Effect of Bromine Addition on Fly Ash Use in Concrete

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ABSTRACT

As utilities plan for mercury control on boilers burning PRB coal, difficulties arise from the lack of chlorine in PRB coal. Chlorine can be replaced by a non-corrosive halogen such as bromine. However, many PRB plants depend on fly ash utilization in concrete for revenue and as an alternative to disposal. Consequently, some emissions control additives may alter properties of ash and concrete, such that the resulting product does not meet performance requirements. If present, this effect could result in lost fly ash markets or legal liabilities in construction projects.

Southern Company, EPRI, and Gallet & Associates, have evaluated this question during bromine addition tests at Alabama Power's Plant Miller. This work is part of an EPRI project to evaluate the fate of bromide/bromine in coal-fired power plants and its potential balance of plant impacts. It includes comprehensive ash and concrete testing. Test conditions include bromine addition to ash in a laboratory environment, in addition to full-scale testing on ash samples from the boiler, where bromine was added to coal over a range of concentrations.

INTRODUCTION

The speciation of mercury in flue gas can affect the ability of various environmental control devices to remove it. Flue gases derived from Powder River Basin (PRB) coal typically contain a high fraction of elemental mercury. This form is insoluble in water and therefore not easily removed across wet scrubbers. Several methods are being investigated by EPRI to oxidize the elemental mercury in flue gas, thereby improving mercury removal across a wet scrubber. These methods include catalytic and chemical injection processes. [1]

EPRI has funded a study to evaluate the fate of bromide/bromine in coal-fired power plant systems and its potential balance of plant impacts, including effects on marketability of fly ash. This paper and paper # 27 report on results obtained from Alabama Power Company's Plant Miller, the first field site to be tested as part of the EPRI project.

The primary use for coal fly ash is in ready-mix concrete, where it replaces a portion (generally in the 20% range) of the cement content and provides silica, alumina, and iron content for concrete. Ash offers cost savings and physical advantages such as greater pumpability, higher long-term strength, and decreased permeability.

As environmental control technologies are considered for implementation at power plants, it is important to carefully examine the effects of process configurations and various additives on the properties of ash and concrete. There have been instances where boiler or ESP additives caused unexpected consequences when the fly ash was used in commercial concrete, such as extremely long set times and undesirable odors. As an example of the importance of this subject, Plant Miller currently sells essentially 100% of the fly ash which is produced at the site. Losing the ability to market this material would result in much higher disposal costs, as well as lost revenue.

EXPERIMENTAL METHODS

Key Properties for Evaluation

This test program was designed to determine the effects of bromine (as $CaBr_2$) on key acceptance properties for concrete – unit weight, slump, air content, compressive strength, and freeze-thaw durability. Unit weight and slump are measures of quality control in concrete mix production. Changes in unit weight or slump height could indicate an undesirable change in mix ingredients – water, sand, cement, ash and aggregate. Homogeneity improves quality and structural integrity of cured concrete. Compressive strength determines load-bearing strength of a concrete product. Air content, or the difficulty in maintaining a specified air content, is a measure of the protection or durability against freeze-thaw cycles. Freeze-thaw durability measures the degree of deterioration in a concrete specimen subjected to alternate freezing and thawing cycles.

Results also served to verify findings from similar testing in 2007 during which bromine was artificially added to ash samples in the laboratory after the samples were collected from ESP hoppers. In this latest work, $CaBr_2$ was added to the coal (at the coal feeders), producing more realistic ash samples for concrete testing. [2]

Test Conditions

Calcium bromide injection testing was performed at Plant Miller on Unit 4, which is a 700 MW pulverized coal unit that fires exclusively PRB coal in a wall-fired furnace. It is equipped with an SCR and cold-side electrostatic precipitator (ESP). Table 1 summarizes the general test conditions surrounding the ash samples which were collected.

A reference sample for all four units was collected in early February prior to any use of $CaBr_2$ in Unit 4 during parametric or longer-term continuous injection tests. Two sets of ash samples were obtained during the six-day period of continuous injection at 25 ppm, with one set of samples obtained during the three-day period for 50 ppm injection. Note that the sample sets at 25 ppm bromine are not expected to exhibit different properties, since differences were related to pilot FGD operation, which is downstream of the ESP. For each sample set, “treated” ash samples (exposed to bromine) were collected at the plant silo # 2, which was isolated to collect ash from Unit 4 only during each test period. The background sample for each test was obtained at the ash marketer's silo and represented Units 1-3 only, which experienced no bromine addition at any time.

Table 1. General Test Conditions for Investigation of Ash Effects

Sample Date	Injection Condition	Sample Type	Sample Location	Units Included	SCR/NH_3
2/06/08	0 ppm on coal	Reference	Headwaters silo	1-4	On / None
3/07/08	25 ppm on coal	Background	Headwaters silo	1-3	On / None
3/09/08	25 ppm on coal	Treated	Plant silo # 2	4	On / None
3/12/08	25 ppm on coal	Background	Headwaters silo	1-3	On / None
3/12/08	25 ppm on coal	Treated	Plant silo # 2	4	On / None
3/15/08	50 ppm on coal	Background	Headwaters silo	1-3	On / None
3/15/08	50 ppm on coal	Treated	Plant silo # 2	4	On / None

Sample Collection and Preparation

Background ash samples from the Headwaters silo were collected directly from the silo's loading spout by filling a 55-gallon drum placed underneath the spout. Since no bromine was added to Units 1-3, it was not necessary to allow for any stratification within the ESP that could be reflected in ash materials sent to the silo. However, "treated" samples from the plant silo could indeed represent stratification within the different rows of ESP hoppers. Consequently, samples for testing were obtained by taking a five-gallon sample from each truckload of ash taken to the landfill as the plant silo was emptied, then creating a composite by physically blending these individual samples.

In order to assure uniformity and reproducibility in the laboratory testing, a protocol was developed outlining procedures for sampling and preparation of raw materials contained in the concrete mix prior to batching, procedures for batching of the raw materials and, finally, procedures for sampling and testing of the batched concrete.

The method for preparing ash materials was particularly important. Background and treated ash from each test period were placed in separate 55-gallon drums. To assure uniformity of the fly ash, ash contained in the drum was blended using a paint mixer attached to a hand-operated rotary drill. [3]

Test Procedures

For reference, the following standardized procedures were employed in preparing and testing representative specimens of ash and ready-mix concrete. Most are included in the following list:

ASTM C-136 *Standard Test Method for Sieve Analysis of Fine and Coarse Aggregates*

Ready Mix USA, LLC Mix Designation A41C4020 Commercial 4000

ASTM C-143 *Standard Test Method for Slump of Hydraulic-Cement Concrete*

ASTM C-138 *Standard Test Method for Density (Unit Weight), Yield, and Air Content (Gravimetric) of Concrete*

ASTM C-231 *Standard Test Method for Air Content of Freshly Mixed Concrete by the Pressure Method*

ASTM C-1064 *Standard Test Method for Temperature of Freshly Mixed Hydraulic-Cement Concrete*

ASTM C-403 *Standard Test Method for Time of Setting of Concrete Mixtures by Penetration Resistance*

ASTM C-39 *Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens*

ASTM C-192 *Standard Practice for Making and Curing Concrete Test Specimens in the Laboratory* and ASTM C-666 *Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing*

ASTM D-6722 *Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Direct Combustion Analysis*

ASTM D-5987 *Standard Test Method for Total Fluorine in Coal and Coke by Pyrohydrolytic Extraction and Ion Selective Electrode or Ion Chromatograph* Methods (note -- extraction method adapted for bromine)

ASTM D-5142 *Standard Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures*

ASTM D-4749 *Standard Test Method for Performing the Sieve Analysis of Coal and Designating Coal Size*

RESULTS

The laboratory program consisted of testing the physical properties of three concrete mixes with 25, 25 and 50 ppm of calcium bromide ($CaBr_2$) by weight in fly ash (SC-02, SC-03 and SC-04). Also included were one concrete mix without fly ash or calcium bromide (i.e. straight cement mix: SC-05); one mix without calcium bromide (reference condition before bromine injection: SC-01); and one mix with fly ash plus calcium chloride (a commonly used concrete additive) in lieu of calcium bromide (SC-06). With the exception of freeze-thaw durability, which is still in progress, all test results are presented in the following subsections.

All mixes were prepared according to a standard mix design used by Ready Mix USA for the Plant Miller ash product and designated as *A41C4020 Commercial 4000.* Specifications for this design are: design strength 4000 psi @ 28 days, air content 3-5%, unit weight 147 pcf, and slump 3-5 inches.

Ash Characterization

Looking at a few basic parameters in Table 2 such as LOI and particle size, it appears that the ash is similar from one test condition to the next. Total mercury and total bromine on the ash surface is relatively unchanged among the background samples for all test periods. However, within each set of samples (treated vs. background) for the same injection condition, mercury and bromine levels were higher for the treated ash, indicating that bromide injection results in increased mercury (and bromine) adsorption on the ash. Additional results shown below provide information regarding whether bromine adsorption leads to performance problems with ash used in concrete applications.

Table 2. Key Properties for Plant Miller Ash

Sample Date	Injection Condition	LOI (%)	Total Hg (mg/kg)	Total Br (mg/kg)	Particle Size (% < 45 μ)
2/06/08	0 ppm - Reference	0.33	0.226	3	84.12
3/07/08	25 ppm - Background	0.21	0.186	1	81.21
3/09/08	25 ppm - Treated	0.24	0.355	6	80.52
3/12/08	25 ppm - Background	0.26	0.157	2	86.36
3/12/08	25 ppm - Treated	0.18	0.236	5	82.95
3/15/08	50 ppm - Background	0.24	0.093	ND	85.02
3/15/08	50 ppm - Treated	0.19	0.530	6	77.75

Compressive Strength

Figure 1 clearly shows that concrete strength for the mixes containing brominated ash (SC-02, 03, 04) is the same or only minimally different at all ages when compared to mixes with no bromine (SC-01), no ash or bromine (SC-05), or ash with calcium chloride (SC-06). [3] Further, all mixes at the standard 28-day strength are well above the design value of 4000 psi. For fewer than 15 strength tests, ACI (American Concrete Institute) requires that the average 28-day strength be greater than the specification value plus 1200 psi (4000 + 1200 = 5200 psi). [3] The bar chart shows that the average strength for SC-02, SC-03, and SC-04 is above 6000 psi, so there is no negative effect on strength. Mixes can also be compared based on rate of strength gain, where all mixes continue to gain strength at all ages. Figure 2 has a separate curve for each age across all mixes. [3] The flatness of each line indicates that the rates of strength gain are very similar.

In summary, results show that the addition of calcium bromide, calcium chloride or fly ash had no negative effect on the specified strength of the mix design.

Figure 1. Compressive Strength vs. Curing Time for All Mixes

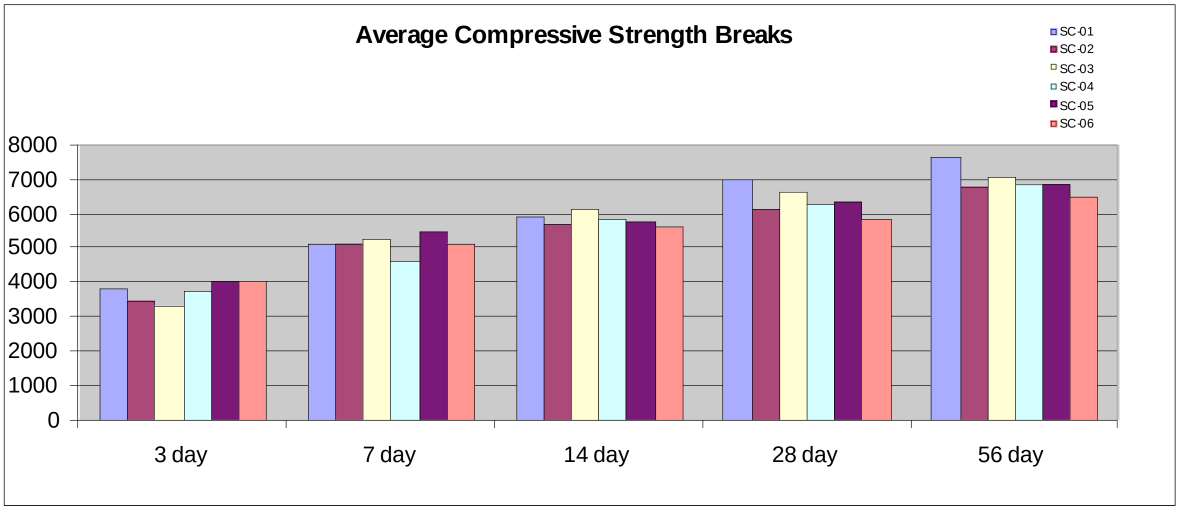
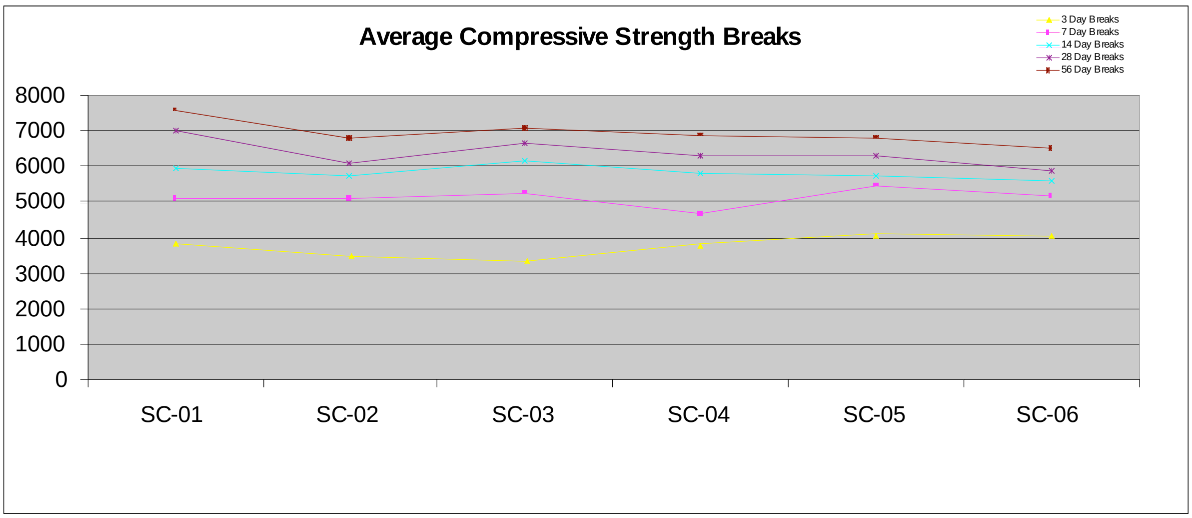


Figure 2. Rate of Compressive Strength Gain for All Mixes



Air Content

The Ready Mix USA design specified an air content between 3 and 5 percent. Table 3 shows that five of the six mixes [3] maintained air content within the specified range without further adjustment of air entraining agents. As noted earlier, proper air content is important to ensure adequate freeze-thaw durability; therefore it is useful to look at these two results together. Unfortunately, freeze-thaw test results are not yet available for this project.   However, at this point, it is safe to say that the presence of calcium bromide on the ash had no appreciable impact on air content of the various mixes.

Table 3. Concrete Mix Properties

Mix	**Air Content (%)**	**Slump (inches)**	**Unit Weight (pcf)**
SC-01	4.8	3.75	148.0
SC-02	4.5	4.25	146.9
SC-03	5.2	3.25	145.9

Slump

Concrete mix slump is indicative of the workability and quality of the concrete product. While three of the mixes in Table 3 had slump values slightly outside the desired range, that is considered a minor issue, especially since compressive strengths showed little variability.

Unit Weight

Unit weight is also an indicator of concrete quality. ASTM C192 states that a series of 10 concrete mixes should not differ by more than 4.1 pcf. Unit weights for the six mixes in this project differed by only 2.7 pcf, indicating that unit weight was not affected by calcium bromide.

Other Properties

Another useful property of fresh concrete is initial and final set time, which indicates the time until hardening takes place. This is important in transport of the mixes, as well as for construction considerations. While not tabulated separately here, it was reported by the lab that initial set times for mixes SC-01, SC-02, and SC-03 ranged from 6 hours, 49 minutes to 6 hours 52 minutes. Final set times ranged from 9 hours to 9 hours, 20 minutes. These tight ranges indicate no significant difference and no effect from calcium bromide on fly ash.

SUMMARY

These project findings indicate that addition of calcium bromide to coal results in some increase of bromide and mercury adsorbed on the fly ash. An evaluation of laboratory results found that subsequent use of the "treated" fly ash in concrete mixes had no impact on the tested physical properties specified in the baseline concrete mix design. This is in agreement with earlier laboratory testing which found that the addition of calcium bromide to mixes containing fly ash had no impact on the air content, compressive strength, set time, slump or unit weight.

REFERENCES

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KEYWORDS

fly ash, bromine, concrete