# Assessing Ash Quality and Performance

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## Introduction

Fly ash for use in concrete is typically specified according to ASTM C618 *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete* [ASTM C618, 2015] and characterized/evaluated using test methods for sampling and testing provided in ASTM C311 *Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete* [ASTM C311, 2013]. Both documents are overseen by the ASTM C09.24 Subcommittee on Supplementary Cementitious Materials. Internationally, other material specifications and tests are used with the purpose of characterizing the same properties discussed in this chapter. References to specific ASTM standards are provided for context.

Within ASTM C618, usable fly ash materials are identified as either Class F or Class C. ASTM C618 also specifies a Class N, which describes natural pozzolan materials. Class F fly ash is historically obtained from burning anthracite or bituminous coal and Class C from burning lignite or subbituminous coal. However, modern combustion processes utilize coal blends to optimize burner operation with respect to efficiency, cost, and air quality and tracing an ash class to a specific coal type is less meaningful. The ASTM C618 specification lists both chemical and physical requirements that the fly ash must meet or exceed. Chemical requirements include a minimum value for the "sum of the oxides" (SUM), which is the sum of the $SiO_2$, $Al_2O_3$, and $Fe_2O_3$ contents, and maximum values for the $SO_3$ content, moisture content, and loss on ignition (LOI) of the fly ash. The latter three values are the same for Class F and Class C fly ashes, making SUM the primary distinction between the two classes. The sum of oxides has a minimum value of 70 % for Class F ash and 50 % for Class C fly ashes. This separation means the CaO content of Class C fly ashes usually exceeds that found in Class F fly ashes, but once again there are exceptions to this comparison. Specified physical requirements include fineness (i.e., maximum amount retained on a 45 µm sieve), strength activity index at 7 d and 28 d, water requirement relative to an ordinary portland cement control mortar, soundness as evaluated using

autoclave expansion, and limits on the maximum variations in measured density and fineness. Finally, the user of the specification may elect to include optional physical requirements that test mixtures with fly ash and portland cement and consider drying shrinkage, variability in air content, control of alkali-silica reaction (ASR), and sulfate resistance. In most of these optional tests, performance is measured relative to a control mixture prepared using cement-only as the cementitious component.

ASTM C618 specifies the minimum requirements for a fly ash, while ASTM C311 provides the procedures for performing the test methods used to evaluate fly ash performance with respect to these requirements. Procedures and calculations are provided for determining moisture, LOI, available alkali, and ammonia content, the oxide composition, the physical properties of density and fineness, and specific performance tests to assess drying shrinkage, soundness, air-entrainment in mortar, strength activity index, water requirement, and effectiveness at mitigating alkali-silica reaction and sulfate attack. Overall, the ASTM C618 and C311 standards have provided an adequate, if not necessarily robust, quality control system for fly ash, but provide little insight into the projected performance of a specific fly ash in a specific concrete mixture. This shortcoming has been recognized for many years and efforts continue to improve the existing standards and to develop more discerning and pertinent test procedures. Some concrete examples of recent efforts in this area will be provided in the loss on ignition (i.e., carbon content) and air entrainment issues and test methods that will be discussed next. The strength activity index will be considered in more detail at the end of this chapter, where alternates will also be discussed.

## Carbon Content and Loss on Ignition

### *Carbon in Fly Ash*

An important characteristic of fly ash is the presence of various forms of carbon intermixed with the fly ash. The carbon resulting from combustion is present in different forms broadly classified as char particles that are typically 5 μm to 50 μm, or soot and carbon black particles that are typically a micrometer or less in diameter. More recently, an additional external source of carbon has been introduced into fly ash. That is, in many power plants, powdered activated carbon (PAC) is commonly added to the combustor exhaust stream to adsorb mercury and other constituents whose emissions are limited by air quality standards.

The combustion of coal is a two-step process where initially gases and highly volatile components are driven out of the coal structure leaving behind a carbon char that burns as a second step. These chars either burn in the combustor, or are carried out of the furnace as un-burnt carbon intermixed in the fly ash (Bailey 1990). These char particles exhibit a wide range of morphologies depending on the coal maceral from which they originated. The texture, porosity and specific surface area of these chars vary with changes in particle morphology. The other class of carbon, soot and carbon black, condenses out of the exhaust stream of the combustor as the stream cools in the exhaust path. It is more difficult to characterize the morphology of these sub-micron soot particles.

The general problem with carbon in fly ash is two-fold. The lesser problem is one of adding color, which affects architectural applications but is generally not a concern for most structures. The far more serious problem is that carbon can readily adsorb organic chemicals such as air entraining admixtures (AEAs) on to its surface. To develop this idea, a brief review of the air entrainment mechanism is provided in the following section.

*Air Entrainment in Concrete*

Air bubbles are purposefully entrained in concrete to provide resistance to cyclic freeze-thaw (F-T) exposure. A detailed discussion of air entrainment and F-T protection is beyond the scope of this discussion and the reader is directed to the numerous textbooks and publications that address the issue. Suffice it to say that in order to provide protection from F-T exposure, a system of properly spaced and sized air bubbles is required in the hardened cement paste matrix. This is accomplished through the use of air entraining admixtures (AEAs). An AEA is an organic compound made from natural sources such as wood resins or tall oil, or they are synthetic chemicals. The AEA has an anionic, hydrophilic “tail” and a non-ionic, hydrophobic “head” as shown schematically in Figure 1a. As shown schematically in Figure 1b, the hydrophilic, anionic polar groups (i.e. head) sorb strongly to the ionic cement particles while the hydrophobic, non-polar portion of the surfactants (i.e. tail) orient towards the solution and stabilize, or entrain, air bubbles and prevent the smaller bubbles from coalescing into larger ones (Bruere 1955).

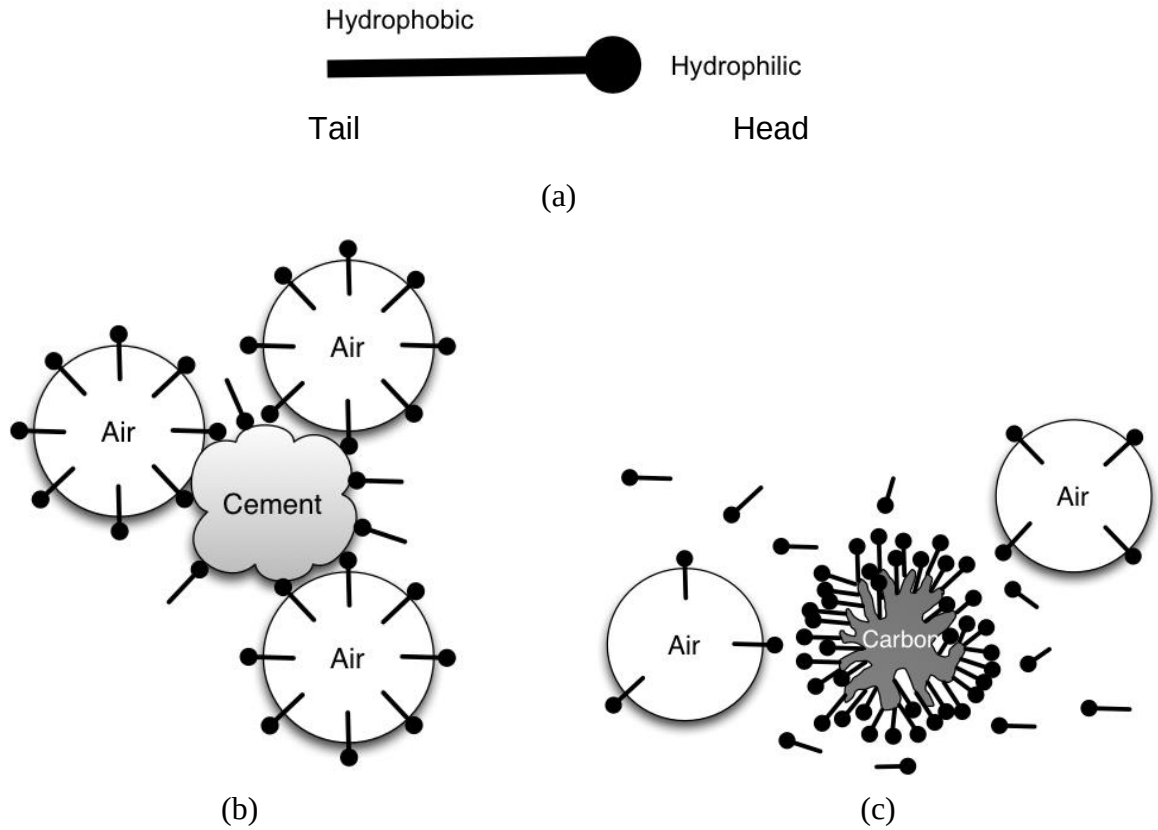



Figure 1. Schematic representation of a) an air entraining admixture (AEA) molecule, b) AEA stabilizing air in a concrete system, c) carbon preferentially adsorbing AEA and rendering the chemical ineffective at entraining air.

*Effect of Carbon on Air Entrainment*

When adsorbent carbon is present, it preferentially adsorbs the AEA, diminishing the residual AEA concentration in the mixture water to a point where effective air bubble stabilization does not occur. This is shown schematically in Figure 1c. To offset this adsorption, a higher quantity of AEA must be added to a concrete mixture containing fly ash to ensure the desired air-void structure formation. However, with variation in carbon content in fly ash, it is difficult to specify the proper amount of air-entrainment required and often the AEA dosage is either inadequate or excessive.

The adsorption potential of carbon is a function of the porosity, surface texture, surface chemistry, and specific surface area of the carbon particles. These properties all vary as the combustion conditions vary. Powdered activated carbon is, by design, highly adsorbent and potentially presents a significant problem when included in a concrete mixture.

*Loss on Ignition Test*

Under current specifications, the abundance of carbon in fly ash is determined by means of a loss on ignition (LOI) test and there are specified maximum limits for LOI in fly ash (i.e., 6 % LOI in ASTM C618). The loss on ignition procedure is provided in ASTM C311, which in turn refers to ASTM C114 *Standard Test Methods for Chemical Analysis of Hydraulic Cement*. In the LOI test, a dry sample of fly ash is ignited at 750 °C until a constant mass is achieved; the percentage loss of mass is calculated and reported as the LOI.

The LOI test is a reasonable predictor of total carbon content when the only volatile phases in the fly ash are unburned, residual carbon. However, materials combusted along with the coal or stack additives can affect the results (Schlorholtz 2006). Other tests for carbon are sometimes used instead of LOI because in addition to being more accurate for total carbon content, they are typically much faster. These include dedicated carbon determination units that work on a LOI principal but selectively analyze only volatilized carbon.

Although the LOI test effectively limits the total carbon in fly ash, it does so without consideration for the type of carbon or its adsorption capacity. Not all carbon forms will exhibit the same adsorption behavior and identifying the carbon form, or more to the point identifying the adsorption capacity, is far more useful than simply specifying the total carbon through limiting the LOI.

## Adsorption Based Tests for Characterizing Carbon in Fly Ash

*Foam Index Test*

The foam index test is used as a quick screening test to estimate the effect of a particular fly ash on the air entrainment of concrete. The test requires observing the stability of the foam produced when the fly ash, or fly ash and cement, and diluted AEA are combined with water and agitated. The test provides a quick indication of possible changes in the amount of AEA required when using the same materials combination in concrete. The foam index test procedure is currently not standardized and numerous variations of the test are reported in the literature. A review of the various published procedures was provided by Harris et al. (2008).

In general, the procedure involves adding diluted AEA solution to the test slurry, agitating the mixture after the addition of the AEA, then visually monitoring the slurry surface for formation of a "stable foam". If the foam is determined to be not stable after a "cycle" (i.e., addition of the AEA solution, agitation, and observation), another cycle is performed. The AEA solution is added drop-wise, usually one drop per cycle, using either a laboratory syringe or a micro-pipet capable of dispensing prescribed-volume, individual drops. This incremental process is continued until a stable foam is observed, which is defined as one that covers the entire surface of the slurry in the test container and persists for a prescribed observation time without dissipating (e.g., 15 s to 60 s, depending on the method used).

How the foam index is expressed varies among users. Many express the foam index simply as the number of AEA solution drops required to achieve a stable foam. Using this approach, a constant AEA solution concentration is used and as will be discussed, a single solution concentration is not optimum for a range of ash types. However, for a consistent fly ash, cement, and AEA materials combination, the number of drops is a measure that can identify variation in that combination. In some cases, the total amount of undiluted AEA, known as the absolute volume of AEA, is determined by a variety of approaches such as weighing the syringe before and after the test and calculating the volume of AEA based on the mass consumed, the solution concentration, and the AEA specific gravity. A more common approach is to simply calculate the absolute volume of AEA as shown in equation 1

$$Absolute\ Volume\ AEA = N_D \times V_D \times C_S \tag{1}$$

Absolute Volume AEA = volume of undiluted AEA added, mL

$N_D$ = Number of drops

$V_D$ = Volume of each drop, mL (typically 0.02 mL to 0.05 mL, determined experimentally)

$C_S$ = Concentration of the AEA solution, mL undiluted AEA per mL solution

Another useful form of the foam index is the relative foam index, which is the ratio of the foam index using cement and fly ash to that of a cement-only test sample, expressed as a percentage. When testing combined fly ash and cement samples, the typical ratio of cement to fly ash is 4:1, although a range of replacement levels are reported, depending on the specific method used.

The foam index test, because of the short contact time and constantly changing solution concentration, does not determine the AEA adsorption at equilibrium and therefore, using the test to predict absolute changes in AEA dosage requires considerable experience with the specific materials being tested. The foam index test is an empirical test and provides an estimate of the instantaneous adsorption capacity of a fly ash. A variation in performing any aspect of the procedure may cause variation in the results. Also, the test is subjective; determination of a "stable foam" varies by operator, as does the agitation energy. However, it is still a useful tool, particularly for simple measurements in the field or ready-mix operation.

Changes to the foam index test have been suggested to improve reproducibility and precision. One suggested change is to select an optimum AEA solution concentration for the fly ash being tested (Sutter et al. 2013). In terms of proportions for an adsorption test, the optimum balance of adsorbent (i.e., fly ash) and adsorbate (i.e., AEA solution) occurs when the lowest possible AEA solution concentration can be used to achieve a stable foam layer in the prescribed time. The best accuracy and reproducibility, and lowest degree of subjectivity, is achieved when an incremental addition represents a small change in the total AEA added. That is, if after some number of cycles the technician performing the test thinks the foam is stable, but he or she is not quite sure, the least subjective test is one where another increment of AEA can be added and another cycle performed to verify that a stable foam has been achieved, and the addition of that extra increment is only a small percentage of the total AEA added. Conversely, if the AEA solution is too dilute, the time required to achieve the end of the test could literally be hours, therefore making the test impractical. High solution strengths increase the error associated with the incremental AEA addition, but reduce total analysis time. Increased quantities of fly ash in the slurry will require a commensurate increase in AEA addition, leading to the problems previously described.

Research on optimal conditions for the foam index test indicate that 12 min to 18 min is the optimal test duration in terms of practicality and AEA addition rate (Sutter et al. 2013). To achieve a foam index result in this time period, the recommended solution strengths are 2 %, 6 %, 10 %, and 15 % air entraining admixture by volume (Sutter et al. 2013), although any concentration can be used. It is necessary to experiment with the different solutions to establish

the correct choice, by discarding test results that take less than 12 min or more than 18 min, and using a lower or higher solution concentration, respectively (Sutter et al. 2013).

Likewise, the agitation time and energy is important as longer agitation times lengthen the test, while shorter agitation times may lead to insufficient initial contact between the AEA and the fly ash. Use of a mechanical agitator has been proposed to reduce the subjectivity of the shaking intensity and length (Sutter et al. 2013).

The foam index test is an assessment of instantaneous adsorption, not the adsorption that occurs at equilibrium. Additionally, the foam index test is not quantitative; it does not directly provide the amount of AEA adsorbed. Therefore, direct measurement of the adsorption isotherm is often more useful for predicting AEA adsorption and performance.

*Adsorption Isotherms*

The fundamental tool for understanding adsorption capacity of organic chemicals onto carbon is the adsorption isotherm. An adsorption isotherm is used to describe the equilibrium between the solid phase and liquid phase concentration of an adsorbate. Determining the adsorption isotherm is a relatively straightforward test than can be performed with conventional laboratory equipment (e.g., flasks, beakers, stir plates). To measure an adsorption isotherm, a mass of adsorbent is mixed with a solution of adsorbate, with initial concentration $C_0$, for a prescribed period of time sufficient for adsorption to occur and reach equilibrium. After the prescribed time, the reduction in solution concentration of adsorbate is determined. This process is repeated for a number of different quantities of adsorbent. Alternatively, the quantity of adsorbent can remain constant with each test and the solution concentration can be varied. The results of this series of tests are plotted on a log-log scale and the data is fit with a power line fit; the slope and intercept of this fit determine the constants for the Freundlich equation shown in equation 2. The driving force for adsorption is the concentration gradient between the solution and the adsorbate on the adsorbent surface and therefore, as shown in equation 2, the adsorption capacity ($q$) is a function of the solution concentration. This is one reason why the foam index test does not achieve a true equilibrium; the solution concentration is constantly being altered by the addition of more AEA solution.

$$q = K \times C^{1/n} \qquad (2)$$

where:

$q$ = mass of adsorbate adsorbed per unit mass of adsorbent, mg/g

$K$= Freundlich isotherm capacity parameter, (mg/g) $(L/mg)^{1/n}$

$C$= Solution concentration, mg/L

$1/n$ = Freundlich isotherm intensity parameter, dimensionless

An example isotherm is shown in Figure 2 for an iodine solution adsorbed by fly ash.

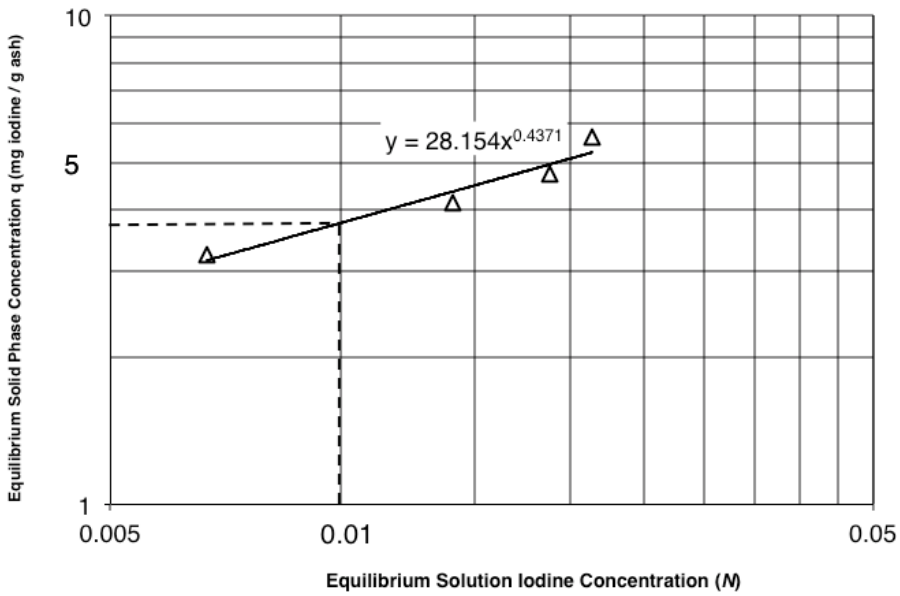



Figure 2. Example of iodine adsorption isotherm for coal fly ash.

*Determination of Fly Ash Iodine Number*

The fly ash iodine number is based on tests developed in the water treatment industry for measuring the adsorption capacity of activated carbon. ASTM D4607 *Standard Test Method for Determination of Iodine Number of Activated Carbon* is designed to characterize quantitatively the adsorption capacity of activated carbons that have a high adsorption capacity. The test serves as a good indication of the microporosity of carbon because an iodine molecule is very small (Sontheimer 1988). The results of an ASTM D4607 test are shown in Figure 2. A standard iodine solution ($C_0$) is contacted with three different masses of activated carbon. The carbon-treated

solutions are filtered to separate the carbon from the solution and the iodine remaining in the filtrate is measured by titration. The amount of iodine removed per gram of fly ash is determined for each mass of fly ash and plotted versus the residual solution concentration on a log-log scale. From the resulting plot, the amount of iodine adsorbed (mg iodine/g fly ash) at a residual iodine solution concentration of 0.01 N is reported as the iodine number of the fly ash. Because of using a standard solution (i.e., iodine), the iodine number provides a relative measure of adsorption capacity that can be used to compare the different adsorption capacities of fly ash materials.

For use with fly ash, the ASTM D4607 test was modified to use a lower initial solution concentration ($C_0$) than recommended for activated carbon (i.e., 0.025 N as compared to 0.1 N) and a lower residual concentration for determining the iodine number (i.e., 0.01 N as compared to 0.02 N). The contact time was also increased (5 min as compared to 30 s) to account for the slower rate of reaction with a more dilute initial concentration.

Treatment of fly ash is required prior to performing the fly ash iodine number test. The purpose of the treatment is to acidify the fly ash and remove any sulfur from the material. Iodine converts to iodide in a basic environment. Therefore, acidifying the fly ash is necessary to ensure that all observed reduction in iodine concentration results from iodine adsorption rather than conversion to iodide. For the developed method, the ash was treated with one cycle of boiling in 5 % wt. HCl.

Although the iodine number test based on a modified version of ASTM D4607 demonstrates well the basic principal of iodine adsorption, the test itself is more rigorous than required for measuring fly ash adsorption. The four-point isotherm approach is useful for accurately determining the adsorption capacity of highly activated carbon. More recent research has been performed to adopt a single-point isotherm method for use with fly ash, based on ASTM D1510 *Standard Test Method for Carbon Black—Iodine Adsorption Number*. The test uses the same ash pretreatment as described for the modified ASTM D4607 test. However, the ash is contacted with a 0.025 N iodine solution and the amount adsorbed at that concentration is taken as the iodine number for the ash (Sutter et al. 2014).

*Determination of Direct Adsorption Isotherm*

An adsorption isotherm for a specific materials combination provides the equilibrium relationship between the solid and liquid phase concentrations of the adsorbate. For the case of

fly ash and AEA, the solid phase concentration represents the mass of AEA sorbed per mass of ash, while the liquid phase concentration represents the residual adsorbate concentration of the solution. To achieve a specific solution concentration, extra AEA must be added to satisfy the adsorption capacity of the fly ash. An adsorption isotherm is unique for the combination of materials; with a given adsorbent, the amount of adsorbate sorbed on the solid is dependent on the properties of the adsorbent as well as the solid. Therefore, to fully characterize the adsorption properties of a system of materials, the isotherm must be established using those specific materials. The iodine number test will characterize the adsorption properties of the solid phase (i.e., fly ash) with iodine but the actual adsorption of AEA will be affected by the AEA used as well as the presence of the cement.

A standard test for determining the adsorption isotherm for activated carbon is ASTM D3860 *Standard Practice for Determination of Adsorptive Capacity of Activated Carbon by Aqueous Phase Isotherm Technique*. This procedure determines the adsorptive capacity of activated carbon for a specific adsorbate species by contacting an aqueous solution of the adsorbate with activated carbon, determining the amount of the constituents removed from solution, and calculating the adsorptive capacity from a Freundlich isotherm plot. This standard procedure cannot be applied directly to the case of AEA adsorption by fly ash because chemisorption by the cement and physical adsorption by the fly ash are taking place at the same time. Therefore, to be applied to fly ash, modifications to the existing standard test are required.

The first modification is to use a mixture of cement and fly ash as the adsorbent. The cement reduces the solution concentration of AEA as shown in Figure 3. When the cement comes in contact with the AEA solution, a portion of the AEA chemisorbs onto the cement almost instantaneously. The amount of chemisorption is independent of the amount of cement above a certain quantity of cement (i.e., 20 g cement) and is independent of the cement type (Sutter et al. 2013). Because the physical adsorption by fly ash is dependent upon the solution concentration, it is required to account for the impact of the cement on the initial solution concentration. Beyond the chemisorption demonstrated, cement shows no appreciable physical adsorption (Sutter et al. 2013).

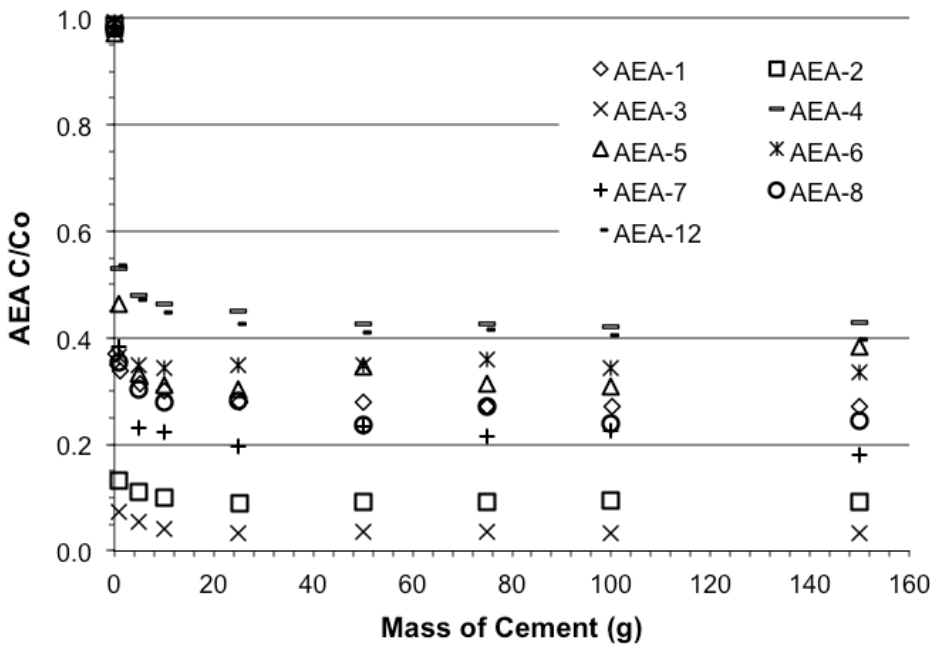



Figure 3. The result of chemisorption of AEA by cement. The AEA concentration in solution after contact is shown as the ratio $C/C_0$ where $C$ is the residual solution concentration after contact and $C_0$ is the initial solution concentration. The amount of chemisorption is dependent on the AEA type and independent of the cement type.

The second modification is to establish how the solution concentration of AEA is determined. ASTM D3860 does not specify an analytical method and generally, the adsorbate is a simple organic chemical and the solution concentration is determined by standard analytical methods. Measuring AEA concentration is more difficult since AEAs are a mixture of complex organics. The chemical oxygen demand (COD) test is often used in water treatment to measure the dissolved organics in water. The test uses extreme oxidation conditions through a strong oxidizing agent (i.e., potassium dichromate $K_2Cr_2O_7$), strong acid (i.e., sulfuric acid $H_2SO_4$), and high temperature (i.e., 150 $^{\circ}$C). Nearly all organic compounds are oxidized to $CO_2$ and measured as milligrams of oxygen consumed per liter of water. Commercially available kits are available to measure COD and this approach provides a reliable and accurate solution for determining AEA concentration in solution (Sutter et al. 2013).

To measure the direct adsorption isotherm, at least three samples of fly ash and cement (40 g fly ash/20 g cement for each test) are contacted with three different concentration AEA solutions for 60 min, the residual AEA concentration is measured, and the adsorbed AEA concentration is calculated. The results are plotted in the same manner as those shown in Figure

2 and the Freundlich isotherm parameters are determined. To use the isotherm, the desired solution concentration ($C_s$) is calculated based on the AEA dosage and the volume of mixing water. The adsorption capacity (q) is calculated or read from the graph and is provided in units of mL/g fly ash. The sum of $C_i$ and q is the estimated dosage of AEA required to achieve the desired solution concentration (Sutter et al. 2013).

*Methylene Blue*

Other sorption-based methods have been investigated. In research by McCarthy et. al. (2012), the adsorption capacity of fly ash was determined by a colorimetric method. A solution of Acid Blue 80 (AB80) was contacted with fly ash, filtered and the filtrate analyzed with a spectrophotometer to measure the concentration of residual AB80. The blue dye was selected as the molecular size is similar to that of AEAs. Good correlation was found between measured adsorption capacity and increases in AEA dosage to produce a target air content in lab-scale mortar and concrete mixtures having the tested fly ashes partially replacing cement. The adsorption capacity results obtained also correlated well with $N_2$ adsorption surface area measurements (BET).

Subsequent work with blue dye was reported by Islam et. al. (2012) investigating AB80 and methylene blue adsorbates. The methylene blue test was derived from a British test method used to evaluate fines in sand and is non-instrumental, relying on a subjective measure of color intensity. Both methods were found to correlate well with $N_2$ surface area measurements and a relationship was found with increased AEA demand when the fly ashes studied were employed in laboratory concrete mixtures. The referenced British test method is similar to ASTM C1777 *Standard Test Method for Rapid Determination of the Methylene Blue Value for Fine Aggregate or Mineral Filler Using a Colorimeter* except the latter employs a spectrophotometer for measuring the concentration of methylene blue. Both papers discussing blue dye adsorbates reported better correlation between adsorption capacity and measured surface area than between adsorption capacity and LOI.

**Particle Size Measurement**

The particle size distribution of fly ash is specified as fineness in ASTM C618. The test method used to measure fineness is ASTM C430 *Standard Test Method for Fineness of*

*Hydraulic Cement by the 45-µm (No. 325) Sieve*. In this test method, the fly ash sample is wet sieved on a 45-µm sieve. To meet ASTM C618, a fly ash must have a maximum of 34 % retained on the 45-µm sieve. The amount of material retained on the 45-µm sieve provides a general indicator of the total amount of fine material present, but this fraction is not indicative of the total material that contributes to the hydration reaction in concrete.

Fineness of fly ash (i.e., particle size distribution) affects the water demand for a given level of concrete workability, as well as the reactivity of the fly ash in concrete mixtures. It is known that specific surface area is related to particle size. Fly ash particles have a greater distribution of smaller particles as compared to portland cement. Because of this, fly ash has a greater specific surface area when compared to cement and replacement of cement by fly ash may result in increased water demand to wet the additional surface area. Reactivity is also affected by particle size. It is well known that a finely divided material will react with a solution faster than a coarser material. Therefore, control of particle size will also impact properties such as strength, rate of strength gain, and ASR mitigation, all being dependent on the fly ash particle reacting with the mixing water of the concrete.

In addition to a sieve analysis, the fineness of fly ash can be determined using an air permeability method, which provides a measure of specific surface area. ASTM C618 does not currently have a specific surface area requirement, but this requirement had been included in older versions of the standard along with the determination of fineness. The specific surface area can be estimated by using ASTM C204 *Standard Test Methods for Fineness for Hydraulic Cement by Air-Permeability Apparatus*, commonly referred to as the Blaine fineness. A Blaine fineness apparatus is used to draw air through a packed powder sample and the specific surface area is calculated knowing the density and the air flow versus time. This method can be used to provide a rapid indication of the average specific surface, which is affected by the particle size distribution. However, it does not provide a direct measure of particle size distribution.

Direct measurement of the particle size distribution for a fly ash is possible using sedimentation, or particle size analyzers based on laser diffraction or X-ray transmission (i.e. X-ray Sedigraph). Sedimentation and particle size analyzers require the material to be analyzed while settling in water or another fluid of known viscosity and density. For Class C ash, this can present special problems due to its cementitious properties. Class C ash will begin to react

hydraulically during the test. Using isopropanol as the carrier fluid can avoid this problem; in fact, isopropanol is the carrier fluid of choice for laser-based PSD analysis of cement-based materials. Laser-based particle size analyzers can also analyze material in air and these can be directly applied. Some sedimentation-based techniques require an extended duration to perform the analysis, whereas rapid tests that can determine the quality and usability of fly ash in minutes are desired. The wide range in particle composition and the presence of porosity in the fly ash (e.g., cenospheres) affects the settling time and skews the particle size distribution. Particle size determination is still an area that needs more research to establish an effective method of determination.

**Analysis for Incompatibilities**

Proper design of a concrete mixture containing fly ash requires that the cement, fly ash, and other powders and any chemical admixtures being combined together are compatible with one another. An improper combination of these materials can lead to mixtures that flash set or conversely, sit for hours without setting; the latter case being due to excessive retardation of the hydration reactions. As will be shown in the examples that follow, one powerful tool for examining materials' compatibility is isothermal calorimetry, as outlined in the ASTM C1679 *Standard Practice for Measuring Hydration Kinetics of Hydraulic Cementitious Mixtures Using Isothermal Calorimetry* [ASTM C1679, 2014]; a similar standard based on semi-adiabatic calorimetry has been recently published by ASTM as ASTM C1753 *Standard Practice for Evaluating Early Hydration of Hydraulic Cementitious Mixtures Using Thermal Measurements* [ASTM C1753, 2015].

*Sulfate Optimization*

Since many fly ashes provide a significant source of aluminate phases and/or their own source of (calcium) sulfates, sulfate optimization can be an issue in producing high-volume fly ash (HVFA) concretes that have desired constructability properties [Niemuth et al. 2012]. The properties affected by sulfate imbalance include setting time and early-age strength development. Portland cements are generally optimized with respect to sulfate content based on measured compressive strengths at a specific target age, such as 7 d or 28 d. This "sulfate optimization" is commonly performed assuming the material will be subsequently employed in a 100 % portland cement concrete mixture. The incorporation of relatively large quantities of fly ash into a

concrete can thus result in systems that are either under-sulfated, over-sulfated, or in fortuitous cases, still properly sulfated.

As examples, Figure 4 and Figure 5 show the influence of additional gypsum (calcium sulfate dihydrate) on the hydration reactions in two different blended cement/fly ash mixtures prepared using the same highly reactive, and retarding, Class C fly ash [Bentz 2010, Bentz et al. 2012b]. In Figure 4, an ASTM C150 Type II/V cement (2.5 % $SO_3$ content by mass) was used, while in Figure 5, the mixtures used an ASTM C150 Type I/II cement (3.27 % $SO_3$ content by mass). As can be seen in Figure 4, for the first cement blended with the fly ash on a 50:50 mass basis, the addition of supplemental gypsum had a pronounced positive effect on the hydration reactions, restoring the shape of the isothermal calorimetry curve to its expected form, but still not eliminating the excessive retardation produced by the use of Class C fly ash. While both the 1 % and 2 % addition levels of gypsum produce reasonable calorimetry curves, with distinct silicate and aluminate hydration peaks, 2 % was selected as the optimum value for subsequent mixtures, based on those mixtures providing a slightly higher cumulative heat release value at 24 h [Bentz 2010]. This higher heat release should correspond to a higher 1 d strength as well [Niemuth et al. 2011]. Conversely, as shown in Figure 5, when the same fly ash is used with a Type I/II cement of higher sulfate content, at a 40:60 fly ash:cement ratio (by volume), a 2 % addition of gypsum only results in a further unwanted retardation of the hydration reactions without significantly altering the shapes of the hydration peaks. Figure 5 also shows the calorimetry results for a paste prepared from just the Class C fly ash and water, indicating its high initial reactivity. The prepared paste generates heat in a noticeable manner, and flash sets in a matter of minutes, but doesn't develop any significant strength beyond that setting point. In both cases, the influences of additional gypsum on the hydration reactions can be observed by using small samples and standardized isothermal calorimetry experiments on paste specimens, as opposed to the more labor-intensive conventional employment of strength testing [Niemuth et al. 2011].

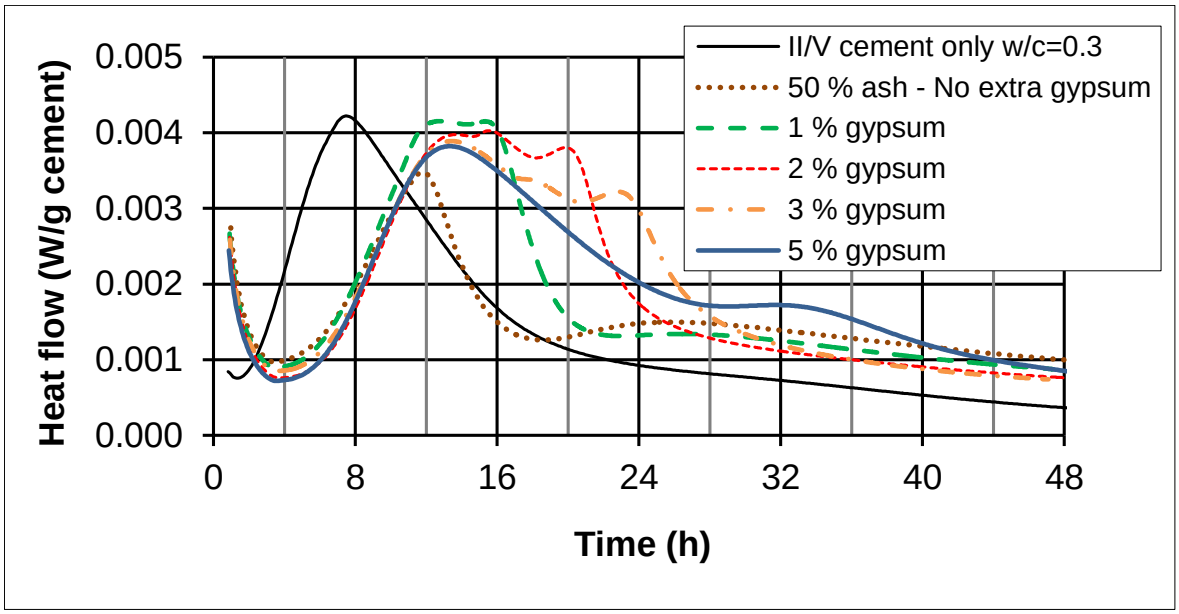



Figure 4. Isothermal calorimetry curves for Type II/V cement/Class C fly ash blends (*w/cm*=0.3) with various addition levels of gypsum [Bentz 2010].

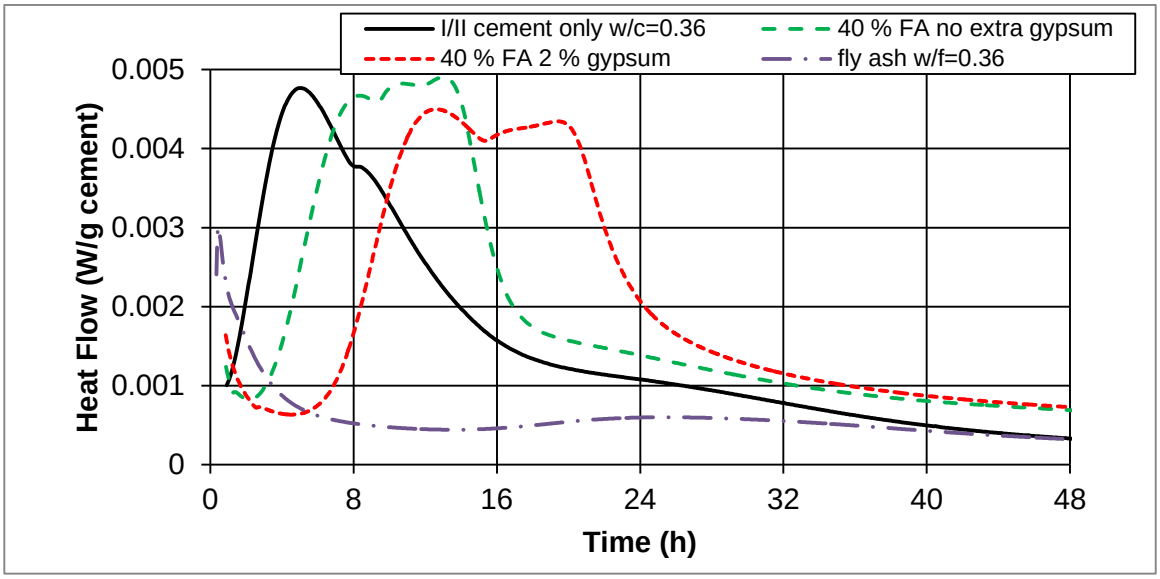



Figure 5. Isothermal calorimetry curves for Type I/II cement/Class C fly ash (FA) blends (*w*/cm=0.36) with and without additional gypsum [Bentz et al 2013a].

*High Range Water Reducer Incompatibilities*

While the previous section focused on incompatibilities due to sulfate imbalance in simple cement/fly ash mixtures without chemical admixtures, additional issues often arise when a high range water reducer (HRWR) is included in the concrete mixtures, along with other admixtures. As shown previously by Roberts and Taylor [Roberts and Taylor 2007], excessive retardation can also be produced by the improper selection of an HRWR; in their particular study, a lignin-carbohydrate water-reducing admixture was being used. A further example of this influence of HRWR on performance is provided in Figure 6, showing the difference in hydration response depending on the selection of HRWR employed in a Type II/V cement/Class F fly ash blended paste (50:50 on a mass basis). While both HRWRs are observed to increase retardation, the performance of HRWR-B would almost certainly be unacceptable from a practical concrete construction viewpoint. In addition to dramatically lengthening the duration of the so-called "induction period", HRWR-B has also modified the basic shape of the peak in the calorimetry curve. The Class F fly ash by itself produced no retardation so any delays in setting time for a blended paste without HRWR would be simply due to a dilution effect (e.g., the blended mixture containing only 50 % of the cement present in the control mixture).

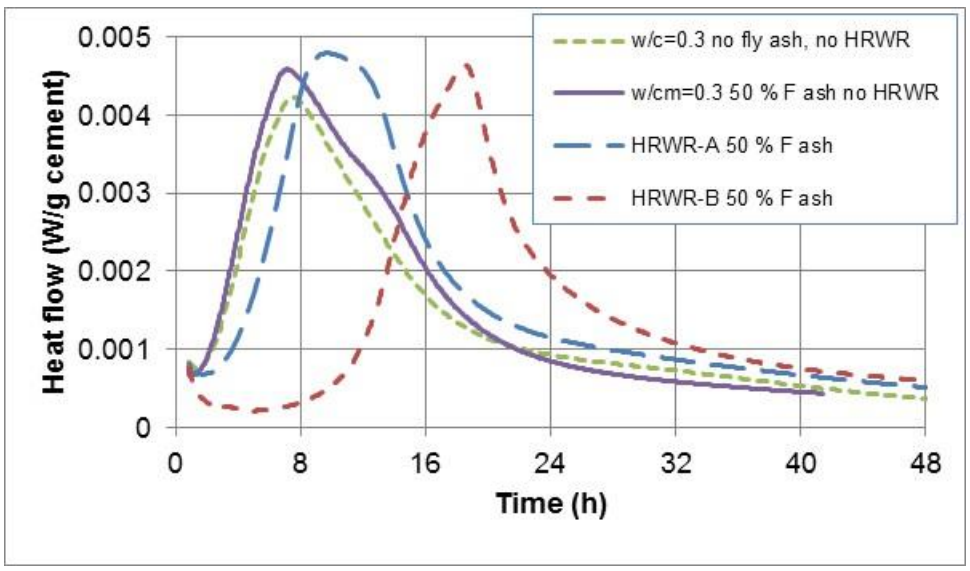



Figure 6. Isothermal calorimetry curves for a Type II/V cement/Class F fly ash blend with (two different) and without an HRWR [Bentz et al. 2013a].

The above examples clearly indicate that calorimetry can be a useful tool in developing HVFA mixtures as it provides diagnostic information about the hydration reactions occurring in

the paste. As complete and useful as this measurement technique is, it cannot readily predict all the important early-age performance issues of cement-fly ash mixtures such as false setting, early stiffening, etc. A more complete picture of how these mixtures will perform will often require additional test methods, such as modified versions of the ASTM C359 *Standard Test Method for Early Stiffening of Hydraulic Cement (Mortar Method*) [ASTM C359, 2013], a mini-slump test (currently under ASTM ballot), and rheometer tests based on the guidance provided in the ASTM C1749 *Standard Guide for Measurement of the Rheological Properties of Hydraulic Cementitious Paste Using a Rotational Rheometer* and elsewhere [ASTM C1749 2012, Roberts and Taylor 2007, Tanesi et al. 2012].

**Setting Time Delays and Their Mitigation**

As cited in the 2012 NRMCA survey [Obla et al. 2012], an issue commonly encountered with HVFA concrete mixtures is their delayed setting, with corresponding delays in finishing and other construction operations.[1] Due to a substantial research effort in recent years, several viable mixture proportioning options have been developed to mitigate excessive delays in setting for fly ash concrete mixtures.

As with conventional portland cement concretes, non-chloride accelerators can be effectively employed to reduce setting times of fly ash concrete mixtures [Cost 2011, Keith and Schindler 2012]. Especially for HVFA concretes, higher dosages may be required to attain target setting times, such as that of a comparable 100 % portland cement concrete mixture. The dosage will also depend on the characteristics of the fly ash, the replacement level, and the expected curing temperatures in a field or pre-cast environment. In general, lower curing temperatures and higher CaO contents in Class C fly ashes require higher dosages and, in some cases, acceptable setting behavior of a 50 % HVFA mixture may not be achievable via this approach [Cost 2011, Keith and Schindler 2012]. Non-chloride accelerators also can be fairly expensive, so economic considerations may sometimes dictate their use in a proposed cement/fly ash mixture.

[1] Low early-age strengths that also influence the timing of construction operations, such as formwork removal, will be considered as a separate issue in a subsequent section of this chapter.

As will be shown in the section to follow, one convenient method that has been already employed in practice for increasing the early-age strength of HVFA concrete mixtures, particularly during the winter construction season, is to switch to an ASTM C150 Type III (i.e., finer particle size) portland cement. In practice, such a change typically has a significantly greater impact on early-age strength development than on initial and final setting times. For example, one recent study [Bentz et al. 2010] indicated that switching to a Type III cement reduced the setting time delays by only about 1 h for two HVFA mortars, one with a Class C fly ash and the other with a Class F. The mixtures originally exhibited a 3 h to 4 h delay in setting relative to a corresponding 100 % portland cement control mortar. However, for these same two HVFA mortars, this switch to Type III cement increased their 1 d compressive strengths by an impressive 60 % on average. If Type III cement is being used to enhance early-age strengths, it is always a good idea to take into consideration its potential contributions to reducing setting time delays as the mixture proportions are being developed and optimized.

Different additions have been investigated for their ability to restore setting times of HVFA mixtures to values typical of those achieved for corresponding 100 % portland cement control mixtures. One study screened numerous candidate powders and identified calcium hydroxide and a rapid set cement as the two most promising candidates [Bentz 2010]. Table 1 provides representative setting times resulting from these additions in HVFA pastes prepared with either a Class C or a Class F fly ash [Bentz and Ferraris 2010]. For both fly ashes, a 5 % calcium hydroxide addition by mass restored the initial and final setting times to be nearly identical to those of the control cement paste (i.e., no fly ash). For the rapid set cement, while a 5 % addition was adequate for the Class F fly ash mixture, a 10 % addition was required for the Class C fly ash. One additional consideration when employing these powder additions is their subsequent influence on compressive strength. While the rapid set cement addition has produced mortars with similar or superior long-term (28 d or 91 d) strengths, as compared to those of the control 100 % portland cement mortar, a significant decrease in 28 d strength on the order of 15 % has been observed for HVFA mortars prepared with Class F fly ash and a 5 % calcium hydroxide addition [Bentz et al. 2010, Bentz 2010]. Still, calcium hydroxide additions have been recently used in practice to produce HVFA concretes (e.g., 70 % replacement of portland cement) that exhibited greater bonding to reinforcing steel when compared to 100 % portland

cement control concrete mixtures [Looney et al. 2012], although the measured compressive strengths of the HVFA mixtures were indeed about 20 % lower than that of the control concrete.

**Table 1. Setting Times for HVFA Paste Mixtures [Bentz and Ferraris 2010]**

| Paste mixture | Vicat initial set | Vicat final set |
|---|---|---|
| Type II/V cement<br>0.67 % HRWR | 5.1 h | 5.9 h |
| 50 % C ash, 2 % gypsum,<br>0.33 % HRWR | 8.2 h | 8.8 h |
| 50 % C ash, 2 % gypsum,<br>5 % CH, 0.33 % HRWR | 5.3 h | 6.0 h |
| 50 % C ash, 2 % gypsum,<br>10 % rapid set cement,<br>0.33 % HRWR | 3.1 h | 4.5 h |
| 50 % F ash,<br>0.87 % HRWR | 8.6 h | 10.2 h |
| 50 % F ash,<br>5 % CH, 0.87 % HRWR | 5.2 h | 5.9 h |
| 50 % F ash,<br>5 % rapid set cement,<br>0.87 % HRWR | 3.3 h | 4.5 h |

In the initial screening study described above, a relatively coarse limestone powder, with a modal particle diameter of about 27 µm, had basically no effect on the early-age hydration response as assessed using isothermal calorimetry [Bentz 2010]. However, subsequent investigations have indicated that limestone powder additions can indeed be quite effective for mitigating setting time delays and increasing early-age strengths in HVFA mixtures, when finer limestone particles are employed [Bentz et al. 2012b, Cost and Bohme 2012, Gurney et al. 2012]. Results when using a fine limestone with a median particle diameter on the order of 1 µm have been particularly promising [Gurney et al. 2012, Bentz et al. 2013b]. The fine limestone particles provide additional surface area for the precipitation and growth of calcium silicate hydrate gel and other products from the cement hydration and pozzolanic reactions. Additionally, the fine limestone particles can also participate in these reactions leading to the formation of stable carboaluminate phases, as opposed to conventional sulfoaluminates. The carboaluminate phases may be stiffer than the sulfoaluminate phases that would be formed in the absence of limestone, further contributing to strength enhancements [Moon et al. 2012].

A study employing four different modal diameters of limestone powders has indicated that the reduction in setting time for a fixed set of mixture proportions is directly proportional to the provided limestone surface area, as quantified by BET surface area measurements [Gurney et al. 2012]. Figure 7 illustrates this linear relation for mixtures with either a Class C or a Class F fly ash, where in some mixtures a portion of the fly ash has been replaced by limestone powder. In this study, titanium dioxide (anatase), with a surface area similar to that of one of the limestone powders, was also included as an inert material to confirm that both the size and chemical nature of the powder material are critical to its ability to accelerate early-age reactions in cement-based materials. While a nano-limestone provided the most significant reduction in setting times, the performance of a fine limestone powder with a 0.7 µm median particle diameter was also quite acceptable.

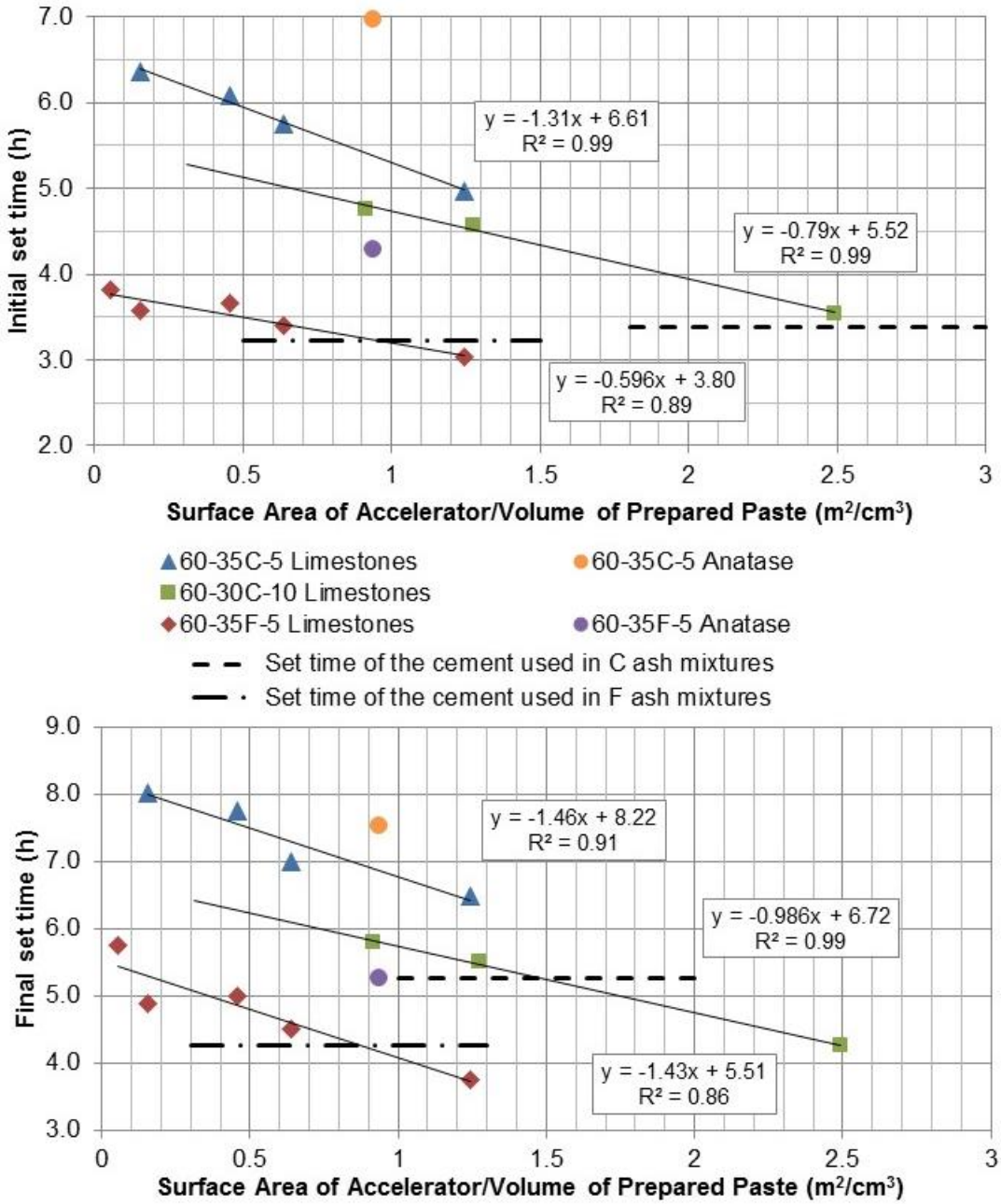


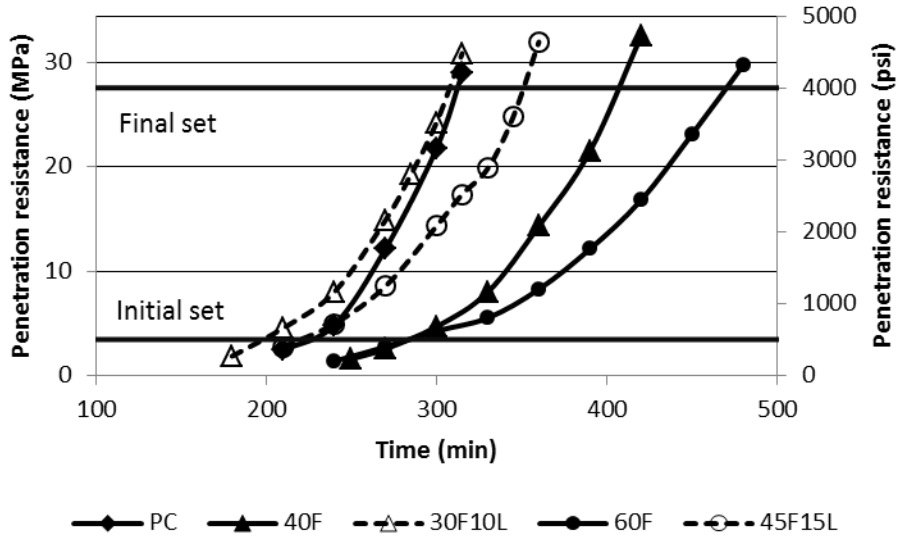

Figure 7. Correlation between initial (top) and final (bottom) setting times and surface areas of the accelerating powders (taken from [Gurney et al. 2012]).

As another example, the same 0.7 µm fine limestone has been subsequently employed in a series of HVFA concrete mixtures [Bentz et al. 2013b], whose mixture proportions are provided in Table 2. As indicated in Figure 8, the replacement of a portion of the fly ash with a fine limestone powder markedly reduces setting time delays in these more sustainable concretes. In addition to their improvement of setting times, the fine limestone powder additions also

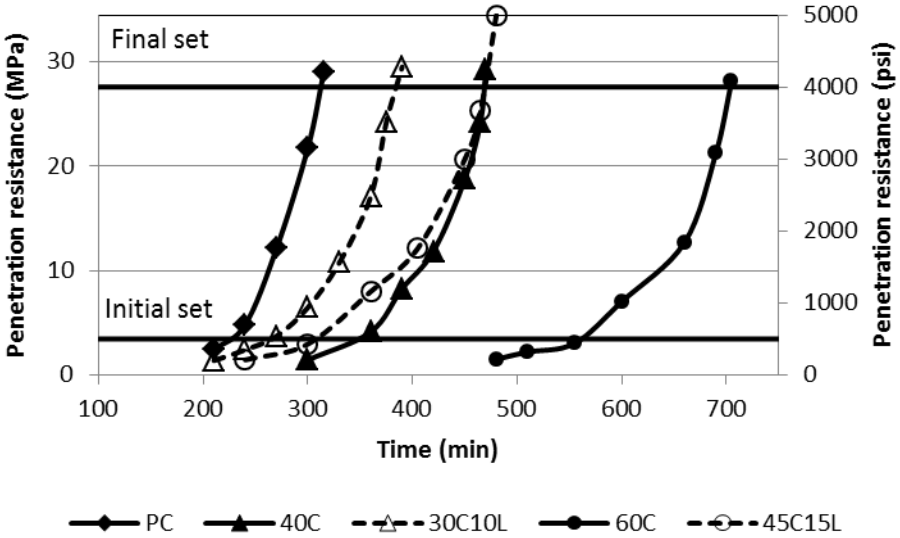
provided substantial benefits to mechanical (strength) and transport (electrical resistivity) properties [Bentz et al. 2013b].

**Table 2. Concrete Mixture Proportions for Study of HVFA with Fine Limestone [Bentz et al. 2013b]**

| Mix ID | Cementitious (kg/m$^3$) [(lb/yd$^3$)] | Type I/II cement (kg/m$^3$) [(lb/yd$^3$)] | Class F fly ash (kg/m$^3$) [(lb/yd$^3$)] | Class C fly ash (kg/m$^3$) [(lb/yd$^3$)] | Limestone 0.7 µm (kg/m$^3$) [(lb/yd$^3$)] | Coarse aggreg. (kg/m$^3$) [(lb/yd$^3$)] | Fine aggreg. (kg/m$^3$) [(lb/yd$^3$)] | Water content (kg/m$^3$) [(lb/yd$^3$)] | *w/cm* | HRWR (fl oz/ cwt) |
|---|---|---|---|---|---|---|---|---|---|---|
| PC | 335 [564] | 335 [564] | | | | 1040 [1750] | 858 [1444] | 134 [226] | 0.40 | 7.7 |
| 40F | 291 [491] | 201 [338] | 91 [153] | | | 1040 [1750] | 858 [1444] | 134 [226] | 0.46 | 3.8 |
| 30F10L | 297 [499] | 201 [338] | 68 [114] | | 28 [47] | 1040 [1750] | 858 [1444] | 134 [226] | 0.45 | 3.8 |
| 40C | 310 [522] | 201 [338] | | 109 [183] | | 1040 [1750] | 858 [1444] | 134 [226] | 0.43 | 3.0 |
| 30C10L | 311 [523] | 201 [338] | | 82 [138] | 28 [47] | 1040 [1750] | 858 [1444] | 134 [226] | 0.43 | 3.0 |
| 60F | 270 [454] | 134 [226] | 136 [229] | | | 1040 [1750] | 858 [1444] | 134 [226] | 0.50 | 3.8 |
| 45F15L | 278 [467] | 134 [226] | 102 [172] | | 41.6 [70] | 1040 [1750] | 858 [1444] | 134 [226] | 0.48 | 3.8 |
| 60C | 298 [501] | 134 [226] | | 163 [275] | | 1040 [1750] | 858 [1444] | 134 [226] | 0.45 | 3.0 |
| 45C15L | 298 [502] | 134 [226] | | 122 [206] | 41.6 [70] | 1040 [1750] | 858 [1444] | 134 [226] | 0.45 | 3.0 |




(a)




(b)

Figure 8. Setting development: a) portland cement mixture and mixtures containing Class F fly ash (45F15L indicates a mixture with 45 % Class F fly ash and 15 % limestone by volume); b) portland cement mixture and mixtures containing Class C fly ash (30C10L indicates a mixture with 30 % Class C fly ash and 10 % limestone by volume) (taken from [Tanesi et al. 2013]).

**Strength Development Issues and Their Mitigation**

The classical approach to increasing concrete strengths, at all ages, is to reduce the water-to-cement ratio (*w/c*) in a portland cement concrete, or equivalently the *w/cm* in a concrete containing fly ash. The advent of HRWRs, also known as superplasticizers in their early days, has permitted substantial reductions in *w/c* or *w/cm* without a significant loss of slump or

workability. Thus, decreasing *w/cm* of an HVFA mixture to obtain more acceptable early-age and 28 d strengths is common practice. For a 100 % portland cement target concrete, with a *w/c* in the range of 0.40 to 0.45, typical reductions in *w/c* when transitioning to a HVFA mixture are on the order of 0.05 to 0.10 [Bentz et al. 2010, Keith and Schindler 2012, Bentz et al. 2013b]. However, when the starting *w/cm* of the target concrete is on the order of 0.3 (e.g., for a high-performance concrete), the *w/cm* of a HVFA mixture that performs similarly may require little or no reduction. For some cement-fly ash combinations, the reduction in *w/cm* necessary to meet targeted 28 d strength levels will still be insufficient to provide adequate early-age strength for timely formwork removal and other construction operations. In these cases, further measures to specifically increase early-age strengths may be necessary.

One such measure that has been employed in practice in HVFA concretes is the use of an ASTM C150 Type III cement, which is more finely ground and may have an increased sulfate content by comparison with an ASTM C150 Type I/II/V cement. Some representative compressive strength results from a study on HVFA mortars are provided in Figure 9 [Bentz et al. 2010]. Using the strengths of the *w/c*=0.40, 100 % portland cement mortar as the target values, the original HVFA mixtures (50:50 by mass) prepared with a reduced *w/cm* of 0.30 fail to achieve the target strengths at 1 d. Only the Class C fly ash mixture reached the target strength at 7 d. However, switching to a Type III cement brought both fly ash mixtures to an acceptable strength level at 1 d and provided strengths that exceeded the target values at ages of 28 d and beyond. Figure 9 is also informative because the 365 d strength values of the HVFA mixtures are approaching the levels of a 100 % portland cement *w/c*=0.3 mortar that itself exhibits a minimal strength increase beyond 28 d. This illustrates the propensity of the longer term pozzolanic reactions to make a significant contribution to later age strength development in these HVFA systems, and supporting the transition from the 28 d testing usually employed for portland cement concretes to later ages (i.e., 56 d or 91 d) for compliance strength testing of HVFA mixtures.

In addition to mitigation of excessive setting time delays, replacement of a portion of the fly ash in an HVFA concrete mixture with a fine limestone powder will also have a beneficial influence on compressive strength values. Figure 10 provides measured compressive strengths for HVFA concretes with and without 1 µm limestone replacing a portion of the fly ash on a

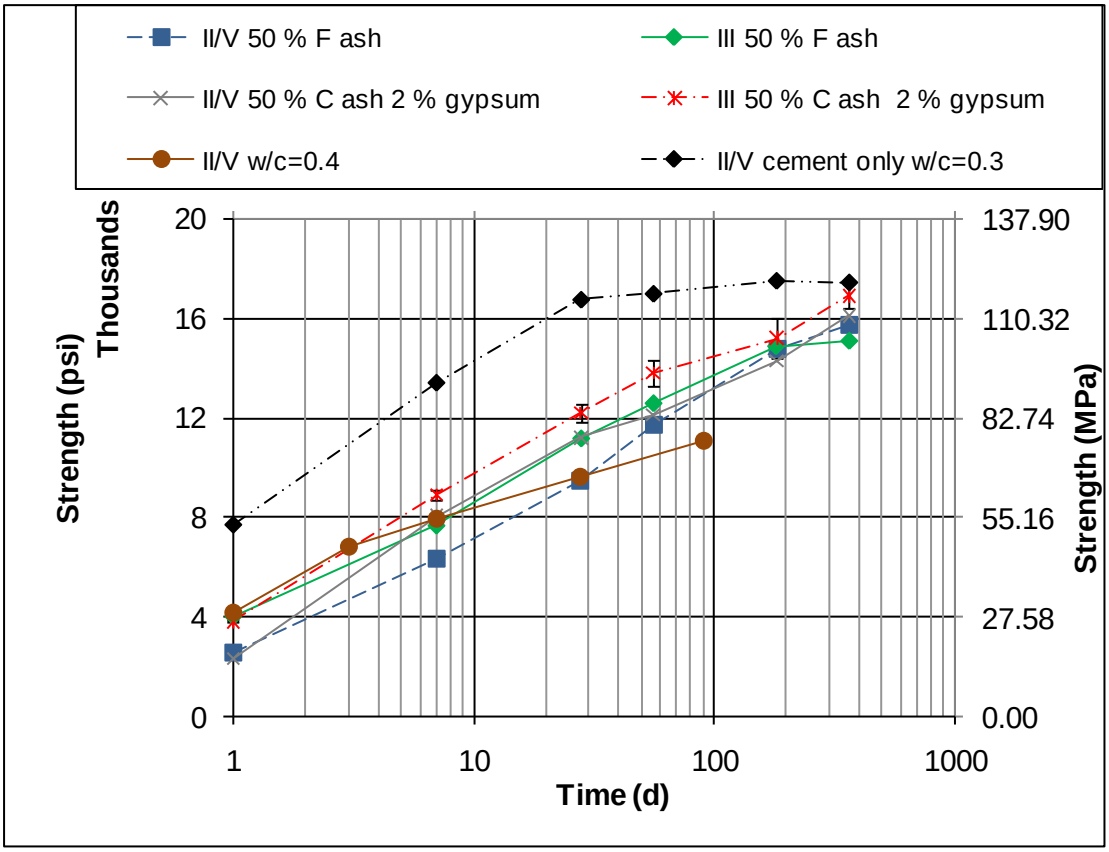



Figure 9 Measured mortar cube compressive strengths vs. age. For the mixtures with fly ash, *w/cm*=0.3 in every case. Error bars (± one standard deviation among three specimens) are provided for the III 50 % C ash 2 % gypsum data to provide an indication of variability (taken from [Bentz et al. 2010]).

volume for volume basis [Tanesi et al. 2013]. All mixtures were prepared with constant volume fractions of water, powders (including cement, fly ash, and limestone), and fine and coarse aggregates. As shown previously in Figure 8, these limestone replacements reduced the setting times of the HVFA mixtures to be nearly equal to those of the control portland cement mixture. With respect to strength at early ages, for both the Class F and the Class C fly ash studied, the fine limestone increases strengths by about 2 MPa (about 300 psi). By 28 d, these strength enhancements have increased significantly, and in the best case, a Class C fly ash HVFA concrete with an initial 28 d strength of 13 MPa (1900 psi) has nearly doubled to 25 MPa (3600 psi) with the incorporation of the fine limestone powder. This strength improvement is likely due to a combination of the acceleration provided by the fine limestone powder (i.e., increased specific surface) and the enhanced formation of stiffer carboaluminate phases [Moon et al. 2012] in this particular cement/Class C fly ash/fine limestone ternary blend. While significant, these

increases still failed to achieve the target strengths of the portland cement concrete. Thus, other measures such as a *w/cm* reduction and/or substitution of a Type III cement would need to be employed, along with the fine limestone replacements for fly ash [Bentz et al. 2013b].

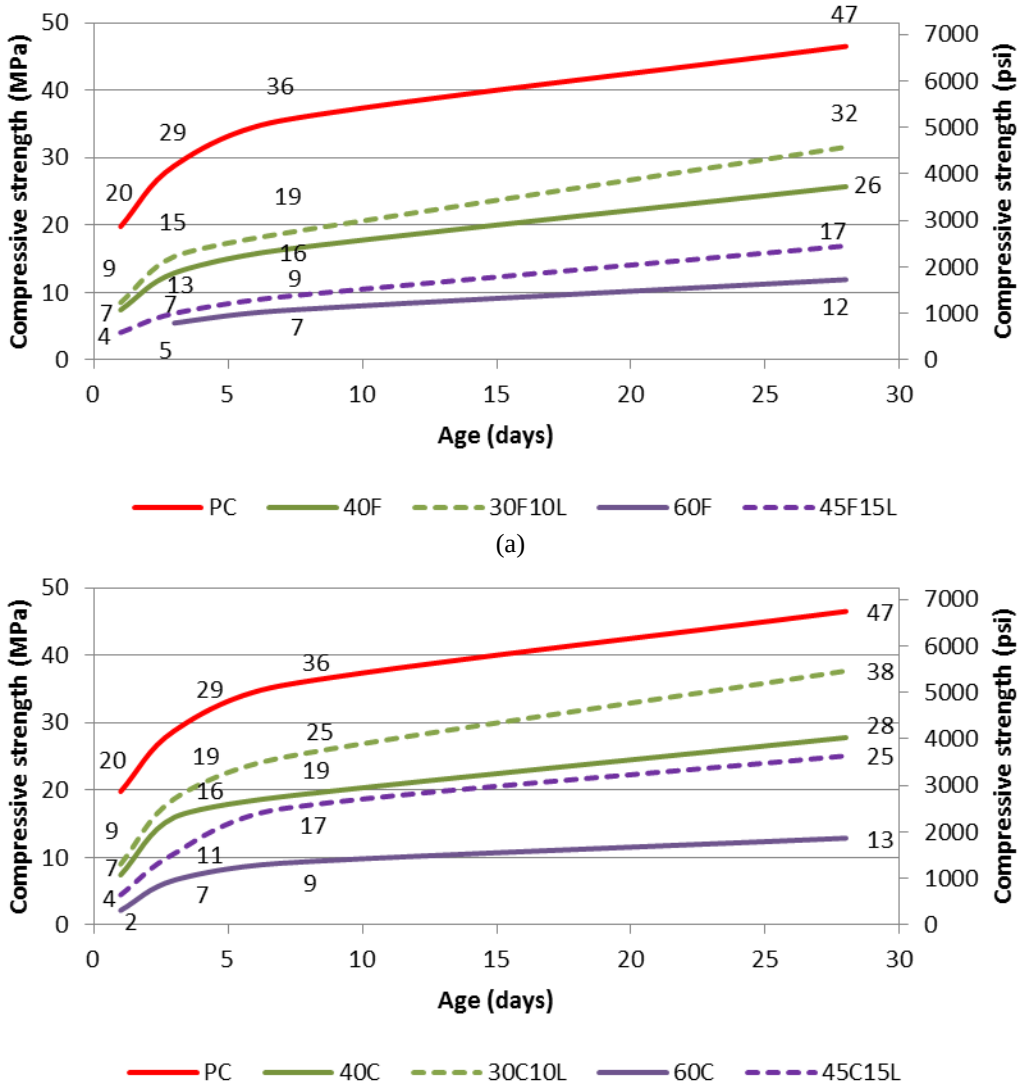



Figure 10. Compressive strength development for concrete mixtures (see Table 2) containing: a) Class F fly ash and b) Class C fly ash (taken from [Tanesi et al. 2013]). Coefficients of variation for three replicate specimens varied from 0.67 % to 2.5 % for the various mixtures. Numbers above lines indicate strengths obtained at testing ages of 1 d, 3 d, 7 d, and 28 d.

*Strength Activity Index Testing*

Some of the issues with the current ASTM C311 Strength Activity Index (SAI) test have been presented in a recent study [Bentz et al. 2012a]. According to the test procedure, for the test mortar, 20 % of the cement is replaced with fly ash on a mass basis and the water content of the mixture is adjusted to give a flow equivalent to the 100 % portland cement control mortar. Because the density of fly ash and cement are quite often substantially different, by as much as 30 % or more in extreme cases, a mass-based replacement alters the volume fractions of water and cementitious materials contained in each mixture subsequently used for strength testing. Adjustment of the water level to provide the same flow as the control mortar further alters these volume fractions. Since water content has a large impact on strength, any beneficial or detrimental impact of the fly ash on strength is confounded with these changes in volume fractions. As has been shown in a recent study [Bentz et al. 2012a], the test could be easily corrected by performing the replacement of cement with fly ash on a volume basis and keeping the water volume content constant. Any changes in flow of the fly ash mortar relative to the control mortar could be measured. If needed, any reductions in flow could be compensated for by using a water reducer. Pursuing this option in the standards committee has been a slow process. Within ASTM, consistency on this testing is lacking as the Annex A1 of ASTM C595 performs its activity index testing with a 35 % volumetric replacement of cement by pozzolan, but still recommends testing at constant flow conditions. An alternate approach to modifying ASTM C311 would be to develop new test methods for evaluating the activity of fly ash and other pozzolans, such as the Keil Hydraulic Index test to be described next.

*Keil Hydraulic Index Test*

The existing SAI test has long been criticized for not effectively evaluating the pozzolanic and cementitious properties of a fly ash. As previously stated, the test involves replacing with fly ash, 20 % by mass of the portland cement in a test sample mixture, preparing mortar cubes, and then comparing the strength of those mortar cubes to control samples prepared with 100 % portland cement. Sutter et al. (2013) demonstrated that replacing 20 % of the cement with an inert filler material actually produces samples that pass the SAI test. Table 3 presents data from their study where three different cements were used and in the case of the test samples, a fine quartz powder was used. The quartz powder had a fineness of 3.2 % and an average

particle size of 7.3 μm. As can be seen, at both 7 d and 28 d, the samples with inert filler exceeded the ASTM C618 SAI specification limit of 75 % of the control.

**Table 3. Results of the strength activity index test with three different cements and a quartz powder**

| Cement Type | Age (days) | 100% Cement Strength (psi) | 20% Replacement Strength (psi) | SAI |
|---|---|---|---|---|
| PC-1 | 7 | 4554 | 3829 | 84 |
| PC-2 | 7 | 4293 | 3408 | 79 |
| PC-3 | 7 | 4090 | 3539 | 87 |
| PC-1 | 28 | 5715 | 4815 | 84 |
| PC-2 | 28 | 5526 | 4235 | 77 |
| PC-3 | 28 | 5134 | 4351 | 85 |

An alternative to the SAI test is the Keil Hydraulic Index test (Keil 1952) that was originally developed for strength activity testing of slag. In this test, the control sample is prepared with a replacement of inert material equal to the replacement of fly ash used in the test sample. For a 20 % replacement of fly ash, the Keil Hydraulic Index (KHI) is calculated as shown in equation 3.

$$Keil\ Hydraulic\ Index = \frac{a-c}{b-c} \times 100 \tag{3}$$

where:

$a$ = the strength of 20 % fly ash/80 % portland cement at time $t$;

$b$ = the strength of 100 % portland cement at time $t$;

$c$ = the strength of 20 % ground quartz/80 % portland cement at time $t$

The difference between this method and the standard SAI test is that the KHI test allows for separation of the pozzolanic and hydraulic effects from the physical filler effects. The Keil Activity can range from 0 % for an inert material to over 100 % if the SCM material develops more strength than the portland cement mixture. A negative value of the KHI indicates the fly ash did not perform as well as the inert filler. Results for the KHI with 8 different fly ash sources are shown in Table 4 (Sutter et al. 2013).

**Table 4. Results of the Keil Hydraulic Index test with eight fly ash sources, four Class F and four Class C, at a 20°% replacement level. The inert filler used was a quartz powder with a fineness of 3.2 % and an average particle size of 7.3 μm. The results are for tests using three different portland cements (Sutter et al. 2013).**

| | KHI - 7 days (%) | | | KHI - 28 days (%) | | |
|---|---|---|---|---|---|---|
| **ID-% Replace.** | **PC-1** | **PC-2** | **PC-3** | **PC-1** | **PC-2** | **PC-3** |
| Class F #1 | -31 | 4 | -43 | 71 | 91 | 66 |
| Class F #2 | 7 | 28 | 26 | 119 | 55 | 34 |
| Class F #3 | 10 | -6 | -24 | 7 | 73 | 39 |
| Class F #4 | 53 | 44 | 26 | 135 | 102 | 109 |
| Class C #1 | 121 | 40 | 84 | 184 | 75 | 171 |
| Class C #2 | 115 | 101 | 80 | 96 | 30 | 72 |
| Class C #3 | 122 | 46 | 110 | 184 | 99 | 153 |
| Class C #4 | 203 | 83 | 41 | 138 | 119 | 130 |

As can be seen in Table 4, the Class F ash sources demonstrated very little to no contribution to strength at 7 d but a measurable increase at 28 d. Conversely, the Class C ash sources demonstrated a significant strength contribution at 7 d and a measurable increase at 28 d. The results of the KHI test align with the known properties of fly ash and provide a clear indication of strength gain, separate of any contributions from a filler effect.

Another issue highlighted by this research is the dependence on the cement type with regards to the KHI test. The same dependence is seen with the standard SAI test. The results of the SAI and KHI tests using the three different cements, plotted against measured compressive strength, are shown in Figures 11 and 12, respectively.

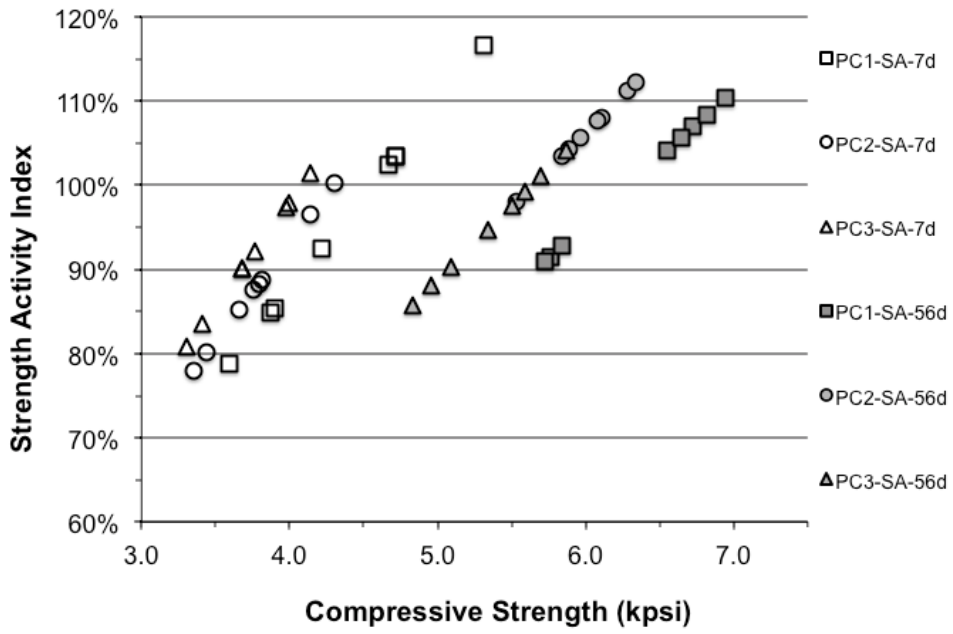



Figure 11. SAI versus compressive strength for a 20 % replacement level for eight fly ash sources, four Class F and four Class C, at a 20 % replacement level. The inert filler used was a quartz powder with a fineness of 3.2 % and an average particle size of 7.3 μm. The results are for tests using three different portland cements (Sutter et al. 2013).

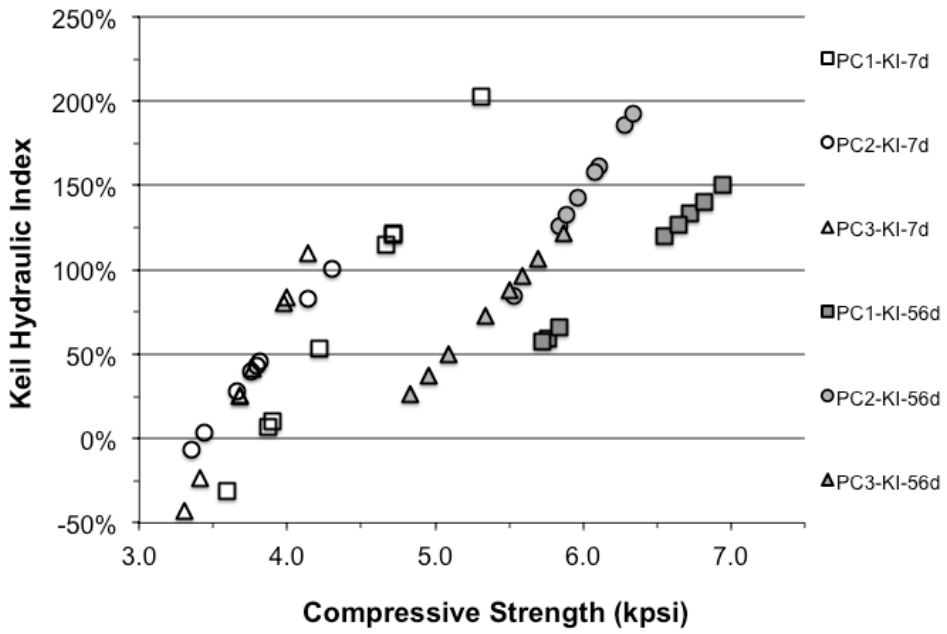



Figure 12. KHI versus compressive strength for a 20 % replacement level for eight fly ash sources, four Class F and four Class C, at a 20 % replacement level. The inert filler used was a quartz powder with a fineness of 3.2 % and an average particle size of 7.3 μm. The results are for tests using three different portland cements (Sutter et al. 2013).

In both tests, PC1 resulted in higher strengths and higher SAI and KHI values as compared to the same ash sources tested with PC2 and PC3. The problem of cement type can now be addressed with the development of the Cement and Concrete Reference Laboratory (CCRL – www.ccrl.us) reference cement, which can be used as a common cement for all strength testing of supplementary cementitious materials.

**Summary**

Fly ash is a heterogeneous material that results from the combustion of coal, primarily to produce electrical power. The process of combustion and the composition of the fuel stream, which is predominately coal, affects the quality and performance of the ash. Because power producers are generating power as a primary product, and fly ash as a residual product, the characteristics of fly ash will change as burning conditions are changed to affect power

production. This variability in ash characteristics presents a challenge to using fly ash in concrete.

A key constituent of fly ash is un-burnt carbon resulting from the combustion process, and carbon added in the form of PAC to help power producers meet emission standards. The carbon is an issue primarily when the concrete produced is air entrained. Air entrainment is accomplished through the use of an air entraining admixture (AEA) and produces concrete that is resistant to cyclic freezing and thawing. Residual carbon in the ash can adsorb the AEA from the concrete mixture water and thereby render them ineffective at entraining air.

The amount of carbon in fly ash has historically been determined by a loss on ignition (LOI) test. Although this test can accurately predict the total amount of carbon present, it does not characterize the adsorption capacity of the carbon. Adsorption capacity can vary widely, and is especially significant when PAC is introduced. Two ash sources with the same LOI can have markedly different adsorption properties.

New tests have been developed to assess adsorption but they have yet to be implemented in any standards or materials specifications. The principal tests currently available are the foam index test, iodine number test, the direct determination of the adsorption isotherm for a specific ash/AEA combination, and the methylene blue-based adsorption tests. The foam index test provides a simple means of evaluating AEA adsorption but it is not quantitative in terms of the amount of AEA adsorbed and it does not evaluate the cementitious system with AEA at equilibrium. Still, it is a useful quick diagnostic test. The iodine number test is an adsorption isotherm-based test that determines the mass of iodine adsorbed from solution per unit mass of fly ash. It is an excellent test for assessing the adsorption capacity of an ash but it does so using iodine, and the adsorption capacity will vary with changes in the adsorbate properties. Nonetheless, it is extremely useful for simply evaluating an ash adsorption or monitoring changes in ash adsorption on a temporal basis. The direct adsorption isotherm provides a quantitative measure of the volume of AEA adsorbed per unit mass of fly ash, in the presence of cement. The cement strongly impacts the system and affects adsorption of AEA by fly ash. The methylene blue adsorption test is relatively new and potentially offers many advantages in terms of simplicity. It provides the same basic information attained from the iodine number test (i.e., it characterizes only the ash).

Particle size is critical to fly ash performance. The smaller particles are more reactive and therefore performance in terms of strength development, ASR mitigation, and sulfate attack mitigation all vary significantly. Current ASTM specification rely only on a sieve analysis to establish the amount of fly ash finer than 45 µm. Other tests exist for measuring particle size distribution but to date, these tests have not been adopted in any fly ash specifications.

One of the performance properties most influenced by fly ash replacement for cement is setting time, particularly for high volume fly ash concretes. Generally, setting times are increased, sometimes dramatically, due to cement dilution, sulfate imbalance, incompatibilities with admixtures such as HRWRs, and/or detrimental influences of fly ash components on early-age hydration reactions. A variety of effective mitigation strategies for these setting time delays have been investigated including additions of calcium hydroxide or a rapid set cement and the replacement of a portion of the fly ash by a fine limestone powder. In the latter case, not only are setting times reduced, early and later age properties (strength and durability) are generally improved as well.

The contribution to strength development is an important property of fly ash. Current ASTM tests assess this property based on a comparison of a control sample prepared with 100 % portland cement to a test sample with 20 % fly ash/80 % portland cement. This strength activity index (SAI) has been criticized because given the specification limits, an inert material can pass the test. Modifications to the SAI test are needed. One proposed modification is the Keil Hydraulic Index (KHI) that compares a control sample prepared with 20 % inert material/80 % portland cement to a test sample with 20 % fly ash/80 portland cement. By doing so, the filler effect of the replacement material is eliminated and the true cementitious and pozzolanic nature of the ash can be measured. Both the SAI and KHI tests are affected by the cement used and therefore any modifications should consider use of a standard cement. Two other deficiencies of the existing SAI test are that is it conducted at constant flow conditions and by replacing cement with fly ash on a mass basis, both of which alter the volume fraction of water in the prepared specimens and are thus confounding influences on the determination of fly ash influence on strength.

## References


ASTM International, ASTM C1749-12 Standard Guide for Measurement of the Rheological Properties of Hydraulic Cementitious Paste Using a Rotational Rheometer, ASTM International, West Conshohocken, PA, 4 pp., 2012.

ASTM International, ASTM C359-13 Standard Test Method for Early Stiffening of Hydraulic Cement (Mortar Method), ASTM International, West Conshohocken, PA, 4 pp., 2013.

ASTM International, ASTM C311/C311M-13 Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete, ASTM International, West Conshohocken, PA, 10 pp., 2013.

ASTM International, ASTM C1679-14 Standard Practice for Measuring Hydration Kinetics of Hydraulic Cementitious Mixtures Using Isothermal Calorimetry, ASTM International, West Conshohocken, PA, 15 pp., 2014.

ASTM International, ASTM D3860-98(2014) Standard Practice for Determination of Adsorptive Capacity of Activated Carbon by Aqueous Phase Isotherm Technique, American Society for Testing and Materials, West Conshohocken, PA, 4 pp., 2014.

ASTM International, ASTM D4607-14 Standard Test Method for Determination of Iodine Number of Activated Carbon, American Society for Testing and Materials, West Conshohocken, PA, 5 pp., 2014.

ASTM International, ASTM C114-15 Standard Test Methods for Chemical Analysis of Hydraulic Cement, American Society for Testing and Materials, West Conshohocken, PA, 32 pp., 2015.

ASTM International, ASTM C150/C150M-15 Standard Specification for Portland Cement, ASTM International, West Conshohocken, PA, 9 pp., 2015.

ASTM International, ASTM C430-08(2015) Standard Test Method for Fineness of Hydraulic Cement by the 45-µm (No. 325) Sieve, American Society for Testing and Materials, West Conshohocken, PA, 3 pp., 2015.

ASTM International, ASTM C618-15 Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete, ASTM International, West Conshohocken, PA, 5 pp., 2015.

ASTM International, ASTM C1753-15 Standard Practice for Evaluating Early Hydration of Hydraulic Cementitious Mixtures Using Thermal Measurements, ASTM International, West Conshohocken, PA, 19 pp, 2015.

ASTM International, ASTM C1777-15 Standard Test Method for Rapid Determination of the Methylene Blue Value for Fine Aggregate or Mineral Filler Using a Colorimeter, American Society for Testing and Materials, West Conshohocken, PA, 4 pp., 2015.

ASTM International, ASTM C204-16 Standard Test Methods for Fineness of Hydraulic Cement by Air-Permeability Apparatus, American Society for Testing and Materials, West Conshohocken, PA, 10 pp., 2016.

ASTM International, ASTM D1510-16 Standard Test Method for Carbon Black-Iodine Adsorption Number, American Society for Testing and Materials, West Conshohocken PA, 10 pp., 2016.

Bailey, J.G., Tate, A., Diessel, C.F.K., and Wall, T.F., "A Char Classification System with Applications to Coal Combustion" *Fuel*, **69** (2), pp. 225-239, 1990.

Bentz, D.P., "Powder Additions to Mitigate Retardation in High Volume Fly Ash Mixtures," *ACI Materials Journal*, **107** (5), 508-514, 2010.

Bentz, D.P., and Ferraris, C.F., "Rheology and Setting of High Volume Fly Ash Mixtures," *Cement and Concrete Composites*, **32** (4), 265-270, 2010.

Bentz, D.P., Ferraris, C.F., De la Varga, I., Peltz, M.A., and Winpigler, J., "Mixture Proportioning Options for Improving High Volume Fly Ash Concretes," *International Journal of Pavement Research and Technology*, **3** (5), 234-240, 2010.

Bentz, D.P., Duran-Herrera, A., and Galvez-Moreno, D., "Comparison of ASTM C311 Strength Activity Index Testing vs. Testing Based on Constant Volumetric Proportions," *Journal of ASTM International*, **9** (1), 7 pp., 2012a.

Bentz, D.P., Sato, T., De la Varga, I., and Weiss, J., "Fine Limestone Additions to Regulate Setting in High Volume Fly Ash Mixtures," *Cement and Concrete Composites*, **34** (1), 11-17, 2012b.

Bentz, D.P., Ferraris, C.F., and Snyder, K.A., "Best Practices Guide for High-Volume Fly Ash Concretes: Assuring Properties and Performance," NIST Technical Note **1812**, U.S. Department of Commerce, September, 2013a.

Bentz, D.P., Tanesi, J., and Ardani, A., "Ternary Blends for Controlling Cost and Carbon Content," *Concrete International*, **35** (8), 51-59, 2013b.

Bruere, G.M., "Air Entrainment in Cement and Silica Paste," *Journal of the American Concrete Institute*, **26** (9), 905-919, 1955.

Cost, V.T., "Concrete Sustainability versus Constructability – Closing the Gap," in Proceedings of the 2011 International Concrete Sustainability Conference, Boston, MA, 2011, available at: http://www.nrmcaevents.org/?nav=display&file=189.

Cost, V.T., and Bohme, P., "Synergies of Portland-Limestone Cements and Their Potential for Concrete Performance Enhancement," in Proceedings of the 2012 International Concrete Sustainability Conference, Seattle, WA, 2012.

Gurney, L., Bentz, D.P., Sato, T., and Weiss, W.J., "Reducing Set Retardation in High Volume Fly Ash Mixtures with the Use of Limestone: Improving Constructability for Sustainability," *Transportation Research Record, Journal of the Transportation Research Board*, No. **2290**, Concrete Materials 2012, 139-146, 2012.

Harris, N. J., Hover, K.C., Folliard, K.J., and M. T. Ley, M.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," *Journal of ASTM International*, **5** (7), 2008.

Islam, G.S., McCarthy, M., Csetenyi, L., and Jones, M., "Investigating Techniques for Evaluating Fly Ash Behaviour in Air-entrained Concrete," Proc. EuroCoalAsh, 2012.

Keil, F., Slag Cements. Proc., 3rd International Symposium on the Chemistry of Cements, Cement and Concrete Association, London, 1952, pp. 530-571.

Keith, K.P., and Schindler, A.K., "Phase II – Task 3 Setting and Temperature Development," Final Report for Project BAA No. DTFH61-08-R-0034 Greatly Increased Use of Fly Ash in Hydraulic Cement Concrete (HCC) for Pavement Layers and Transportation Structures, 2012.

Looney, T.J., Arezoumandi, M., Volz, J.S., and Myers, J.J., "An Experimental Study on Bond Strength of Reinforcing Steel in High-Volume Fly-Ash Concrete," *Advances in Civil Engineering Materials*, **1** (1), 17 pp., 2012.

McCarthy, M., Islam, G.S., Csetenyi, L., and Jones, M., "Colorimetric Evaluation of Admixture Adsorption by Fly Ash for Use in Air-entrained Concrete," *Materials and Structures*, **45** (12), 1793–1803, 2012.

Moon, J., Oh, J.E., Balonis, M., Glasser, F.P., Clark, S.M., and Monteiro, P.J.M., "High Pressure Study of Low Compressibility Tetracalcium Aluminum Carbonate Hydrates $3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}11H_2O$," *Cement and Concrete Research*, **42**, 105-110, 2012.

Niemuth, M.D., Barcelo, L., and Weiss, J., "Effect of Fly Ash on Optimum Sulfate Levels Measured Using Heat and Strength at Early Ages," *Advances in Civil Engineering Materials*, **1** (1), 18 pp., 2012.

Obla, K.H., Lobo, C.L., and Kim, H., "The 2012 NRMCA Supplementary Cementitious Materials Use Survey," *Concrete Infocus*, Summer 2012.

Roberts, L.R., and Taylor, P.C., "Understanding Cement-SCM-Admixture Interaction Issues," *Concrete International*, **29** (1), 33-41, 2007.

Schlorholtz, S. M., Chapter 43 – Supplementary Cementitious Materials. In Significance of Tests and Properties of Concrete and Concrete-Making Materials (J. Lamond, and J. Pielert eds.), ASTM STP 169D, American Society for Testing and Materials, West Conshohocken, Pa., 2006, pp. 495-511.

Sontheimer, H., Crittenden, J.C., and Summers, S., Activated Carbon for Water Treatment. Karlsruhe: DVGW-Forschungsstelle and American Water Works Association, 1988, pp. 102. ISBN 3-922671-20-9.

Sutter, L. L., Hooton, R. D., and Schlorholtz, S., "Methods for Evaluating Fly Ash for Use in Highway Concrete," NCHRP Report 749, National Cooperative Highway Research Program, Transportation Research Board of the National Academies, Washington, DC, 2013, 54 pp.

Sutter, L.L., Vruno, D., Anzalone, G.C., and Dong, J., "Laboratory Study for Comparison of Class C Versus Class F Fly Ash for Concrete Pavement," Final Report, 0092-12-04, Wisconsin Highway Research Program. Madison, Wisconsin, USA, May, 2014. 153 pp.

Tanesi, J., Ardani, A., Meininger, R. and Nicolaescu, N., "Evaluation of High-Volume Fly Ash (HVFA) Mixtures (Paste and Mortar Components) Using a Dynamic Shear Rheometer (DSR) and Isothermal Calorimeter," Report No. PB2012-112546, National Technical Information Service, Springfield, VA, 2012.

Tanesi, J., Bentz, D.P., and Ardani, A., “Enhancing High Volume Fly Ash Concretes Using Fine Limestone Powder,” in ACI SP-294: Advances in Green Binder Systems, Minneapolis, MN, October, 2013.