A Fly Ash Carbon Treatment for Producing a Marketable Product from Activated Carbon Contaminated Fly Ash

Russell Hill, Zhaozhou Zhang and Brian Shaw[1]

[1]Boral Material Technologies, 45 NE Loop 410, San Antonio, TX, 78216

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ABSTRACT

In the near future, utilities are expected to comply with anticipated restrictions on allowable mercury emissions. The current best available practice for mercury capture from flue gas is based on the injection of a powdered, activated carbon. In many cases, the mercury laden carbon will be captured along with fly ash in the ash collection system. This situation leads to ash that is contaminated with small amounts of mercury and varying levels of activated carbon. This paper reports on the performance of a fly ash chemical treatment approach for mitigating against the negative impact that activated carbon has on air entrainment in concrete. The process is based on the controlled application of proprietary chemical formulations to the contaminated ash. The formulations consist of assorted sacrificial agents designed to interact with carbon, and through a number of mechanisms, minimize the carbon's negative influence on air entrainment. This technology is particularly well suited for addressing carbon contamination levels that are too low for the more traditional beneficiation technologies to be effective.

Introduction

In the near future, utilities are expected to comply with anticipated restrictions on allowable mercury emissions. The current favored practice for mercury capture from flue gas is based on the injection of a powdered activated carbon.[1,2,3] In many cases, the mercury laden carbon will be captured along with fly ash in the ash collection system. This situation leads to ash that is contaminated with small amounts of mercury and varying levels of activated carbon. Several studies have suggested that the mercury contamination should not preclude fly ash use in concrete applications; however the activated carbon can be a significant hindrance to ash use in concrete.[4,5,6] Due to its high adsorptive capacity for organics, such as the surfactants used as air entraining admixtures, very low contamination levels of activated carbon can render fly ash unsuitable for use in air entrained concrete. Various fly ash beneficiation technologies already exist for reducing the impact that native ash carbon has on air entrainment performance; however these technologies are typically based on removing carbon from the ash and are most effective when applied to materials with relatively high carbon contents. Their efficiency at remedying ash that may only be contaminated with carbon contents of less than one percent remains questionable. This investigation was conducted to quantify the impact that various powdered activated carbons (PAC's) would have on air entrainment in concrete. Laboratory testing was conducted that was designed to quantify the effects of PAC contamination that might be expected as a result of mercury capture. The performance of different commercial air entraining admixtures in the PAC contaminated mixtures was also investigated, as well as the influence of a number of common concrete chemical admixtures.

The same experimental strategy was pursued to investigate the potential benefit of a new class of chemical admixtures which can neutralize the detrimental influence of carbon on concrete air entrainment. These admixtures, labeled “sacrificial admixtures,” are not air-entraining themselves, and perform through a number of mechanisms including sacrificing to carbon and thereby satiating the carbon's adsorption capacity.[7,8] The present work focuses on the efficacy of a particular combination of sacrificial agents formulated specifically to address the severe challenge of mitigating against PAC contamination. The chemical treatment of the PAC-fly ash with a sacrificial agent is referred to herein as PACT (Powdered Activated Carbon Treatment).

Experimental

Materials

Three samples of commercial-grade PAC, produced by different manufacturers were sourced representing materials actually used in field trials. Select physico-chemical properties are presented in Table 1. Four commercially available air entraining admixtures were selected to represent a cross section of chemistries used in practice. The PACT product tested is a proprietary combination of sacrificial admixtures that was developed specifically for activated carbon.

A Type I low alkali cement was used in all concrete testing in combination with a number 57 limestone coarse aggregate and a siliceous river sand. The fly ash used was derived from the combustion of lignite coal with intermediate calcium oxide content (~12%) and low loss on ignition value (<1%). This ash was specifically chosen for the minimal impact it has on air entrainment.

PAC Contaminated Fly Ash Sample Preparation

PAC contamination levels were reached by adding the appropriate mass of carbon to the raw fly ash and mixing on a spinning drum mixer for a minimum of 24 hours. Mixing adequacy was validated by extracting numerous samples from the treated fly ash drum using a sampling thief. Loss on ignition (LOI) values were then determined with correction for the fly ash inherent LOI value and PAC ash content. The LOI testing was conducted according to ASTM C 618 except the ignition temperature used was 900C.This process was found reliable for producing homogeneous ash samples with the desired level of carbon contamination.

Concrete Mixture Design, Mixing and Testing

Laboratory concrete mixtures were designed based on mixtures containing 517pcy of total cementitious and 25% fly ash by direct replacement. The fine aggregate represented 35% of the total aggregate**.** Air entraining admixture dosages were adjusted as needed to produce multi-point curves typically producing air entrainment values ranging from 3 to 12%.

Concrete mixing was conducted using one and half cubic foot mixtures in a standard rotary laboratory mixer. The mixing sequence was consistent with typical laboratory protocol and followed 3 minutes of mixing, 3 minutes at rest and 2 minutes of additional mixing cycle. The materials were batched in the order of aggregates and partial water, followed by cement and fly ash, followed by admixtures and remaining water to achieve the desired consistency. The water content used was adjusted so that the slump for all mixtures was in the range of 4 to 6 inches. Air testing was conducted in accordance with ASTM C 231 – Pressure Meter B Method. Unit weight measurements (ASTM C 138) were also conducted on each sample.

Results and Discussion

The properties of the PAC are depicted in Table 1. Typical values for fly ash carbon are provided as reference for select parameters. The high BET total surface area for all of the activated carbons relative to fly ash carbon is readily apparent. This is not surprising given that these materials were specifically designed to aggressively adsorb mercury from an extremely dilute gas stream. It is unlikely that all of the PAC surface area measured by BET is available to the relatively large surfactant molecules used as AEA's. The influence of carbon pore size distribution i.e. micro vs. meso porosity is also considered an important carbon property and is under investigation but not reported here. Carbon surface chemistry is also known to significantly influence carbon/adsorbate interaction[9]. Moreover the conditions for adsorption from a liquid phase are also controlled by solute/solution interactions.[10] It is the combined influence of all of these mechanisms that result in the phenomena of adsorption from a liquid phase, the scope of which is well beyond this paper. Rather, in this work we report the net implication of such interactions through their affect on air entrainment.

Table 1

Name	Humidity (%)(1)	S/S (M^2/g)	Ash (%) (2)	Density (g/ml)	C (%)	H (%)	O (%)	N (%)	S (%)	Brominated
PAC-A	8.1	356	26.9 30	2.16	56±1.3	1.2±12	2.1±72	12±5.8	1.4±3.2	Yes
PAC-B	ND	ND	ND	ND	ND	ND	ND	ND	ND	Yes
PAC-C	1.7	639	9.4 15	2.15	79±0.9	0.4±10	0	11±24	1.5±23	Yes

(1) By oven
(2) From TGA analysis

Test results presented in Figures 1 and 2 highlight the influence that commercial PAC's can be expected to have on air entraining admixture demand in concrete. The data indicate that the fly ash only mixture has a relatively minor impact on air entrainment, while all three PAC's decrease air dramatically. The air response curves in Figure 1 show that a high dosage of AEA is required to first presumably fulfill the PAC's capacity for surfactant adsorption, after which additional AEA dosage produces the expected air response. Note however, that the PAC response curves' slopes are generally somewhat reduced relative to the cement only control and reference fly ash mixture suggesting residual impact of PAC on air entrainment through continued adsorption or other mechanisms as reported elsewhere.[11,12] Figure 2 indicates that one percent of PAC contamination will increase the AEA demand 4 to 5 times. The dosage demand curves for PAC contaminated fly ash are generally linear and have a much stronger slope than observed for the fly ash contaminated with native carbon. All of the PACT samples have a strong negative effect on air entrainment, although the PAC-B product is slightly less detrimental. The large increase in air demand combined with the extreme sensitivity to PAC fluctuations will not be manageable by the ready mix concrete industry under most circumstances.

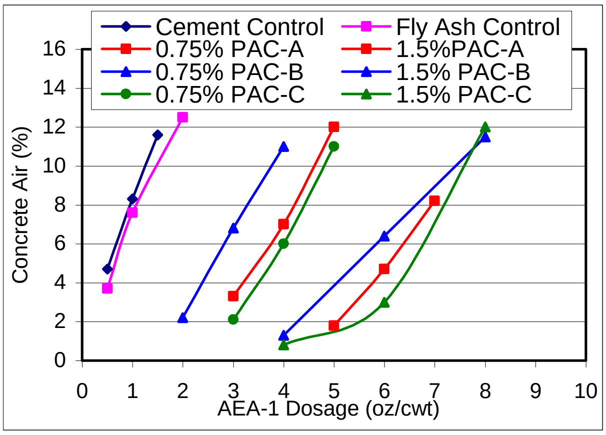

FIG. 1 Impact of Various PACs on Air Response Curves

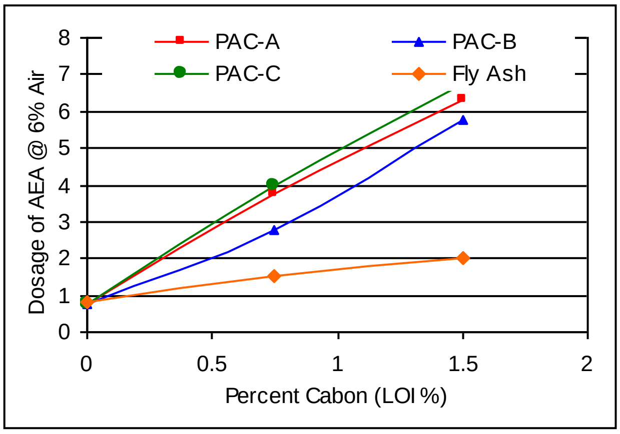

FIG. 2 Impact of PACs on AEA Demand for 6% Concrete Air

Figure 3 presents the results from testing mixtures made with PAC – with various commercial AEA's. Similar results were found for the other PAC samples. The figure reports AEA dosing in terms of ounces per hundred weight of cementitious (oz/cwt) as is common in the construction industry. The same data has been reported normalized to account for the difference in chemical concentration of each admixture in Figure 4. This approach allows one to better distinguish performance differences between commercial products related to chemistry as opposed to concentration. There are a couple of noteworthy points from the normalized data. First, the dosage required to reach what we are calling carbon saturation (the point where one begins to see a response in air content to dosage increase) is much higher for sample AEA-3 than the other products. This implies that at least some of the chemical constituents of this product have a higher propensity to be adsorbed by PAC than the chemicals used to formulate the other products. On the other hand, once the carbon adsorption capacity is apparently satisfied, AEA-3 produces an air response curve that looks similar to that produced by AEA-1 and AEA-4, suggesting similar surfactant/air entraining properties neglecting the impact of carbon. This performance can be contrasted with the behavior exhibited by AEA-2. This surfactant is very similar to products AEA-1 and AEA 4 with respect to the dosage required to saturate carbon; however once this point is reached the air response curve is almost exponential. This volatile behavior is unique to AEA-2 and indicates that this surfactant’s air entraining properties differ from all other AEA’s. These differences are possibly related to AEA chemistry and are being investigated further.

The depiction of data in Figure 3, with no normalization, actually provides a more accurate portrayal of what the concrete practitioner will be faced with in the field. Again we note a large difference in both dosage requirements and air response to dosage adjustments between the various AEA’s. The performance spread seen for various products is exacerbated by the demands imposed by the PAC contamination. This data clearly presents the challenge that concrete producers will face when attempting to utilize PAC contaminated fly ash.

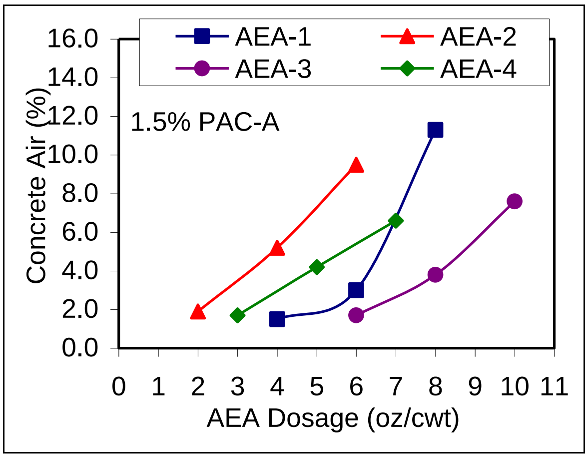

FIG. 3 Concrete Air Response Curves for Various Commercial AEA's Tested with Fly Ash and 1.5% PAC-A

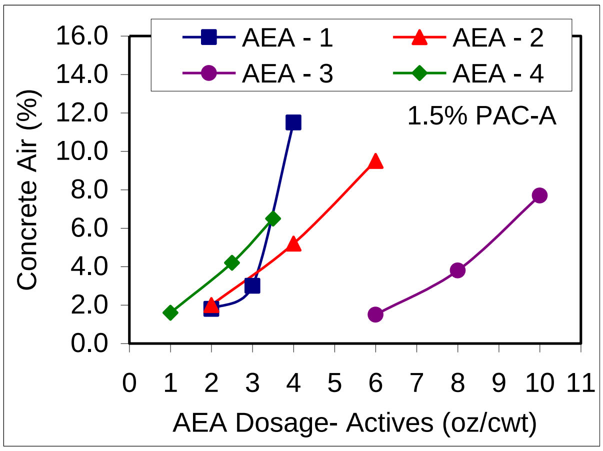

FIG. 4 Concrete Air Response Curves with Data Normalized for AEA Actives Concentration

This situation is further complicated by the use of chemical admixtures as would be common under real world conditions. Figure 5 provides evidence that admixtures such as water reducers will probably reduce the AEA demand for concrete made with PAC contaminated fly ash, however issues may arise around the fact that different admixtures obviously have varying effects on the air response curves and that there are literally scores of chemical admixture products in use.

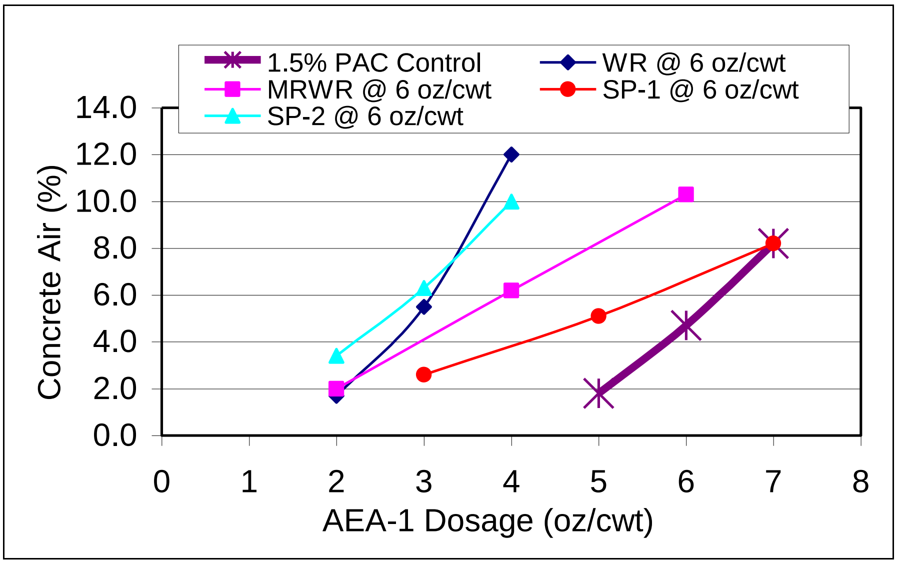

FIG. 5 Influence of Common Chemical Admixtures on Air Response Curves for Fly Ash with 1.5% PACT-A

The forgoing paints a clear picture of the difficulties that PAC contaminated fly ash will create as a raw material for concrete production. Issues surrounding contamination by unwanted residual coal char and air entrainment problems have plagued the fly ash marketing industry for years. This situation was escalated in the mid 1990's when many utilities converted to low NOx combustion technologies that typically increased carbon contents in fly ash. In response to increased quality challenges, new research was conducted to investigate air entraining issues in the late 1990's and early 2000.[13,14,15] A number of fly ash beneficiation technologies were proposed as a means for improving ash quality. A few of these technologies have been successfully commercialized over the last decade including carbon reduction by thermal and triboelectic means and carbon passivation by chemical means.[16,17,18]

With respect to PAC contamination, the practicality of removing relatively small quantities of carbon from ash by segregation is questionable. Moreover, a beneficiation system based on carbon removal would have to be extremely efficient because any residual carbon not removed would continue to represent a substantial problem. Carbon reduction by combustion is plausible, but many of the thermal processes rely on high fly ash-carbon content to serve as a fuel to sustain the combustion process. Activated carbon contamination levels will vary, but typically result in less than 3% additional carbon, thus this technology would be limited only to ash sources that already contain relatively high carbon contents.

Carbon modification by chemical means offers an advantage in this situation since it can be applied to treat low carbon contents on an as-needed basis and at the dosage level required to meet the performance requirements of the ash at a given time. This technology was commercialized in 2003 by Boral as FACT™ (Fly Ash Carbon Treatment) and has been successfully demonstrated in the field on over 2.5 million tons of ash. The drawback to this technology is that it does not remove carbon, but reduces its impact on air entrainment through a number of mechanisms including "sacrificing" to satiate the fly ash-carbon's adsorption capacity. The special chemicals used as sacrificial admixtures are unique in the fact that they are highly attracted to carbon but have little impact on air entrainment (not surfactants) or cement hydration properties. It is this technology's lack of intrinsic air entraining properties that allows it to be used in practice. In the plant, the material is applied to the flowing ash stream in the form of an atomized spray as the ash is being loaded into the transport truck for delivery. The correct dosage is controlled through application software and is initially determined based on performance testing. Because the chemicals react strongly with carbon but have little influence on other performance issues, including air entrainment, the standard dosage is based on the worst case carbon scenario for a particular plant. This provides a safety factor should the ash quality vary more than expected and makes the technology practical for real world applications.

Initial attempts to utilize FACT technology to treat PAC contaminated fly ash quickly identified a real performance gap (Figure 6). The technology showed promise for only very low levels of PAC contamination (<1%). Clearly an improved approach was needed. After two years of research that involved screening over 85 specially selected chemicals, and running over 1000 concrete trial batches, a new formulation was derived that was tailored to address the more demanding performance requirements of activated carbon. This technology was identified as PACT – Powdered Activated Carbon Treatment.

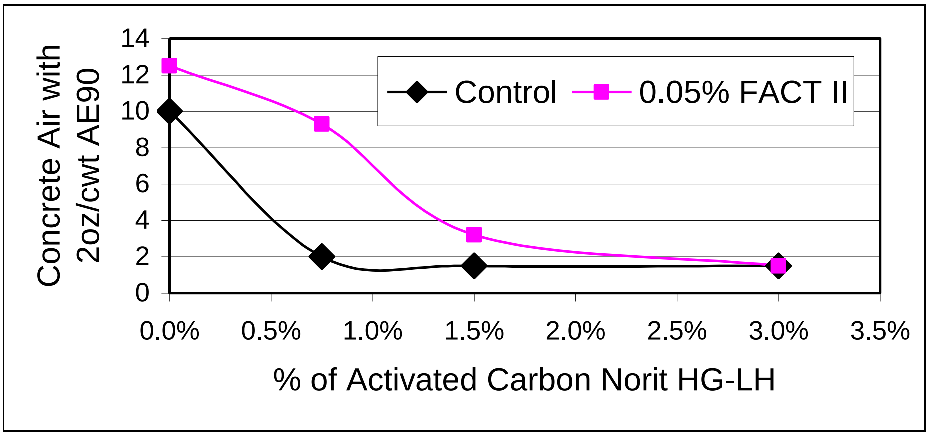

FIG. 6 FACT Performance with Fly Ash Containing Various PAC Concentrations Relative to Untreated Ash.

The effectiveness of PACT is demonstrated in Figure 7 where the PACT treated samples' performance was improved to match the targeted zone. The target zone represents what one should expect for concrete made with uncontaminated fly ash. Treatment with this formulation is seen to be effective for samples with higher than 3% activated carbon contamination, a level which would certainly be untenable otherwise. Figure 8 displays how the use of PACT minimizes the influence of varying PAC concentrations on air entrainment. Results varied by less than 2% in air content over a PAC contamination range of 0 to 3%. This compares well to the large variation (>9%) of the same mixtures without treatment. These results demonstrate that this new technology addresses the two primary issues associated with activated carbon contamination.

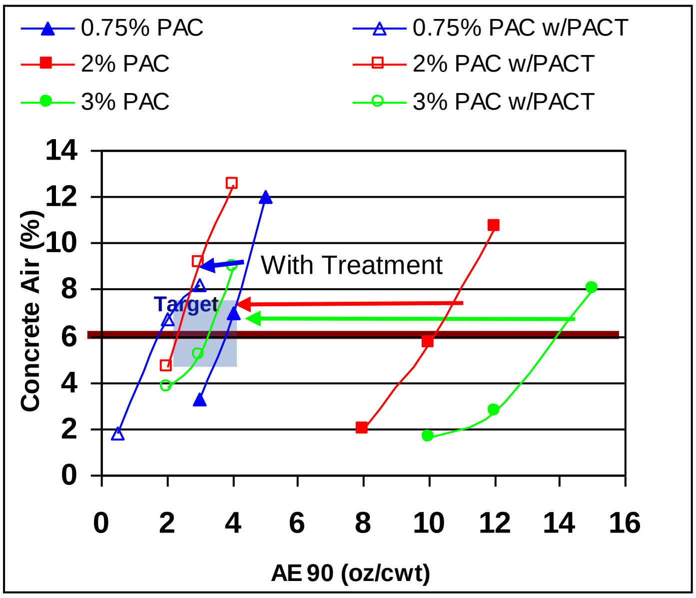

FIG. 7 PACT reduces AEA demand to acceptable levels.

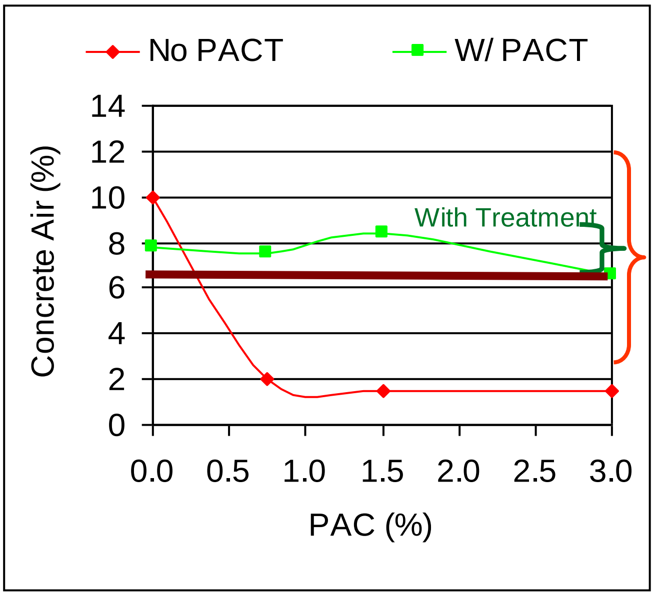

FIG. 8 PACT reduced the impact of varying carbon.

Conclusion

The commingling of powdered activated carbon in fly ash will have severe consequences for ash use in air entrained concrete. Small levels of contamination (<0.5%) are likely to render the ash unmarketable in many markets. Beneficiation by treatment of the ash with formulated compositions consisting of proprietary ingredients including sacrificial admixtures offers a practical means for making PAC contaminated fly ash marketable. One technology, identified as PACT, was shown to be effective at carbon contamination levels as high as 3%. The air entraining admixture dosage demand for the treated samples is comparable to uncontaminated fly ash. The variation in air content as a single air entraining admixture dosage caused by varying PAC contamination levels from 0 to 3 percent was less than 2%. This range of air fluctuation was far less than the variation seen in the untreated samples and would be consistent with the type of variation seen in the field for standard concrete mixtures.

This product is an improvement of a technology that has been in place for over six years designed to address fly ash-carbon issues. The new technology shows considerable promise as a practical beneficiation technology for powdered activated carbon contaminated fly ash. Additional work is underway to validate air void parameters, freeze/thaw performance, and other criteria and to prepare the technology for full commercialization.

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