QA/QC AND VARIABILITY OF CCBS RELATING TO MINE APPLICATONS

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Abstract

Coal combustion products (CCPs), namely, fly ash, bottom ash, and flue gas desulfurization materials, continue to be used in increasing amounts in construction and mining applications such as cementing, grouting and concrete applications, road base construction, soil amendments, backfills, soil cements, solidification and stabilization processes, and controlled low strength material fills. Depending on the specific application, the role of CCPs in a material mix design can vary from that of an economical extender to an active, and essential, key component. The performance of a CCP in many applications will be a direct function of the chemical and physical properties of the CCP itself. For instance, the chemical properties of fly ash are a determining factor when judging its suitability for use in cementing and concrete applications, while physical properties such as granulometry, bulk density, and compacted density can be critical for grouts, fills, and base products. The physico-chemical properties of coal combustion products are a derivative of fuel chemistry and the processing and combustion regimes used during firing. This presentation will briefly describe various CCPs and identify common characteristics that can be used as general indicators of product consistency. Typical relationships between chemical and physical parameters will be highlighted, as well as trend lines and measures of variability in chemical and physical properties. Potential ramifications due to shifts in utility operating programs will be noted. A number of examples will be provided demonstrating measures developed to establish the appropriateness of a particular CCP for specialized applications, with emphasis placed on measuring the correct parameter for a given use. Quality control and quality assurance schemes and protocols common to the industry also will be briefly outlined.

Introduction

Coal combustion products, namely, fly ash, bottom ash, and flue gas desulfurization materials, continue to be used in increasing amounts in construction and mining applications such as cementing, grouting and concrete applications, road base construction, soil amendments, backfills, soil cements, solidification and stabilization processes, and controlled low strength material fills. Depending on the specific application, the role of coal combustion products (CCPs) in a material design can vary from that of an economical extender to an active, and essential, key component. The performance of a coal combustion product in many applications will be a direct function of the chemical and physical properties of the CCP itself. For instance, the chemical properties of fly ash are a determining factor when judging its suitability for use in cementing and concrete applications, while physical properties such as granulometry, bulk density, and compacted density can be critical for grouts, fills, and base products. The physico-chemical properties of coal combustion products are a derivative of fuel chemistry and the processing and combustion regimes used during firing.

Fly Ash

Fly ash is produced as a by-product of burning coals that have been crushed and ground to a fineness of 70 to 80 percent passing a 75-mm (No. 200) sieve. After combustion, much of the noncombustible, inorganic components residing in coal condense in the exhaust gas stream as tiny, glassy spheres. These mostly alumino-silicate spheres will range from several hundred microns in diameter to sub-micron size.

Fly ash is the most widely utilized coal combustion product. The American Coal Ash Association (ACAA-2000) estimates that more than 20,000,000 of the 63,000,000 tons (31%) of fly ash produced annually are effectively utilized. The primary application for fly ash (more than 60 percent of the material used) is as a replacement or addition to cement in concrete and related applications. The National Ready Mix Association (Oct. 2000) estimated that just over 50 percent of all ready mix concrete contained fly ash. Concretes made with fly ash used on average a cement replacement rate of 18-19 percent. The success of fly ash in areas of cement and concrete can not be explained by assuming that fly ash is used simply as a nonfunctional filler material. Rather the successful penetration of fly ash in these markets is attributable to the many benefits offered by its use. Improved workability, increased ultimate strengths, and enhanced durability are properties offered by fly ash that can not always be achieved by using cement alone.

These attributes are a direct consequence of the physico-chemical properties of fly ash. The alumino-silicate glass in fly ash will undergo dissolution and limited solubilization in a high pH environment, such as exist in a portland cement-based concrete pore solution. Silica and to a lesser extent alumina anions released from the ash will interact with calcium made available from cement to precipitate and polymerize forming calcium silicate gel (CSH). (Note that in the absence of high pH activators such as calcium and alkali hydroxides provided by cement, fly ash will not provide any strength development). This gel will be very similar in composition and structure to the CSH formed by the hydration of portland cement itself. Calcium silicate gel is essentially the "glue" that binds the aggregate together in concrete and is responsible for concrete setting and strength gain. The fly ash reaction, termed pozzolanic reaction after a location in Italy known for providing natural volcanic pozzolans, consumes calcium hydroxide (a cement reaction by-product) to produce additional binding CSH gel. When the calcium hydroxide, which is susceptible to attack by some aggressive agents, is removed and more CSH gel is created, a less permeable and potentially stronger concrete is made. This concrete will be better able to withstand attack by aggressive agents such as sulfates, alkalis, chloride ingress, and penetration of water.

In recognition of the widespread use of fly ash in cementitious applications, the American Standards Testing Materials Association (ASTM) developed standards specifically addressing coal fly ash for use as a concrete admixture. The specification was first introduced in the 1950s and has since undergone a number of modifications to reflect changes in both testing methods and the types of available fly ash. The current designation for the specification is *ASTM C 618-00 – Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Concrete*. This specification provides chemical, physical, and performance criteria for coal fly ash use in concrete. This specification references *ASTM C 311-00 -Sampling and Testing Fly Ash or Natural Pozzolans for Use as a Mineral Admixture in Portland-Cement Concrete* for guidance on sampling and testing methods.

ASTM C 618 recognizes two distinct coal fly ashes: Class F and Class C. These fly ashes are distinguished by differences in chemical requirements as seen in Table 1. The distinction provided by ASTM is related only to the sum of the oxides: SiO_2, Al_2O_3, and Fe_2O_3. In practice, the reduced sum of the oxides presented by Class C fly ash are directly proportional to an increase in calcium content reported as CaO, and sometimes an associated increase in magnesium reported as MgO. This can easily be discerned from a comparison of the chemistry of typical fly ashes provided in Table 2.

Fly ash chemistry is a direct consequence of the residual constituents of the combusted coal. Subbituminous coals will typically produce high-CaO, Class C fly ash while bituminous coals produce low-CaO, Class F fly ash. Lower rank coals such as lignite tend to produce fly ash with chemistry intermediate to the two classes and may be classified as either Class C or F depending on performance. These differences in elemental composition obviously influence both the mineralogy and the glass composition of the fly ash. Class F fly ash tends to contain a small proportion of non-reactive crystalline materials such as quartz and mullite. This ash will contain a relatively well ordered glass component that will vary in concentration based on coal chemistry and combustion conditions. A high proportion of glass is associated with increased reactivity.

The presence of higher concentrations of calcium leads to the formation of additional crystalline compounds in Class C fly ash. A number of these compounds such as tricalcium aluminate, dicalcium silicate, and anhydrite are cementitious in their own right and are, in fact, found in cement. The glass phase of Class C fly ash is also more highly substituted and thus reactive. These differences result in Class C fly ash possessing both pozzolanic and cementitious properties. This ash will react with water without an activator to undergo setting and limited strength development. Class C fly ash will typically generate more heat and more strength in concrete at a given dosage level than Class F fly ash; however, the concrete's resistance to attack by aggressive agents such as sulfates or alkalis may be compromised. In the case of sulfate attack, the reduced durability is due to the susceptibility of the Class C fly ash itself to sulfate attack.

The topo-chemical nature of the fly ash hydration process suggests that reactivity is determined not only by chemical composition, but also by available surface area as well. As such, maximum particle size and, more specifically, particle size distribution (which controls surface area) are critical to performance. Particle size distribution not only influences reactivity but impacts rheological performance of materials like grouts. Fly ash fineness and particle size distribution are influenced by both fuel source and processing (i.e., coal grinding). In addition to a limit on maximum allowed particle size (fineness), ASTM C 618 specifies other physical testing such as loss on ignition (a measure of residual carbon) and specific gravity.

Performance testing such as the strength activity index, which compares the compressive strength of control mortar cubes to mixes made by partially replacing cement with fly ash, is used (in addition to other performance tests) to benchmark both performance and consistency.

ASTM C 618 is designed to identify important differences in fly ash that have been determined critical for concrete applications by relying on a combination of chemical and performance testing. The specification further offers simple, rapid testing (LOI, SG, Fineness) to provide a measure of product uniformity and for identification of changes in fuel, combustion, or processing that can impact quality. Physical testing of grab samples must be conducted daily on each 400 tons of fly ash produced, while chemical and performance testing is conducted on composite samples monthly or every 3,200 ton production basis.

The typical fly ash quality program will incorporate the testing philosophy proposed by ASTM C 618. Quality control at an established facility will consist of rapid uniformity testing (fineness, LOI, etc.) of production site samples allowing for go/no-go decisions on material acceptance or beneficiation (air classification, selective collection, blending) prior to acceptance for storage. Tests such as LOI and fineness are quite sensitive to changes in fuel feed or plant processing and are used to trigger more detailed investigations. Dispatched loads will be sampled and tested on a frequency consistent with ASTM as a minimum requirement. Chemical and performance testing generally will be conducted on a less frequent basis, again in accordance with ASTM C 618 stipulations. The chemical testing is used to detect any major changes in composition that could result in modifications in fly ash performance. Generally chemistry will be quite consistent unless a dramatic change is made in fuel chemistry or some alternative material is added into the combustion system, e.g., sodium carbonate for precipitator enhancement. Performance testing will identify changes related both to compositional and physical changes in the fly ash, e.g., coarsening of fly ash will result in lower strength activity index values. More aggressive sampling and testing intervals are often mandated depending on product consistency and performance demands.

Additional testing outside the scope of ASTM may be employed at specific sites or for certain applications that have unique requirements. Examples of such testing are foam index testing for air entrainment issues; particles size distribution or Blaine fineness as a measure of reactivity or rheological performance; free lime content for heat development and reactivity, pH and buffering capacity, and total or leachable metal concentrations. These types of tests are initiated due to the specific requirements of a particular application.

The simplicity of the quality program based on ASTM C 618 specifications and the testing procedures of ASTM C 311 warrants some discussion. It should be emphasized that this system has been determined adequate for monitoring coal fly ash for use in concrete and was developed over an extensive time period. Ash sources other than coal fly ash may be suitable for concrete application, but the existing testing scheme is not necessarily sufficient to make that determination. In the case of alternative materials or applications such as grouts, fills, mineral filler, stabilization, etc., the typical fly ash quality system will provide notification of any disruption in ash production that could signify a change in material characteristics. However, depending on the performance demands of a product for its intended final use, standard quality programs may not be monitoring all pertinent parameters. In these cases, consideration should be given to the material demands for a specific job and suitable quality measures should be instituted on agreement between the supplier and customer. An example would be the routine measure of fly ash pH and periodic TCLP testing for fly ash used in stabilization projects or general geotechnical performance data.

Guidance and recommended testing methods for specific fly ash properties can be found in other ASTM specifications such as *ASTM D 5759-95 - Characterization of Coal Fly Ash and Clean Coal Combustion Fly Ash for Potential Use; ASTM E 1861-97 - Use of Coal Combustion By-Products in Structural Fills;* and *ASTM E 2060 – Use* *of Coal Combustion Products for Solidification/Stabilization of Inorganic Wastes.* More specialized testing techniques also may be developed for the particular needs of individual projects.

Bottom Ash and Flue Gas Desulfurization Materials

Bottom ash represents the agglomerated ash particles formed in pulverized coal boilers that are too large to be carried in the flue gases and impinge on the boiler walls or fall through open grates to ash hoppers at the bottom of the boiler. These materials may be accompanied by boiler slag that is a glassy slag material sometimes distinguished from bottom ash. The chemical composition of these materials will be similar to fly ash. If one combines bottom ash and boiler slag into one category, the ACCA reports that approximately 7,000,000 tons of the 20,000,000 tons of bottom ash and boiler slag produced per annum are utilized.

Bottom ash can range in appearance from an almost glassy to a more textured visceral product. Particle sizes can range from quite coarse (3/8 plus) to that of fine sand. The material typically has a lower bulk density than similarly graded coarse-grained soils and will place and compact in a manner similar to non-cohesive coarse soils or fine aggregate. This material has found use as an aggregate in masonry applications and road base and stabilization work. Grinding and grading can produce specific gradations.

There are no specific ASTM specifications that apply to the production of bottom ash. In practice, specifications are typically formulated around the performance demands of a specific project. Common quality measures include: gradation, chemical composition, pyrite content, bulk density, specific gravity and hardness or friability. It should be stressed that the performance of these products can be generalized, but materials may vary from source to source. Full characterization of products should be established during a complete material evaluation process. When CCBs are to be used in a designed system such as a structural fill, sufficient design and testing should be conducted to ensure performance and appropriate quality. The program should be arranged to reflect the material properties required for the specific project. Broad guidance can be found in the previously referenced ASTM specifications: E 1861 and E2060.

Flue gas desulfurization (FGD) materials consist primarily of calcium sulfate dihydrate or calcium sulfite hemihydrate, although fly ash may be commingled depending on plant processing schemes. The sulfate form has found use in applications that commonly employ gypsum such as wallboard and cement manufacture. In these applications important criteria include: purity, crystalline particle size, speciation, specific impurities, and moisture levels. FGD materials also have been used as soil amendments and in stabilization and fill operations. In these cases, consideration must be given to the localized environment where the products will be used. Once sufficient testing is conducted to ensure that these materials are suitable for a given application, an appropriate quality program can be instituted.

Conclusion

The quality programs based on ASTM C 618 and C 311 effectively allow for determining the suitability of coal fly ash for concrete and cementing applications. Programs based on these criteria are also responsive to changes in fuel and combustion or processing schemes that might influence chemical or physical characteristics of fly ash not specifically monitored under current specification guidelines. The quality of coal fly ash for use in alternative applications, or the utilization of other combustion products, is best monitored by a combination of sampling and testing procedures based on ASTM C 618 and other referenced specifications and by developing relevant testing protocols based on the particular performance demands of the application.

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numerous conferences. He holds a B. S. in Chemistry from the University of East Texas and a PhD in Analytical Chemistry from the University of North Texas. His university research focused on the hydration of fly ash and the impact that various inorganic materials had on these reactions.

Table 1. ASTM C 618 Requirements.

Chemical Requirements	F	C
Silicon Dioxide (SiO_2) plus Aluminum Oxide ($A1_2O_2$), min %	70.0	50.0
Sulfur Trioxide (SO_3) max %	5.0	5.0
Moisture Content, max %	3.0	3.0
Loss on Ignition, max %	6.0	6.0

Supplementary Optional Chemical Requirements	F	C
Available alkalis, as equivalent as Na2O, max %	1.5	1.5

Physical Requirements	F	C
Fineness		
Amount retained when wet-sieved on 45um (No. 325), sieve, max %	34	34
Strength Activity Index		
With portland cement, @ 7 days, min percent of control	75	75
With portland cement, @ 28 days, min percent of control	75	75
Water requirement, max percent of control:	105	105
Soundness:		
Autoclave expansion or contraction max %	0.8	0.8
Uniformity requirements:		
The density and fineness of individual samples shall not vary from the average established by the 10 preceding tests if the number is less than 10, by more than:		
Density, max variation from average %	5	5
Percent retained on 45 um (No. 325) max variation, percentage points from average	5	5

Table 2. Chemistry of Various Fly Ash Types.

	Bit. Class F	Lignite Class F	Sub. Class F	Portland Cement
Silicon Dioxide (SiO_2)	55.2	55	35	22
Aluminum Oxide (Al_2O_3)	28.6	23	20	4
Iron Oxide (Fe_2O_3)	6.9	4	6	3
Sum of Oxides	**90.7**	**82**	**61**	**29**
Calcium Oxide (CaO)	1.7	10	28	66
Magnesium Oxide (MgO)	0.8	2	5	1
Sulfur Trioxide	0.1	0.3	1.5	2.7
Loss on Ignition (LOI)	4.2	0.2	0.2	0.9