Beneficiation and Utilization of Fly Ash Containing Mercury Impregnated Activated Carbon

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ABSTRACT

Mercury emission control technologies are being installed at various coal-fired power plants across the nation. The most promising mercury control technology employs activated carbon injection into the flue gas to adsorb the mercury; thus, causing the fly ash collected at the power plant to be unusable for concrete applications. In response to this, Ceramatec and its colleagues have successfully developed a chemical-encapsulation process for beneficiating the fly ash for continued use as a partial portland cement replacement in concrete applications. Ceramatec's process works effectively for both Class C and F ash types. Our research has demonstrated that the encapsulation mechanism not only prevents the adsorption of air-entraining agents added to concrete mix designs, but encapsulation also provides an extra barrier layer to prevent the leaching of the captured mercury. Consequently, this new treated ash is not environmentally hazardous, and it does not interfere with the functionality of the organic additives common to concrete mix designs.

INTRODUCTION

More than half of the electricity generated in the U.S. is produced by coal-fired facilities. These power plants produce about 125 million tons of coal combustion products (CCPs) annually, including fly ash, which is the non-combustible mineral portion of coal.[1,2] The production of CCPs has been increasing in step with the increasing demand for electricity, creating a more urgent need to minimize the impact of these waste products on the environment. Fly ash has seen increasing use as a partial replacement for portland cement in concrete for over 30 years (~14 million tons annually in 2007),[1,3] because there are several significant benefits to using fly ash in concrete:

1. For power plants, it reduces disposal costs while actually increasing revenues through the sale of fly ash;
2. For concrete manufacturers, it can dramatically improve product performance (higher strength, decreased permeability, increased durability, better workability, etc.) while actually reducing costs, since the fly ash is less costly than portland cement; and
3. For the benefit of society at large, greenhouse gas emissions are reduced by minimizing the production of portland cement, while the number of landfills needed for the disposal of fly ash is also reduced.

The EPA and/or state legislatures intend to control mercury emissions from coal-fired electric utilities, and enforcement is expected to begin in 2009 for some areas of the US.[1] For the majority of coal-fired power plants without scrubbers, the most mature retrofit technology available today for Hg-control is the injection of sorbents such as powdered activated carbon (PAC) into the flue gas upstream of the particle control devices (PCDs).[4] After injection, existing particle control equipment (either an ESP or a fabric filter) will collect the mercury-containing sorbent along with the fly ash. Generally speaking, however, the fly ash collected after activated carbon injection for mercury control, will not only have a much higher mercury content (a few µg/g to ~100µg/g), but also an increased carbon content (potentially up to ~30wt%), when compared to conventional fly ash. Unfortunately, the utilization of activated carbon injection technology for Hg-control has several negative impacts on the potential use of fly ash in concrete including:

1. Fly ash samples with even low concentrations of activated carbon will adsorb organic molecules (particularly air entraining agents (AEAs)) added to concrete mix designs; and
2. The effect of increased carbon content on the strength characteristics of the concrete material is relatively unknown at this point.

It is well known in the industry that most fly ash materials contain a certain amount of natural unburned carbon from coal combustion. And over the last 30 years concrete industry professionals have adapted their concrete mix designs to enable the incorporation of fly ash with unburned carbon into the concrete mix. Despite this, fly ashes with carbon contents higher than 1 - 2% (measured by loss on ignition, LOI) are not typically used in concrete applications due to poor performance of the concrete mix.

Therefore, the inclusion of activated carbon (in addition to the unburned carbon) to the fly ash will dramatically impact the performance of the concrete mix designs. This is primarily due to the fact that activated carbon has significantly higher adsorptive capacity, when compared to unburned carbon, due to its high surface area and porosity. Therefore, injection of activated carbon for mercury control essentially eliminates the use of fly ashes for concrete applications.[5] Hence, there is an urgent need to develop novel, high-volume beneficiation technologies for fly ash containing activated carbon from mercury control technologies to ensure the continued use of fly ash in concrete.

In response to this problem, Ceramatec has worked with the DOE (Phase II SBIR) to develop an encapsulation method for treating the fly ash to mitigate the deleterious effects of the mercury and activated carbon, which are captured with the fly ash materials of interest. Ceramatec has demonstrated that the encapsulation process can prevent the adsorption of intentionally-added organics, particularly AEAs, in concrete mix designs. Furthermore, this encapsulation process provides a barrier layer around the Hg-laden carbon; thus, further preventing the leaching of the adsorbed heavy metals.

EXPERIMENTAL

Ceramatec is developing a chemical-based treatment process for the remediation of fly ashes containing elevated amounts of activated carbon and mercury from coal-fired power plants. The chemical treatment process is proprietary to Ceramatec, and has been applied for patent protection. The treatment process involves the addition of an aqueous-based chemical additive to the high-carbon fly ash material. Once the solid and liquid components are thoroughly mixed, the slurry is then re-granulated to a powder form by drying the slurry. After re-granulation, the dried powder can be used in concrete applications in an identical manner as current materials in concrete applications.

Foam Index Test. The foam index test is used to determine the interference effects of carbon in fly ash on the amount of air-entrained in concrete. Added organics to concrete mixes typically include air entraining agents (AEA) that help to stabilize microscopic air bubbles within the concrete mix. The foam index test determines the amount of AEA needed for concrete mixes containing fly ash materials. Foam index testing at Ceramatec is performed by adding 16 g of ordinary portland cement, 4 g of fly ash, and 50 mL of DI water to a 125 mL glass jar. This mixture is shaken by hand for 1 minute. The AEA (Darex II, Grace) is diluted 1:20 using DI water, and it is added dropwise to the jar. After each addition the jar is capped and shaken for ~15 seconds, then the foam layer is observed. The minimum amount of AEA needed to form a stable foam layer (e.g. bubbles exist over entire surface) for 45 seconds is the FOAM INDEX SCORE (FI) of the cement mixture.

Compression Testing. Compression tests were performed on cement, mortar, and concrete mixtures using several sources of fly ash. Compression strength specimens were cast into cylindrical molds (4” dia. × 8” tall) or into 50 mm cubes. The specimens were tested using an Instron mechanical testing apparatus, and were performed at a local independent concrete test facility (CMT Engineering, Salt Lake City, UT).

RESULTS and DISCUSSION

Several samples of high-carbon fly ashes from various DOE-sponsored mercury-control experiments were obtained for testing using our chemical treatment process. Each of the incoming samples were measured for: 1) carbon interference using the foam index test, 2) average surface area, 3) mean particle size, and 4) chemical analysis (including mercury content). The testing results for the as-received samples are shown in Table 1.

Table 1. Foam Index Testing Results of Incoming Fly Ash Samples

Fly Ash ID	Si-Al-Fe Total wt%	Surface Area (m^2/g)	LOI wt%	Foam Index Avg.	Hg ug/g
1	63.4	10.66	2.5	99	1.1
2	83.3	2.20	1.82	43	11.7
3	71.8	14.64	3.37	330	17.5
4	64.1	42.06	11.38	918	6.5
5*	N/A	11.02	20.33	162	N/A

*Sample contained only unburned carbon material

Table 1 also shows the measured LOI values for each fly ash received. Fly ash samples 1 – 4 were from activated carbon injection experiments, whereas sample 5 only contains natural unburned carbon collected with the fly ash. Figure 1 is a plot of the foam index score as a function of the measured LOI, which does not follow a linear behavior due to the high adsorptive capacity of the activated carbon. This implies that in the age of Hg control via activated carbon injection, LOI is no longer suitable for predicting the impact of various fly ash materials on concrete performance. We have

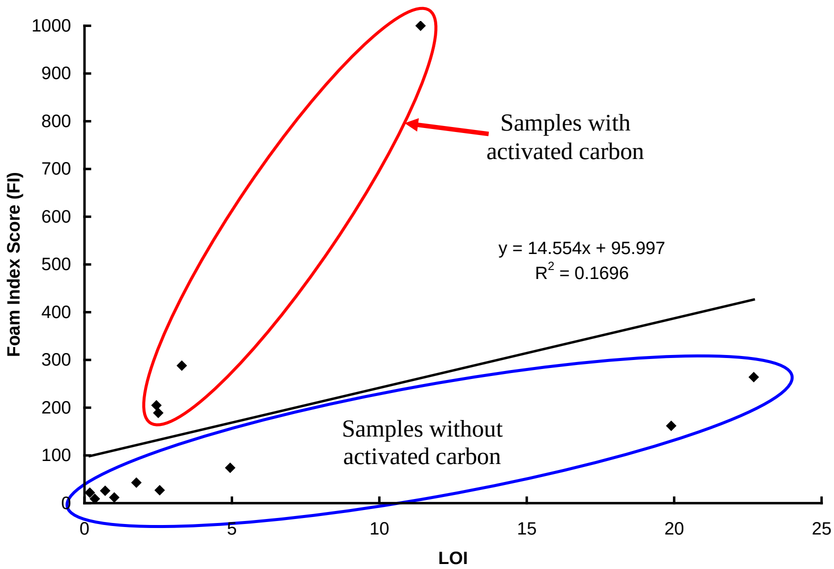

Figure 1. Foam Index Score as a function of LOI in fly ash samples.

found that a more accurate way to predict the foam index score of a particular fly ash sample containing activated and unburned carbon is to plot foam index score as a function of measured surface area.

Figure 2 shows a plot of foam index score as a function of particle surface area. The linear fit results obtained for numerous samples of fly ash show very nice correlation. Using this analysis allows us to quickly estimate foam index scores that are irrespective of the type of carbonaceous materials contained within the fly ash materials.

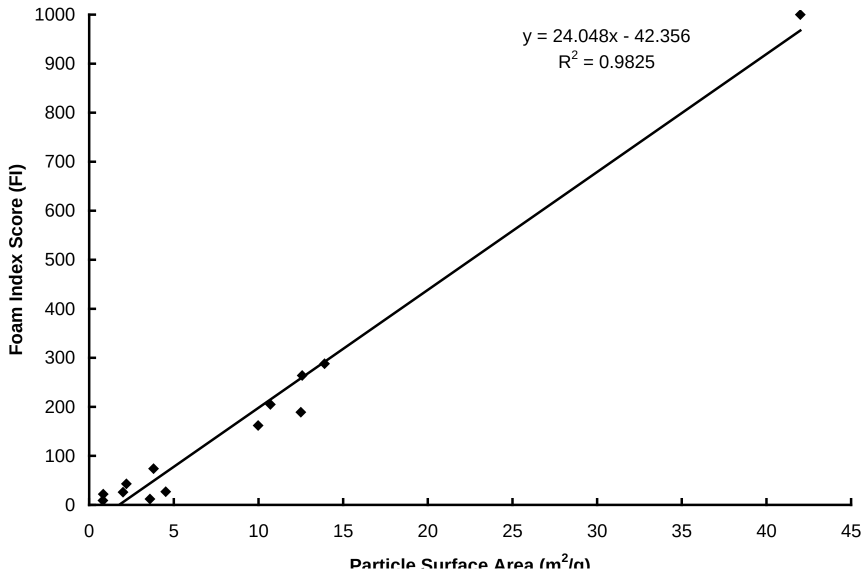

Figure 2. Foam Index Score as a function of particle surface area.

Ceramatec Treatment Process. Ceramatec's proprietary treatment process is a *chemical* treatment process designed to encapsulate the carbonaceous material to prevent adsorption of the organic molecules added to the concrete mix. For each of the fly ash samples obtained, the treatment solution was thoroughly mixed with the fly ash to form a slurry. After mixing, the slurry was injected into a labscale spray dryer with an inlet temperature of 200°C and an outlet temperature of 100°C. The dried powder was

Table 2. Foam Index Testing of Fly Ash Samples After Applying Ceramatec's Treatment Process

Sample Number	LOI (%)	Foam Index (Before)	Foam Index (After)
1	2.5	98	16
2	1.8	43	8
3	3.3	288	17
4	11.4	918	90
5*	20	162	32

then foam index tested to quantify the degree of encapsulation of the carbon material. The resulting ash had a moisture content of ~1%. Table 2 shows the results of the post-treatment foam index testing. Table 2 shows that for our treatment process that the foam index score decreases by an average of ~85%, relative to the untreated fly ash samples. These results are important because this shows that by chemically treating the fly ash, the negative impact of carbon can be minimized; thus, allowing the fly ash to be beneficially used in concrete applications despite the high-carbon content.

Concrete Tests Using Treated Fly Ash. To verify that the performance of the concrete is not degraded when adding the high-carbon treated fly ash to a concrete mix, we started by fabricated samples of mortar cubes (50 mm) for compression testing. Cubes were fabricated according to practices outlined in ASTM C311. Three samples of each type were fabricated by mixing sand with various cement mixtures. The cement mixtures studied were: 1) 100% portland cement (PC), 2) 80% PC – 20% commercially available class C fly ash (FA), and 3) an 80% PC - 20% treated Class C fly ash containing activated carbon (TFA). Figure 3 shows the results of the compression tests for these samples, where the black bars represent samples made using 100% PC, the blue bars represent an untreated low-carbon class C fly ash typically used in the concrete industry today, and the red bars represent treated fly ash containing high carbon content from mercury control experiments. The compression tests were recorded after 7, 28, and 56 days of curing in a humidity and temperature controlled chamber. Figure 3 clearly shows that the fly ash samples (treated or untreated) have similar compression test values after 7 and 28 day cures. These mortar cube samples

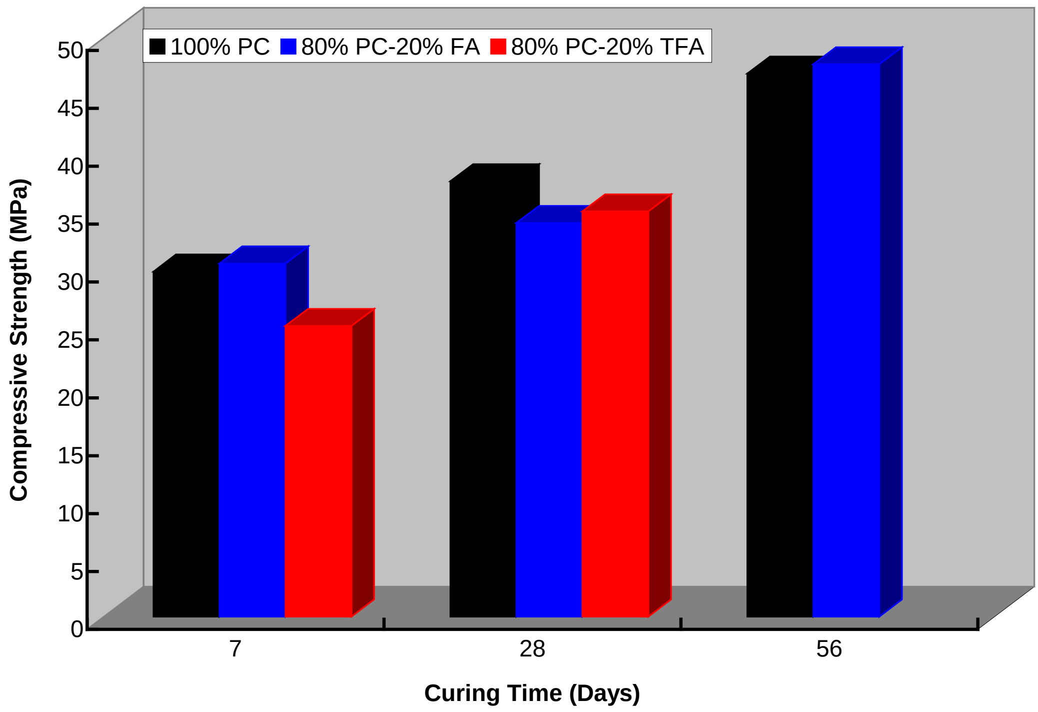

Figure 3. Compression testing results for 2" mortar cubes for a) 100% portland cement mix (black), b) 80% portland cement with 20% untreated fly ash (blue), and c) 80% portland cement with 20% treated fly ash (red).

were made using the treated ash from sample #1 (Table 2) only. The important thing to note here is that using a high-carbon fly ash did not show any reduced compressive strength of the mortar cube. However, significantly more testing is required using treated fly ash samples from many more power plant sources to fully demonstrate this technology. In addition we must expand our testing to include concrete cylinders that contain varying amounts of the treated fly ash in the concrete mix design.

CONCLUSIONS

Ceramatec has demonstrated the ability to chemically treat fly ashes with high carbon contents for use in concrete applications. The treatment process works with natural unburned carbon or injected activated carbon for mercury control. The treated ash materials show good foam index scores, and increased compressive strength in mortar and concrete tests.

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