sources and the number of drops required to reach a stable foam. The data in Figures 2-4 shows that the use of the foam index test to predict the AEA dosage requirement for a concrete mixture of 6% air content is applicable in traditional, reclaimed, and blended fly ash.

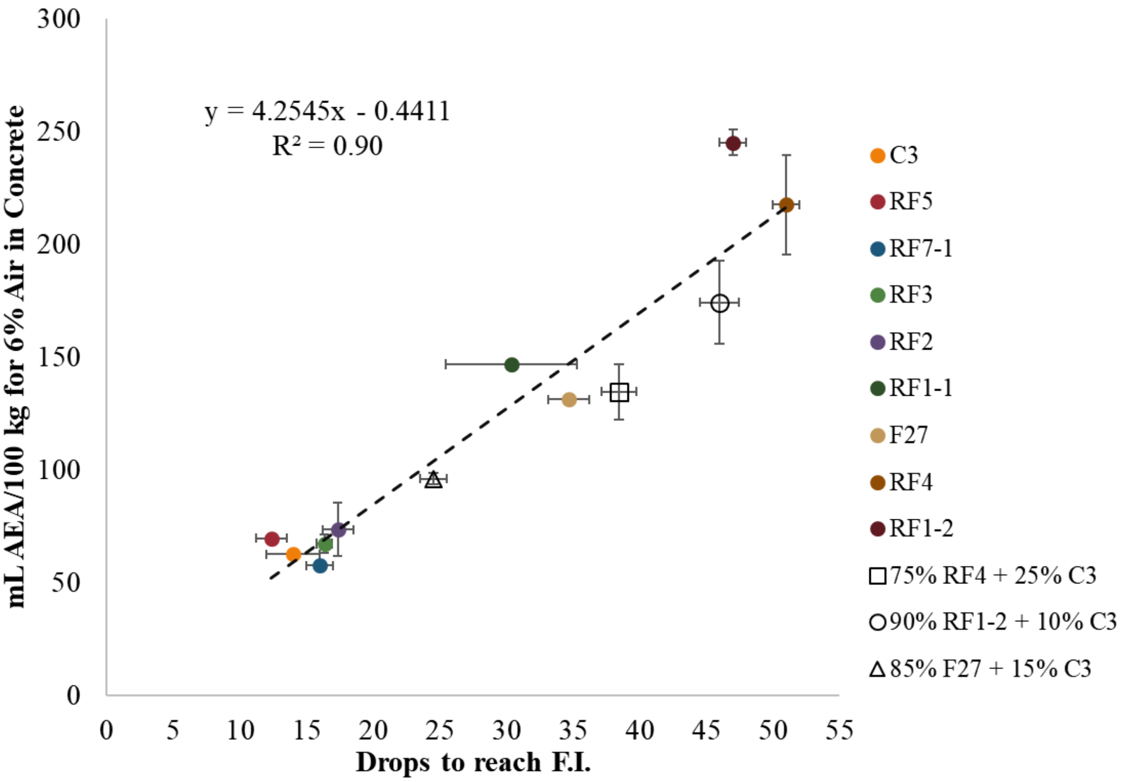

Figure 2-3: AEA dosage vs. the number of drops to reach foam index

2.4. PRACTICAL IMPLEMENTATIONS

Understanding the impacts of AEA used in concrete mixtures containing fly ash will improve the ability to achieve the desired air content. As this study shows fly ash can change the AEA demand by 3.5x in concrete. This high variability is problematic for concrete producers in terms of both cost of admixture as well as challenges with consistent AEA dosages. Previous studies have shown an ability to use the foam index test to predict the amount of AEA dosage required for different fly ash mixtures [7]. The results of this work show that the use of the foam index test to create a preliminary AEA dosage for concrete of similar volume and mixture proportions could be applied to reclaimed or blended ashes that do not meet specifications as well as traditional fly ash. By testing new fly ash with the foam index test, the impact the AEA dosage has on air content can be predicted. This provides a dependable preliminary AEA dosage in concrete to reach the desired air content that is more reliable than the existing LOI test. The procedure used to sequentially add AEA to a concrete mixture can also be used to determine the performance of these materials in a concrete mixture.

2.5 CONCLUSIONS

This work investigated the ability of the foam index test to predict the AEA dosage in concrete mixtures containing fly ash. Each mixture used a 20% replacement of either traditional, blended, or reclaimed fly ash. The following conclusions were found:

- Blended and reclaimed fly ash can be used in air entrained concrete and performs similarly to traditional fly ash.
- The LOI did not serve as a useful test to use to predict AEA demand in a concrete mixture for reclaimed fly ash.
- The foam index test used proves to be a reliable method to evaluate the AEA demand of traditional, blended, and reclaimed fly ash.
- The foam index test used shows a linear correlation ($R^2 = 0.90$) to the AEA dosage required to create 6% air in a concrete mixture. These studies show the usefulness of the foam index test to predict the slope of AEA dosage with increase in air content. This continues to show promise of this test to serve as a tool to

predict the impacts that traditional, reclaimed, and blended fly ash have on the AEA dosage required to achieve the desired air content.

This work shows that the foam index test shows great potential to be used as a performance based test to evaluate reclaimed and blended fly ash performance.

CHAPTER III

RATE OF HEAT EVOLUTION FOR RECLAIMED FLY ASH

3.1 INTRODUCTION

The hydration of cementitious particles is an exothermic reaction that occurs over multiple stages [18]. Previous studies have shown that the addition of fly ash materials has the ability to reduce the heat of hydration [19]. This heat reduction is especially important for mass concrete elements. The American Concrete Institute (ACI) defines mass concrete as any volume of structural concrete in which the member being cast can lead to undesirable thermal stresses as a result of the heat of hydration [20]. These are typically members with a minimum dimension of 1 meter, or 3 feet [21]. These elements can achieve very high internal temperatures that can cause adverse hydration reactions. The large temperature gradients cause these elements to be susceptible to cracking when the formwork is removed. The reduction in heat of hydration with the addition of fly ash can lessen the problem of heat rise in mass concrete placements without sacrificing long-term strength [17]. Although fly ash has proven to be a resourceful addition to concrete mixtures, the annual production of fly ash from coal combustion plants is steadily decreasing per year [3]. With dwindling supplies of available fly ash, reclaimed fly ash may become a valuable resource to reduce the heat of hydration in concrete.

3.1.1 Aim of this Investigation

Isothermal calorimetry is a rapid testing method that measures the amount of thermal power required to keep a specimen at near isothermal conditions [18]. This analysis is used to monitor the amount of exothermic reaction in a cementitious specimen during the hydration stages. There is little knowledge on the changes in heat of hydration for reclaimed fly ash in comparison to traditional fly ash currently meeting ASTM C618 specification [22]. This test will provide insight into the behavior of reclaimed and blended fly ash in comparison to traditional fly ash. This study will analyze the isothermal calorimetry results of twenty-seven different fly ash materials at two replacement levels.

3.2 EXPERIMENTAL METHODS

3.2.1 Laboratory Materials & Mixture Design

One ASTM C 150 [10] Type I Portland cement source was used. A conventional mixture of 100% cement was tested to compare 20% and 40% fly ash replacements with each source. Table 3-1 shows the mixture proportions for each test.

Table 3-1. Mixture Proportions

Mixture	w/cm	Cement (g)	Fly Ash (g)	Water (g)	Paste (%)
OPC	0.45	5.000	0.000	2.250	100
20% Fly Ash	0.45	1.000	4.000	2.250	100
40% Fly Ash	0.45	2.000	3.000	2.250	100

The chemical composition of the cement will affect the hydration process. The Bogue compounds have a unique contribution to the total heat of hydration. The main compounds that affect hydration are C_3A and C_3S [19]. Table 3-2 shows the Bogue calculations, which approximates the proportions of the four main compounds in Portland cement clinker.

Table 3-2: Type I cement Oxide Analysis and Bogue calculations

Oxide %											Bogue Calculation			
SiO_2	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**SO_3**	**Na_2O**	**K_2O**	**TiO_2**	**P_2O_5**	**SrO**	**C_3S**	**C_2S**	**C_3A**	**C_4AF**
62.1	21.1	4.7	2.6	0.2	2.4	-	3.2	0.3	-	-	56.7	17.8	8.2	7.8

Twenty-seven fly ash sources were used in this chapter. Each fly ash source was evaluated with the automated scanning electron microscope (ASEM) to determine the proportion of 11 chemical oxides (SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, SO_3, Na_2O, K_2O, TiO_2, P_2O_5, SrO) for each fly ash material. All of the fly ash used in this chapter are classified as Class F based on the ASTM C618 requirements. One of the main specifications for this ash is the limitation of the calcium oxide content to less than 18 percent. The chemical oxides and classification for each source as a percent of the total source are reported in Table 3-3.

Table 3-3: Fly Ash Oxide Analysis

	Oxide %										
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O_5	SrO
RF1-1	53.04	25.31	11.45	3.36	0.52	0.93	0.35	4.39	0.41	0.18	0.03
RF1-2	57.57	23.51	10.12	2.82	0.49	0.48	0.21	3.85	0.67	0.19	0.05
RF1-3	52.39	22.24	11.18	4.98	0.45	3.94	0.18	3.80	0.78	0.01	0.06
RF1-4	61.59	19.64	11.25	1.98	0.38	0.64	0.22	3.32	0.77	0.03	0.19
RF2	57.55	30.47	5.15	1.45	0.26	0.07	0.03	3.43	1.05	0.06	0.49
RF4	53.50	26.22	9.91	4.62	0.70	0.35	0.08	3.53	0.51	0.14	0.42
RF5	57.88	27.51	6.62	2.37	0.24	0.17	0.13	4.08	0.59	0.03	0.38
RF8	54.75	30.48	8.37	1.79	0.17	0.03	0.03	3.22	0.84	0.07	0.24
BF1	50.63	20.16	4.44	15.99	3.88	0.84	1.11	2.22	0.49	0.05	0.17
BF2	55.58	19.82	5.30	12.61	2.60	0.34	0.60	2.55	0.41	0.05	0.15
BF3	55.26	22.96	3.60	12.72	2.22	0.87	0.05	1.41	0.77	0.01	0.15
BF7	46.54	23.06	4.49	17.63	4.14	0.88	1.22	1.11	0.67	0.12	0.14
BF8	55.74	23.72	3.83	12.00	2.52	0.23	0.04	1.25	0.62	0.00	0.04
F1	48.76	23.79	7.39	12.53	2.97	0.48	0.86	2.05	0.78	0.09	0.29
F2	50.40	20.91	3.89	17.09	3.69	0.54	1.04	1.37	0.70	0.05	0.32
F3	48.81	26.62	6.65	9.30	1.95	0.28	1.75	1.93	1.46	0.14	1.10
F4	45.34	27.39	4.00	14.61	3.59	0.70	1.48	0.65	1.09	0.37	0.76
F5	53.18	25.36	11.21	2.06	0.19	0.89	0.97	4.43	0.71	0.03	0.96
F6	51.87	25.71	12.32	2.50	0.32	0.67	1.61	4.13	0.66	0.05	0.16
F9	48.27	25.01	5.86	12.59	3.32	0.49	1.33	1.77	1.12	0.18	0.06
F20	54.04	29.29	8.24	1.37	0.41	0.01	0.07	4.51	1.19	0.60	0.19
F22	52.31	21.06	19.66	1.74	0.44	0.05	0.47	3.61	0.62	0.02	0.01
F23	58.36	26.41	8.26	1.11	0.20	0.07	0.57	4.26	0.69	0.04	0.01
F24	49.92	21.55	22.84	0.93	0.23	0.15	0.36	3.30	0.67	0.01	0.02
F25	54.76	20.93	16.38	1.44	0.60	0.39	0.24	4.80	0.35	0.07	0.02
F26	55.54	28.60	7.63	1.84	0.77	0.07	0.10	4.54	0.76	0.10	0.03
F27	52.88	23.86	12.25	5.26	0.39	0.61	0.40	3.36	0.47	0.12	0.39

3.2.2 Sample Preparation

The cement and fly ash were combined in a glass ampoule and mixed by hand. The water was added to the cementitious material with a syringe and mixed again by hand. Next, the ampoule was placed in a vibratory mixer and vibrated at 1000 rpm for 60 seconds.

3.2.3 Isothermal Calorimetry Testing

Isothermal calorimetry testing was performed per ASTM C1702 [9] for all mixtures. Testing was conducted with a TAM Air 8-channel isothermal calorimeter with glass ampoules. A cement only mixture was used for the control mixture with a w/cm ratio of 0.45. The remaining tests consisted of fly ash at either a 20% or 40% replacement of cement. The heat evolution was measured for 48 hours. The isothermal calorimetry results presented for each fly ash represent the average of two samples.

When the glass ampoules are lowered into their respective chamber at the start of the isothermal calorimetry test, the temperature of the chambers is disturbed. Due to this, TAM Air requires a thirty-minute baseline to be established at the beginning of the test. ASTM C1702 defines the baseline as the "time-series signal from the calorimetry when measuring output from a sample of approximately the same mass and thermal properties as a cement sample, but which is not generating or consuming heat" [24]. This disturbance can cause the initial rate of heat evolution data to start at different magnitudes. To accurately compare graphs with a fly ash replacement, each data point was moved to the starting point of the 100% OPC testing. This starting point is defined as the minimum value at the beginning of the rate of heat evolution dataset. The average minimum value is at a time of 1.66 hours and at a rate of heat evolution of 0.318

milliwatts per gram of paste material. Each following rate of heat evolution data set with a fly ash replacement was adjusted to have an initial starting point at the average minimum value. The magnitude of the heat evolution from the initial value to the maximum value is not affected by this adjustment.

3.2.4 Calculations Behind Isothermal Calorimetry Testing

The results of the isothermal calorimetry test can be summarized with the total heat of hydration measured in Joules per gram. The first derivative of the total heat of hydration results provides the rate of heat evolution in milliwatts per gram (Joules per second per gram). The second derivative of the total heat of hydration results is used to find the maximum value on the rate of heat evolution in milliwatts per second per gram (Joules per second per second per gram).

When the rate of heat evolution graph starts to decline, this is where the peak value is found. The peak value is the point where the maximum rate of heat evolution value occurs. The derivative of this graph is used to calculate the time the maximum rate of heat evolution value occurs, or where the slope is zero. Figure 3-1 shows the rate of heat evolution graph as the first derivative, or $\frac{\mathrm{dH}}{\mathrm{dt}}$. The time in hours that the peak value occurs can be found by using the second derivative plot, or $\frac{\mathrm{d^2H}}{\mathrm{dt^2}}$. The number of hours required for the data set of the second derivative to reach zero is the same amount of hours the peak value occurs for the first derivative.

The setting of concrete typically takes place during the acceleratory period, which corresponds to the positive slope of the first derivative graph. The maximum point of the first derivative graph is representative of the end of this acceleratory period. The transition from a positive to a negative slope on the rate of heat evolution plot is considered the peak value. The maximum value can be used to estimate the relative set time between two materials [25].

The total heat of hydration represents the amount of heat given off from the sample at a 48-hour time interval. The higher total heat of hydration represents an increase in potential temperature rise in a concrete element [19]. The total heat of hydration is found at time intervals of 12, 24, and 48 hours. The values for the 48-hour time interval are analyzed further in this paper and the remaining time intervals are shown in the appendix.

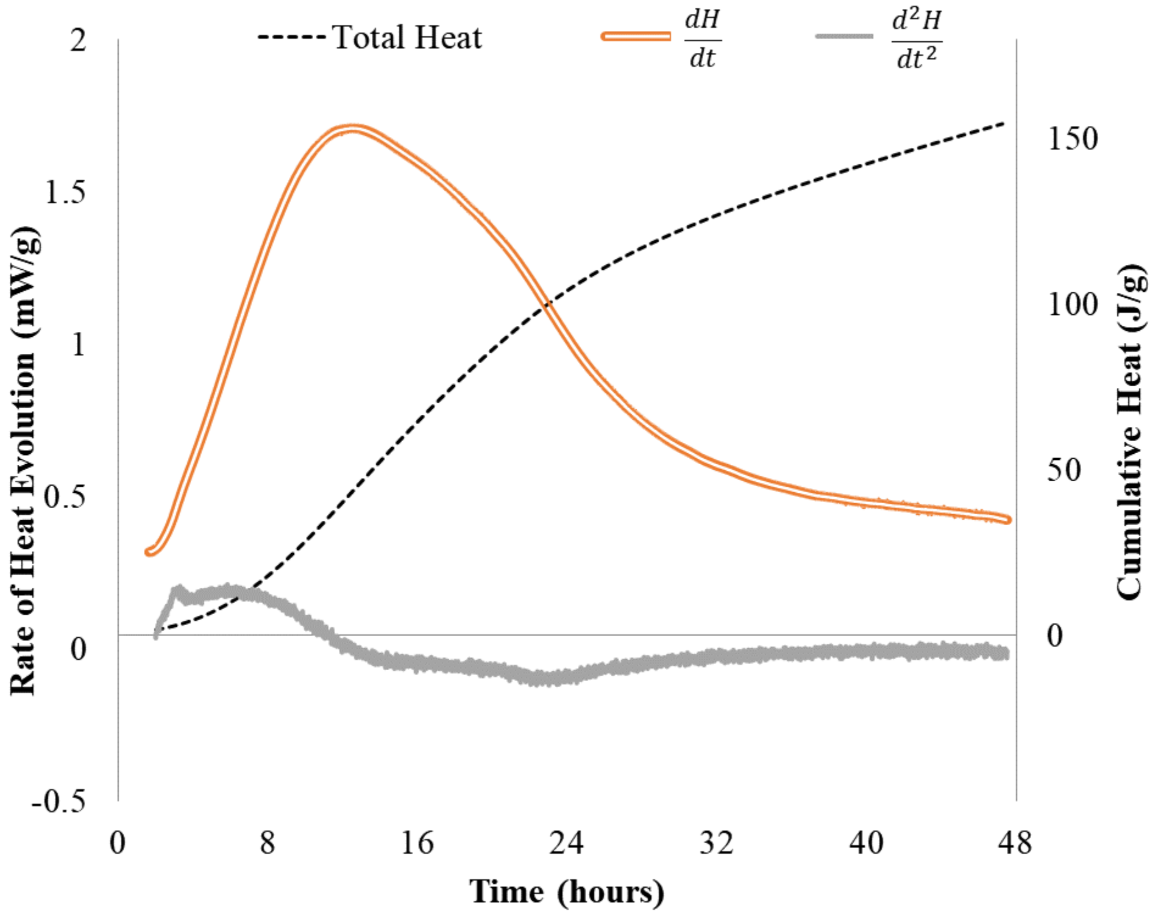

Figure 3-1: Analysis of the total heat of hydration.

3.2.5 Statistical Analysis Using T-Test & Quartile Analysis

There is little knowledge on the changes in heat of hydration for reclaimed fly ash in comparison to traditional fly ash currently meeting ASTM C618 specification. Two analysis methods are chosen to determine the similarity between reclaimed and blended fly ash with traditional fly ash are the Student's t-test and quartile analysis. These techniques are then also used to more deeply examine the fly ash that are outliers.

3.2.5.1 Student's t-test

A t-test is a type of inferential statistic used to determine if there is a significant difference between the means of the two groups. The Student's t-test will compare the statistical significance between the traditional Class F fly ash and the reclaimed and blended Class F fly ash. For this study, a 2-tailed type 3 t-test was performed. The 2 tailed shows the statistical significance in both directions. Since the total heat of hydration could increase or decrease from the traditional Class F fly ash, a 2-tailed test was used. A type 3 test was used since the data set is heteroscedastic, or the scatter plot has variation [26]. The equation for the Student's t-test is shown below where m is the total heat of hydration for traditional Class F fly ash, μ is the heat of hydration for the fly ash being investigated, s is the standard deviation from all traditional Class F fly ash, and n is the number of traditional Class F fly ash.

$$T = \frac{m - \mu}{\frac{s}{\sqrt{n}}}$$

Equation 3.1 – Student's t-test

This test will be used to first determine similarity between reclaimed and blended fly ash and traditional fly ash. The test will also be used to investigate how fly ash with only certain oxide contents perform

3.2.5.2 Oxide Analysis

The amount of heat released is dependent on the chemical composition of the cement material as well as the fly ash materials [19]. The analysis of these fly ash is focused on the chemical composition of each fly ash. The following oxide parameters are used to better understand the performance of each fly ash in regards to the total heat of hydration.

This analysis focused on calcium oxide, sulfur trioxide, the oxide ratio, and the alkali equivalent. These oxides were chosen due to their ability to increase the total heat [27], delay hydration reactions [19], or increase the pH level [27]. Equation 3.2 shows the oxide ratio calculations where equation 3.3 shows the alkali equivalent calculations.

$$\frac{\mathrm{CaO}}{\mathrm{SiO_2} + \mathrm{Al_2O_3}}$$

Equation 3.2 – Oxide ratio

$$\mathrm{Na_2O} + 0.685\mathrm{K_2O}$$

Equation 3.3 – Alkali equivalent

The content of each parameter was divided by the median value into a high and low classification. The median was selected in order to have a large enough sample size for each parameter. Table 3-4 summarizes the division of each parameter.

Table 3-4: High and low oxide classification

Parameter	
low CaO	0-5%
high CaO	5-18%
low SO3	0-0.4%
high SO3	0.4-4%
low oxide ratio	0-0.05
high oxide ratio	0.05-0.3
low alkali equivalent	0-2.6
high alkali equivalent	2.6-5

3.2.5.3 Quartile Analysis

A quartile analysis was performed to find outliers in the oxide content. This analysis divides the data set into four groups to measure the distribution of the values above and below the mean [28]. The upper and lower limit of the dataset is found with the inner quartile range. Any data point that falls above or below these limits is considered an outlier [29]. The quartile analysis was used to compare the oxide content of the reclaimed and blended Class F fly ash with traditional Class F fly ash. Each quartile was calculated using the quartile function in MS Excel.

3.3 RESULTS AND DISCUSSION

3.3.1 Repeatability of Isothermal Calorimetry Measurements

Sixteen different tests were completed with Portland cement mixtures to determine the repeatability of the method and also establish a minimum value of the test. This minimum value created a starting point for the remaining fly ash tests to ensure the magnitude of the rate of heat evolution was calibrated. This allowed the variation of the test and equipment to be established. To gain a better understanding of how the testing can vary over the 48-hour time interval, the average and standard deviation were taken for 16 tests every 12 hours. The results of these tests are shown in Figure 3-2 and Table 3-5. The results of this test showed that the total heat of hydration at 48 hours differed by a maximum value of 7.4 Joules per gram, which is within the limitation of ASTM C1702.

These measurements create standard for the expected standard deviation between two tests of the same material. Since each fly ash material was tested twice for heat evolution, the standard deviation was then compared to the 100% OPC test. This ensured the values received from tests with the same fly ash material were consistent and provided quality control to the test.

Table 3-5: Deviation in Rate of Heat Evolution and Total Heat of Hydration plots

Time (hours)	Average Heat (mW/g)	STD	COV	Average Total Heat of Hydration (J/g)	STD	COV
12	1.95	0.04	2.05	50.59	1.39	2.75
24	0.96	0.02	2.08	117.79	3.37	2.86
36	0.46	0.03	6.52	145.69	2.69	1.85
48	0.35	0.01	2.86	162.69	2.50	1.54

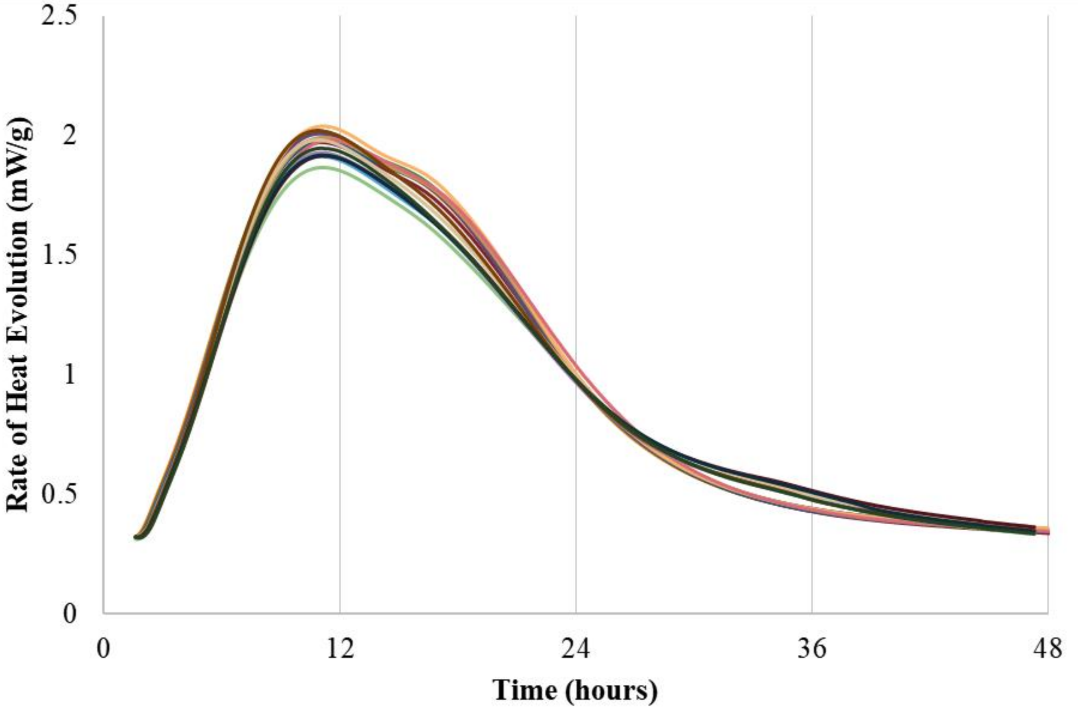

Figure 3-2a: Rate of Heat Evolution results for 16 OPC only experiments

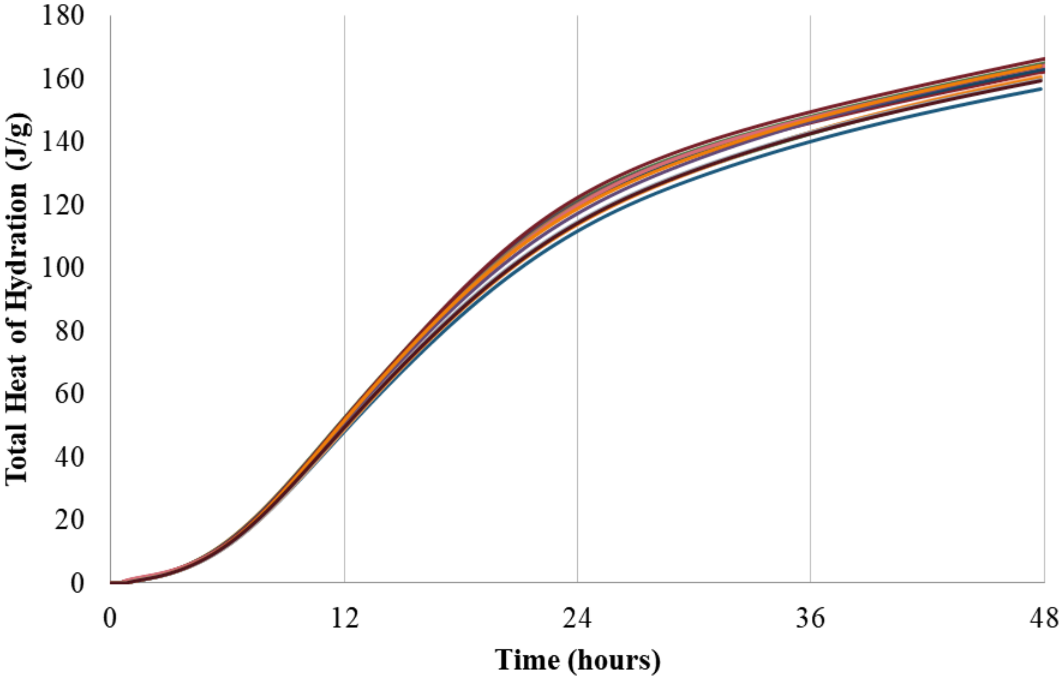

Figure 3-2b: Total Heat of Hydration results for 16 OPC only experiments

3.3.2 Impacts of Water Reducer on the Rate of Heat Evolution

The rate of heat evolution can provide insight into the time required for concrete to begin to set. However, there are several outside factors in a concrete mixture that affect the setting time that is outside of the scope of this study. Figure 3-3a shows the impact that water-reducing admixtures have on the setting time, where Figure 3-3b shows the impact that water-reducing admixtures have on the total heat of hydration. A cementitious material with Type I Portland cement and 40% Class F fly ash replacement was tested for isothermal calorimetry. Additional mixtures were measured with a mid-range water reducer and a high-range water reducer.

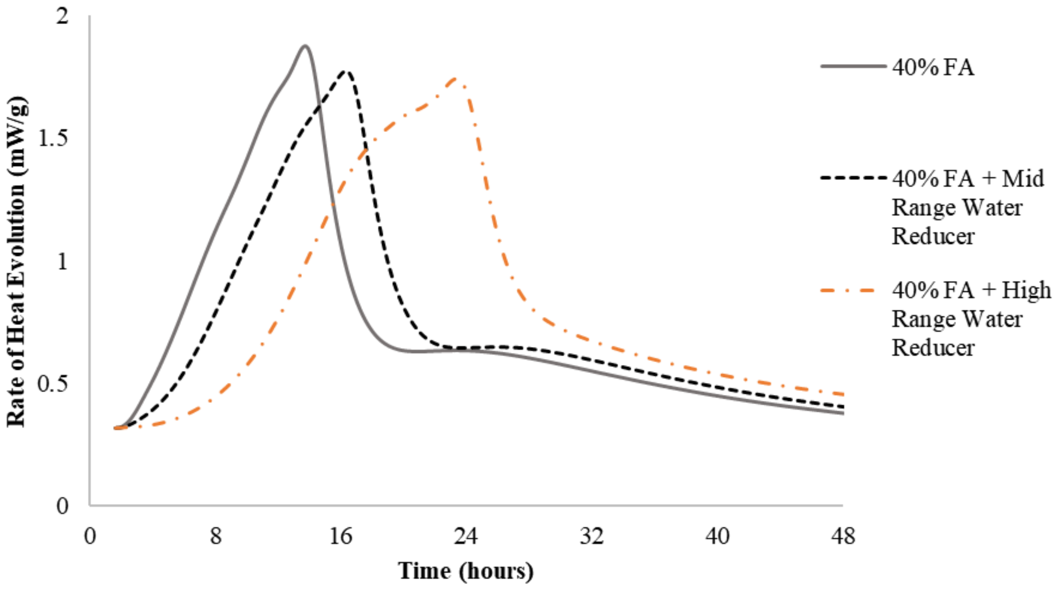

Figure 3-3a: Impact of Water Reducing Admixtures on Rate of Heat Evolution

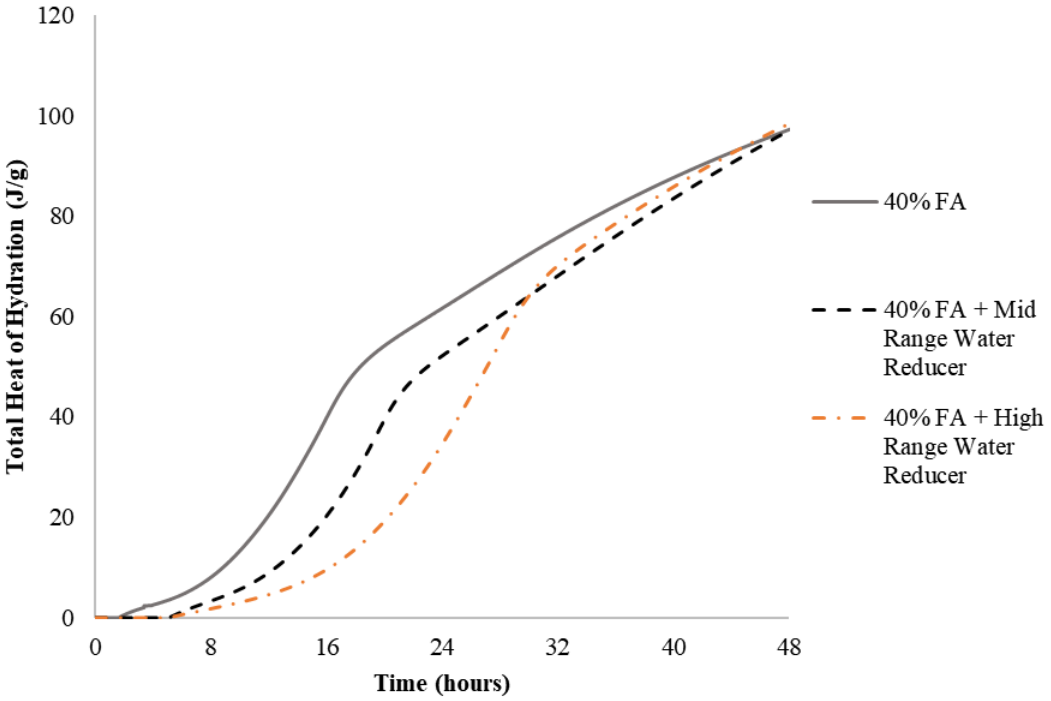

Figure 3-3b: Impact of Water Reducing Admixtures on Total Heat of Hydration

The results of Figures 3-3a show the change in peak time increase from two to twelve hours depending on the type of water reducer used. Since the use of water-reducing admixtures with different intensities in a concrete mixture is common in the industry, the time to peak values from an isothermal calorimetry test without the use of admixtures can be misleading. Figure 3-3b shows that although the heat evolution is affected by the water reducing admixtures, the total heat of 48 hours has very similar values. The total heat of hydration in Joules per gram for 40% fly ash, 40% fly ash plus mid-range water reducer, and 40% fly ash plus high range water reducer are 97.3, 97.07, and 98.4 respectively. These values fall within the expected standard deviation of the OPC samples tested above, and are considered similar testing values. Due to this, the total heat of hydration will be the focus of this chapter as opposed to the rate of heat evolution.

Figure 3-4 shows the total heat of hydration at 48 hours for each fly ash. These values show the total heat given off from the cementitious combination of cement with a fly ash replacement of either 20% or 40%. The figure displays a horizontal line for the average total heat of hydration of 163 J/g for the 100% OPC testing.

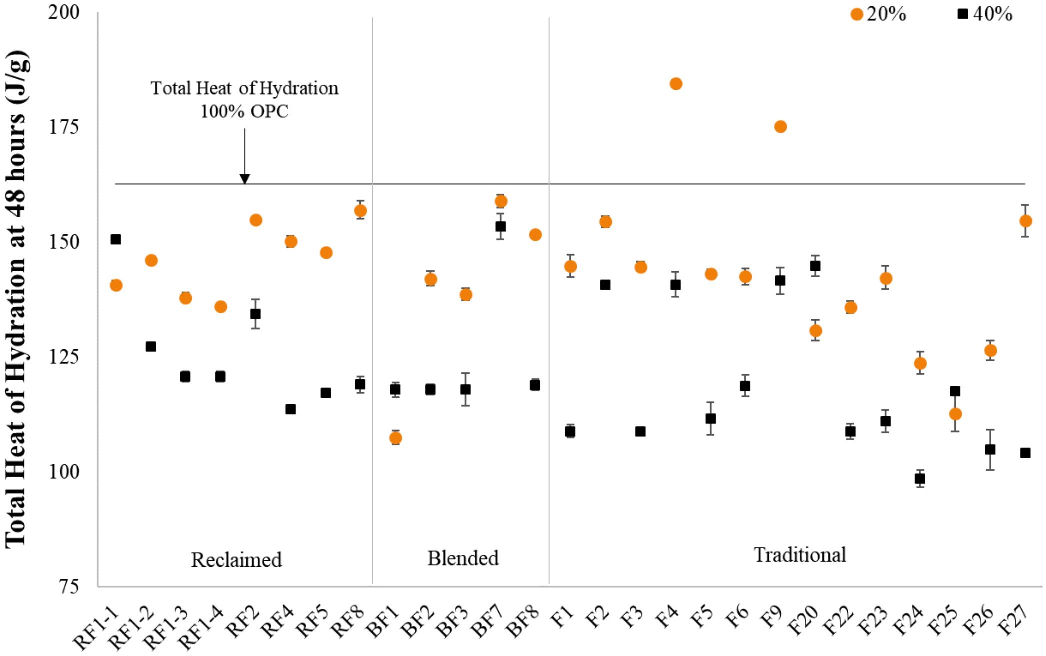

Figure 3-4: Total Heat of Hydration at 48 hours

3.3.3 STATISTICAL ANALYSIS

There is little knowledge on the changes in heat of hydration for reclaimed fly ash in comparison to traditional fly ash currently meeting ASTM C618 specification. The addition of fly ash in a concrete mixture is known to reduce the total heat of hydration. The two analysis methods chosen to determine the similarity between reclaimed and blended fly ash with traditional fly ash are the Student's t-test and quartile analysis.

3.3.3.1 Student's t-test

A t-test is a type of inferential statistic used to determine if there is a significant difference between the means of the two groups. The Student's t-test will compare the statistical significance between the traditional Class F fly ash and the reclaimed and blended Class F fly ash. For this study, a 2-tailed type 3 t-test was performed. First, a Student's t-test was conducted to compare the number of statistically similar traditional Class F fly ash. Then the reclaimed and blended Class F fly ash were tested to see the statistical similarity of traditional Class F fly ash. The amount of fly ash that passed the t-test as a percent of the total data set was shown in Table 3-6 and Figures 3-5a and 3-5b shows a graphical representation of the data points that are considered statistically similar.

The solid lines in Figures 3-5a and 3-5b show the average total heat of hydration for traditional Class F fly ash at 20% or 40% where the points within the dashed lines are considered statistically similar or statistically different with a 95% confidence interval. The reclaimed and blended Class F fly ash had a 77% statistical similarity to traditional fly ash, which means 10 of the 13 fly ash in this study have a total heat of hydration statistically similar to traditional Class F fly ash for both 20% and 40% replacement. This shows that the reclaimed and blended Class F fly ash are statistically similar to traditional Class F fly ash due to the greater percent passing value.

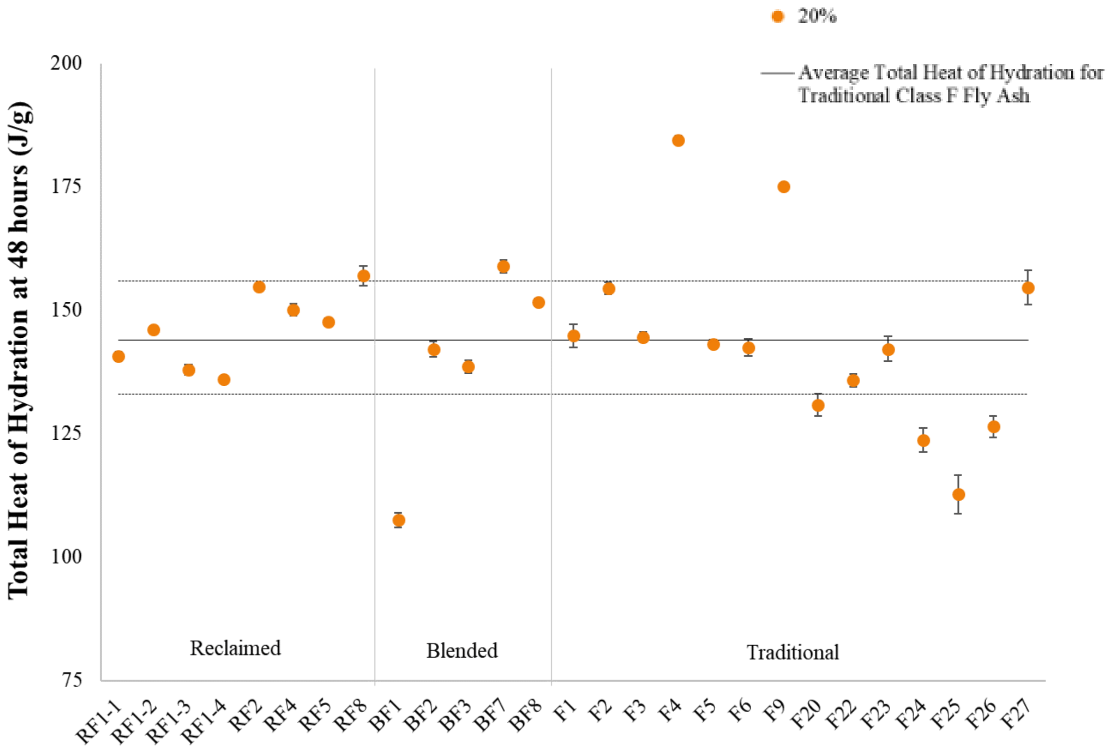

Figure 3-5a: Results of Student's t-test with 20% Class F fly ash replacement

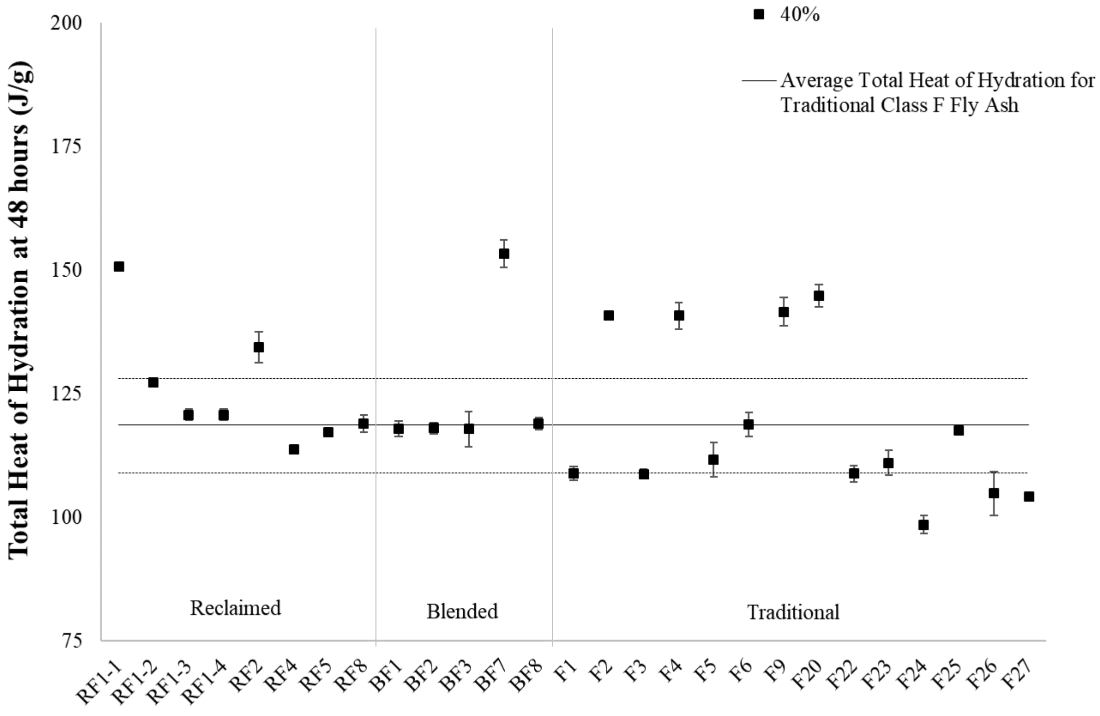

Figure 3-5b: Results of Student's t-test with 40% Class F fly ash replacement

Table 3-6: Student's t-test results of reclaimed and blended Class F fly ash in comparison to traditional Class F fly ash

Percent of total fly ash passing the Student's t-test			
Fly Ash Analyzed	Parameter	20% Replacement	40% Replacement
Traditional	All	57%	29%
Reclaimed/Blended	All	77%	77%

To learn more about the outliers, additional Student's t-test are done with CaO, SO_3, alkali equivalent and the ratio of oxide content. If separating the fly ash by these parameters either significantly improves or reduces the percent passing the Student's t-test then this could provide greater insight into the importance of these oxides.

The results of the Student's t-test shown in Table 3-7 show a significant statistical similarity in fly ash with an alkali equivalent below from 0-2.5. There is a less significant increase in statistical similarity in fly ash with a calcium oxide content from 5-18% in comparison to the alkali equivalent. This means that fly ash with these chemical contents provide even higher statistical similarity than just using a typical reclaimed or blended fly ash. This means that if a fly ash has this characteristic then it is more likely to perform like a typical Class F fly ash and would not be considered an outlier. This creates a potential correlation between the ability to predict a statistical similarity between Class F fly ash that is either traditional, reclaimed, or blended since these values are higher than 77% of the overall results. On the other hand, the separation by sulfate content provided unreliable results since the statistical similarities ranged from 0% to 83% for a sulfur oxide content below 0.4%. The change in similarity based on the percent fly ash replacement shows that the sulfate content does not provide significant insight to the performance of the fly ash with 20% replacement in this group.

Table 3-7: Student's t-test results of reclaimed and blended Class F fly ash based on oxide content

			Percent of total fly ash passing the Student's t-test	
Fly Ash Analyzed	**Parameter**	**Value**	**20% Replacement**	**40% Replacement**
Traditional	All	-	57%	29%
Reclaimed/Blended	All	-	77%	77%
Reclaimed/Blended	low CaO	0-5%	38%	63%
Reclaimed/Blended	high CaO*	5-18%	80%	80%
Reclaimed/Blended	low SO_3	0-0.4%	0%	83%
Reclaimed/Blended	high SO_3	0.4-4%	29%	71%
Reclaimed/Blended	low oxide ratio	0-0.05	33%	67%
Reclaimed/Blended	high oxide ratio	0.05-0.3	43%	86%
Reclaimed/Blended	low alkali equivalent*	0-2.6	100%	100%
Reclaimed/Blended	high alkali equivalent	2.6-2	40%	60%

*high CaO content and low alkali equivalent show an increase in statistical similarity from the previous Student's t-test of 77%

3.3.3.2 Quartile Analysis

A quartile analysis was created to find outliers in the oxide content. The quartile analysis was used to compare the oxide content of the reclaimed and blended Class F fly ash with traditional Class F fly ash. The previous Student's t-test proved statistical similarity for reclaimed and blended Class F fly ash. The potential outliers remaining from this analysis are BF1, BF7, RF1-1, RF2, and RF8. There was not a unique chemical composition of the potential outliers from the Student's t-test according to the quartile analysis. The results of this analysis are shown in the appendices with bolded oxide contents that are considered outliers. There was not a correlation between the potential outliers from the Student's t-test and the outliers found from the quartile analysis. This shows that more complex analysis is required to predict the performance of the total heat of hydration for Class F fly ash based on the oxide content.

3.4 PRACTICAL IMPLEMENTATION

The results of the Student's t-test show that reclaimed and blended Class F fly ash have great potential to be classified alongside traditional Class F fly ash based on total heat of hydration at 48 hours according to the 77% passing from the Student's t-test. The use of reclaimed and blended Class F fly ash is expected to perform similarly with traditional Class F fly ash according to the parameters tested in this study for total heat as measured by isothermal calorimetry. This establishes the usage of reclaimed and blended fly ashes to lower heat and also shows that isothermal calorimetry is a reliable measurement tool for these materials.

3.5 CONCLUSION

The use of isothermal calorimetry provides the availability for rapid testing to compare the impact of the heat of hydration with reclaimed, blended, and traditional Class F ash. The results of these tests can begin the baseline for performance based specifications for traditional, reclaimed, and blended fly ash material. This can allow materials that are currently being stored as waste to be implemented in concrete mixture.

The results of this chapter are as follows:

- 77% of the reclaimed and blended Class F fly ash showed a similar total heat of hydration at 48 hours for both 20% and 40% replacement according to the Student's t-test
- The statistical similarity increased from 77% to 80% for fly ash with a calcium oxide content greater than 5% but less than 18%
- The statistical similarity increased from 77% to 100% for fly ash with an alkali equivalent from 0 to 2.6
- The oxide content shows promise in fly ash materials with a high calcium oxide content and low alkali equivalent due to the similarity of the total heat of hydration values from the Student's t-test
- The quartile analysis was not a reliable method to predict the outliers of the total heat of hydration based on the oxide content
- This shows that reclaimed and blended fly ashes have very similar performance to traditional Class F fly ash in their total heat at 48 h. This makes these materials strong candidates for use in mass concrete applications.

3.6 FUTURE WORK

Additional testing is required to better understand the variability in heat of hydration for reclaimed, blended, and traditional Class F fly ash for total heat of hydration. Further analysis on the impact of chemical oxide content with total heat of hydration is also recommended.

CHAPTER IV

CONCLUSION

4.1 SUMMARY

This thesis was composed of two rapid testing methods to understand the behavior of reclaimed and blended Class F fly ash in comparison to traditional Class F fly ash. A total of 30 types of fly ash sources were used in this study.

The overall study has shown both isothermal calorimetry and the foam index test are useful to evaluate performance of reclaimed and blended fly ash in concrete. The results of these tests can be used for performance based specifications to allow the use of reclaimed and blended Class F fly ash alongside traditional Class F fly ash. This will provide an adequate supply of reliable fly ash in the industry.

Conclusions from Chapter 2:

- Blended and reclaimed fly ash can be used in air entrained concrete and performs similarly to traditional fly ash.
- The LOI did not serve as a useful test to use to predict AEA demand in a concrete mixture for reclaimed fly ash.
- The foam index test used proves to be a reliable method to evaluate the AEA demand of traditional, blended, and reclaimed fly ash.
- The foam index test used shows a linear correlation ($R^2 = 0.90$) to the AEA dosage required to create 6% air in a concrete mixture. These studies show the usefulness of the foam index test to predict the slope of the dosage curve. This continues to show promise of this test to serve as a tool to predict the impacts that traditional, reclaimed, and blended fly ash have on the AEA dosage required to achieve the desired air content.

Conclusions from Chapter 3:

- 77% of the reclaimed and blended Class F fly ash showed a similar total heat of hydration at 48 hours for both 20% and 40% replacement according to the Student’s t-test
- The statistical similarity increased from 77% to 80% for fly ash with a calcium oxide content greater than 5% but less than 18%

- The statistical similarity increased from 77% to 100% for fly ash with an alkali equivalent from 0 to 2.6
- The oxide content shows promise in fly ash materials with a high calcium oxide content and low alkali equivalent due to the similarity of the total heat of hydration values from the Student's t-test
- The quartile analysis was not a reliable method to predict the outliers of the total heat of hydration based on the oxide content
- This shows that reclaimed and blended fly ashes have very similar performance to traditional Class F fly ash in their total heat at 48 h. This makes these materials strong candidates for use in mass concrete applications.

REFERENCES

[1] Benhelal, Emad, et al, et al. "Global strategies and potentials to curb CO2 emissions in cement industry." *Journal of cleaner production* 51 (2013): 142-161.

[2] Samad, S., and A. Shah. "Role of binary cement including Supplementary Cementitious Material (SCM), in production of environmentally sustainable concrete: A critical review." *International journal of Sustainable built environment* 6.2 (2017).

[3] ACAA. (2016). 2015 Production and Use Survey Results News Release. Retrieved from https://www.acaa-usa.org/Publications/Production-Use-Reports

[4] ASTM C618 *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete*.

[5] Tyler, Ley. "Determining the Air-Entraining Admixture Dosage Response for Concrete with a Single Concrete Mixture." *Recent Advancement in Concrete Freezing-Thawing (FT) Durability*. ASTM International, (2010).

[6] Ley, T., Harris, N. J., Folliard, K. J., Hover, K. C.; "Investigation of Required Air Entraining Admixture Dosage in Fly Ash Concrete," ACI Concrete Materials Journal, Vol. 105, 5,September 2008, pp. 494-498

[7] Harris, N.J., Hover, K.C., Folliard, K.J., Ley, T.; "The Use of the Foam Index Test to Predict AEA Dosage in Concrete Containing Fly Ash: Part I-Evaluation of the State of Practice," ASTM Journal of Testing and Evaluation, (2008), doi: 10.1520/JAI101601.

[8] Harris, N.J., Hover, K.C., Folliard, K.J., Ley, T.; "The Use of the Foam Index Test to Predict AEA Dosage in Concrete Containing Fly Ash: Part II-Development of a standard test method: apparatus and procedure," ASTM Journal of Testing and Evaluation, (2008), doi: 10.1520/JAI101602.

[9] Harris, N.J., Hover, K.C., Folliard, K.J., Ley, T.; "The Use of the Foam Index Test to Predict AEA Dosage in Concrete Containing Fly Ash: Part III-Development of a standard test method—Proportions of materials," ASTM Journal of Testing and Evaluation, (2008), doi: 10.1520/JAI101603.

[10] Diaz-Loya, Ivan, et al. "Extending Supplementary Cementitious Material Resources: Reclaimed and Remediated Fly Ash and Natural Pozzolans." *Cement and concrete composites* 101 (2019): 44-51.

[11] ASTM C33-18, Standard Specification for Concrete Aggregates (2018)

[12] ASTM C138, Standard Test Method for Density Unit Weight, Yield, and Air Content "Gravimetric of Concrete," (2001)

[13] ASTM C231-03, "Standard Test Method for Air Content of Freshly Mixed Concrete by the Pressure Method," (2003).

[14] ASTM C150/C150M-20 "Standard Specification for Portland Cement" (2020).

[15] ASTM C143 "Standard Test Method for Slump of Hydraulic-Cement Concrete" (2020)

[16] ASTM C260 "Standard Specification for Air-Entraining Admixtures for Concrete" (2016).

[17] American Coal Ash Association. “Fly Ash Facts for Highway Engineers.” *U.S. Department of Transportation/Federal Highway Administration*, (2003).

[18] Gartner, E. M., et al. "Hydration of Portland cement." *Structure and performance of cements* 2 (2002): 57-113.

[19] Schindler. “Heat of Hydration Models for Cementitious Materials.” ACI materials journal 102.1 (2005): n. pag. Print.

[20] *ACI 301-16: Specifications for Structural Concrete*. American Concrete Institute.

[21] Alper, J. Benjamin, et al. “Mass Concreting.” *STRUCTURE Magazine*, www.structuremag.org/?p=12993.

[22] ASTM C618 *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete*.

[23] Abualrous, Yasar, et al. "MAT-759: PARTICLE SIZE ANALYSIS AS A MEANS TO BETTER UNDERSTAND THE INFLUENCE OF FLY ASH VARIABILITY IN CONCRETE." (2016).

[24] ASTM C1702 Standard Test Method for Measurement of Heat of Hydration of Hydraulic Cementitious Materials Using Isothermal Conduction Calorimetry

[25] Hu, Jiong, Zhi Ge, and Kejin Wang. "Influence of cement fineness and water-to-cement ratio on mortar early-age heat of hydration and set times." *Construction and building materials* 50 (2014): 657-663.

[26] Hayes, Adam. “T-Test Definition.” *Investopedia*, 22 Mar. 2020

[27] Skibsted, Jørgen, and Morten D. Andersen. "The effect of alkali ions on the incorporation of aluminum in the calcium silicate hydrate (C–S–H) phase resulting from Portland cement hydration studied by 29 Si MAS NMR." *Journal of the American Ceramic Society* 96.2 (2013): 651-656.

[28] Liberto, Daniel. “Quartile Definition.” *Investopedia*, Investopedia, 20 Apr. 2021, www.investopedia.com/terms/q/quartile.asp.

[29] “How to Find Outliers in Excel.” *AbsentData*, 3 Apr. 2018, www.absentdata.com/how-to-find-outliers-in-excel.

APPENDICES

Table A-1: Raw data from air entrained concrete mixtures

	Foam Index		SAM #		Phoenix (w/cm)		Dosage Curve	mL AEA/100kg cm for 6% air	
	Average	STD			Batched	Actual	R^2	Average	STD
C3	14.0	2.0	-	0.17	0.45	0.45	0.9578	62.40	1.74
			0.12	-	0.45	0.44	0.9768		
RF5	12.3	1.2	-	0.13	0.45	0.49	0.975	69.52	0.07
			0.10	-	0.45	0.43	0.9843		
RF7-1	16.0	1.0	-	-	0.45	0.41	0.9152	57.38	0.31
			0.09	-	0.45	0.42	0.9982		
RF3	16.3	0.6	0.10	0.09	0.45	0.47	0.9949	67.15	4.13
			0.19	0.05	0.45	0.53	0.9849		
RF2	17.3	1.2	0.13	-	0.45	0.45	0.975	73.37	11.82
			-	0.20	0.45	0.45	0.9826		
F27	34.7	1.5	0.42	0.22	0.45	0.44	0.964	131.14	0.18
			0.14	-	0.45	0.46	0.9363		
RF4	51.0	1.0	0.14	0.13	0.45	0.42	0.9453	217.43	21.95
			0.15	0.19	0.45	0.46	0.8999		
RF1-2	47.0	1.0	0.19	0.19	0.45	0.45	0.9586	245.11	5.80
			0.17	0.13	0.45	0.45	0.9699		
RF1-1	30.3	4.9	0.12	0.21	0.45	0.45	0.9965	146.66	12.30
			0.22	-	0.45	0.45	0.9993		
75% RF4 + 25% C3	52.7	1.5	0.18	0.15	0.45	0.43	0.9381	134.62	1.45
			0.09	0.08	0.45	0.47	0.9151		
90% RF1-2 + 10% C3	63.0	1.0	0.17	0.17	0.45	0.44	0.9946	174.13	18.54
			0.17	-	0.45	0.44	0.9959		
85% F27 + 15% C3	24.5	0.7	-	-	0.45	0.52	0.9674	95.92	2.56
			0.13	0.18	0.45	0.58	0.9609		

Table A-2: Standard deviation of oxide content

	Oxide %										
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O_5	SrO
RF1-1	1.59	0.31	2.44	0.51	0.24	0.11	0.03	0.46	0.08	0.14	0.02
RF1-2	1.36	1.26	2.77	0.20	0.17	0.16	0.04	0.07	0.29	0.17	0.01
RF1-3	0.02	1.10	2.00	0.94	0.09	0.02	0.10	0.20	0.26	0.00	0.02
RF1-4	3.90	1.36	1.95	0.05	0.02	0.13	0.10	0.86	0.35	0.00	0.17
RF2	0.18	0.99	1.14	0.45	0.01	0.03	0.02	0.02	0.37	0.05	0.11
RF3	2.58	2.18	2.57	2.24	0.10	0.17	0.02	0.05	0.21	0.00	0.14
RF4	0.35	0.28	3.78	3.66	0.03	0.28	0.07	0.14	0.04	0.04	0.21
RF5	3.63	0.22	1.34	2.32	0.01	0.19	0.15	0.15	0.23	0.02	0.22
RF6-1	3.46	1.26	3.17	0.49	0.42	0.09	0.02	0.51	0.17	0.27	0.11
RF6-2	1.44	1.52	2.91	0.27	0.15	0.22	0.11	0.10	0.26	0.03	0.00
RF7-1	2.53	0.09	2.66	0.82	0.23	0.04	0.01	0.09	0.23	0.00	0.33
RF7-2	1.35	2.54	0.22	0.42	0.05	0.19	0.08	0.13	0.89	0.00	0.03
RF8	0.89	0.17	0.61	0.33	0.04	0.03	0.04	0.15	0.12	0.04	0.06
RF9	3.31	0.59	0.17	2.15	0.03	1.37	0.27	0.33	0.22	0.05	0.02
RF10	6.54	1.04	0.72	2.05	0.70	0.49	0.87	0.12	0.11	0.40	0.21
RF11	0.34	0.87	0.13	0.14	0.49	0.09	0.04	0.24	0.00	0.10	0.05
BF1	5.09	0.71	0.11	3.59	0.59	0.36	0.01	0.19	0.06	0.03	0.03
BF2	1.17	0.11	0.61	1.40	0.13	0.15	0.22	0.57	0.01	0.02	0.16
BF3	1.96	0.84	0.79	3.16	0.17	0.79	0.02	0.13	0.14	0.01	0.06
BF7	0.04	0.98	0.35	0.76	0.04	0.15	0.13	0.12	0.10	0.03	0.01
BF8	0.40	0.84	0.01	0.21	0.04	0.08	0.01	0.09	0.01	0.00	0.02
F1	1.03	0.65	1.22	1.05	0.47	0.22	0.10	0.07	0.13	0.01	0.00
F2	2.20	0.95	0.24	0.55	0.24	0.07	0.11	0.00	0.03	0.05	0.05
F3	0.22	0.48	0.99	0.96	0.29	0.07	0.17	0.35	0.20	0.06	0.08
F4	0.35	0.24	0.11	0.12	0.03	0.25	0.09	0.01	0.13	0.02	0.15
F5	1.49	0.49	1.27	0.01	0.05	0.14	0.06	0.35	0.01	0.01	0.09
F6	0.08	0.38	0.39	0.50	0.06	0.09	0.08	0.04	0.12	0.02	0.58
F9	-	-	-	-	-	-	-	-	-	-	-
F20	0.65	0.65	1.41	0.43	0.02	0.00	0.07	0.57	0.74	0.52	0.23
F22	3.78	0.23	3.06	0.93	0.39	0.07	0.08	0.73	0.37	0.00	0.01
F23	0.13	0.12	0.80	0.40	0.05	0.09	0.12	0.19	0.00	0.02	0.00
F24	1.49	0.12	2.34	0.33	0.04	0.10	0.18	0.32	0.04	0.01	0.02
F25	0.97	1.01	0.19	0.19	0.01	0.04	0.10	0.14	0.08	0.04	0.01
F26	0.31	0.36	0.00	0.53	0.02	0.04	0.01	0.38	0.21	0.04	0.01
F27	0.53	3.05	7.10	2.76	0.40	0.09	0.39	0.39	0.11	0.07	0.25

Table A-3: Results of outliers from quartile analysis based on oxide content

Fly Ash	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O_5	SrO	Oxide Ratio	Alkali Equivalent
RF1-1	53.04	23.79	11.45	3.36	0.52	0.93	0.35	4.39	0.41	0.18	0.03	0.04	3.36
RF1-2	57.57	20.91	10.12	2.82	0.49	0.48	0.21	3.85	0.67	0.19	0.05	0.035	2.85
RF1-3	52.39	26.62	11.18	4.98	0.45	**3.94**	0.18	3.80	0.78	0.01	0.06	0.07	2.78
RF1-4	**61.59**	27.39	11.25	1.98	0.38	0.64	0.22	3.32	0.77	0.03	0.19	0.02	2.49
RF2	57.55	25.36	5.15	1.45	0.26	0.07	0.03	3.43	1.05	0.06	0.49	0.02	2.37
RF4	53.5	25.71	9.91	4.62	0.7	0.35	0.08	3.53	0.51	0.14	0.42	0.06	2.50
RF5	57.88	25.01	6.62	2.37	0.24	0.17	0.13	4.08	0.59	0.03	0.38	0.03	2.92
RF8	54.75	29.29	8.37	1.79	0.17	0.03	0.03	3.22	0.84	0.07	0.24	0.02	2.24
BF1	50.63	21.06	4.44	15.99	3.88	0.84	1.11	2.22	0.49	0.05	0.17	0.23	2.64
BF2	55.58	26.41	5.30	12.61	2.60	0.34	0.60	2.55	0.41	0.05	0.15	0.17	2.35
BF3	55.26	21.55	3.60	12.72	2.22	0.87	0.05	1.41	0.77	0.01	0.15	0.16	**1.01**
BF7	46.54	20.93	4.49	17.63	4.14	0.88	1.22	1.11	0.67	0.12	0.14	0.25	1.98
BF8	55.74	28.60	3.83	12.00	2.52	0.23	0.04	1.25	0.62	0.00	0.04	0.15	**0.90**
F1	48.76	23.86	7.39	12.53	2.97	0.48	0.86	2.05	0.78	0.09	0.29	0.17	2.27
F2	50.40	25.31	3.89	17.09	3.69	0.54	1.04	1.37	0.70	0.05	0.32	0.24	1.98
F3	48.81	23.51	6.65	9.30	1.95	0.28	1.75	1.93	1.46	0.14	**1.10**	0.12	3.07
F4	45.34	22.24	4.00	14.61	3.59	0.70	1.48	0.65	1.09	**0.37**	0.76	0.20	1.93
F5	53.18	19.64	11.21	2.06	0.19	0.89	0.97	4.43	0.71	0.03	**0.96**	0.03	4.01
F6	51.87	30.47	12.32	2.50	0.32	0.67	1.61	4.13	0.66	0.05	0.16	0.03	4.43
F9	48.27	26.22	5.86	12.59	3.32	0.49	1.33	1.77	1.12	0.18	0.06	0.17	2.55
F20	54.04	27.51	8.24	1.37	0.41	0.01	0.07	4.51	1.19	**0.60**	0.19	0.02	3.17
F22	52.31	30.48	19.66	1.74	0.44	0.05	0.47	3.61	0.62	0.02	0.01	0.02	2.95
F23	58.36	20.16	8.26	1.11	0.20	0.07	0.57	4.26	0.69	0.04	0.01	0.01	3.49
F24	49.92	19.82	**22.84**	0.93	0.23	0.15	0.36	3.30	0.67	0.01	0.02	0.01	2.62
F25	54.76	22.96	16.38	1.44	0.60	0.39	0.24	4.80	0.35	0.07	0.02	0.02	3.53
F26	55.54	23.06	7.63	1.84	0.77	0.07	0.10	4.54	0.76	0.10	0.03	0.02	3.21
F27	52.88	23.72	12.25	5.26	0.39	0.61	0.40	3.36	0.47	0.12	0.39	0.07	2.70

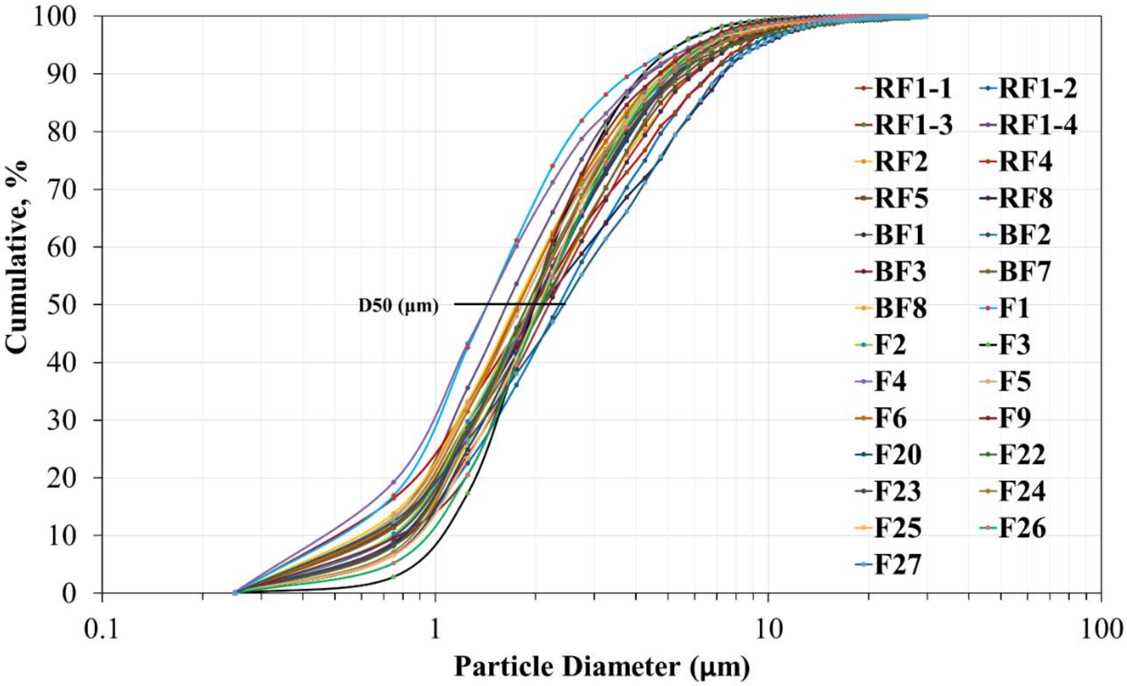

Figure A-1 Cumulative Particle Size Distribution

Table A-4: D50 values from Cumulative Particle Size Distribution

Fly Ash	D50 (μm)
RF1-1	2.20
RF1-2	2.60
RF1-3	2.02
RF1-4	1.87
RF2	2.37
RF4	2.23
RF5	2.32
RF8	2.36
BF1	2.25
BF2	2.22
BF3	2.44
BF7	2.35
BF8	2.00

Fly Ash	D50 (μm)
F1	1.68
F2	2.15
F3	2.24
F4	1.68
F5	2.06
F6	2.03
F9	2.20
F20	2.28
F22	2.13
F23	2.22
F24	2.17
F25	2.29
F26	2.30
F27	2.67

VITA

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