CONCRETE APPLICATIONS USING HIGH-CARBON FLY ASH FROM THE TOXECON™ BAGHOUSE

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ABSTRACT

We Energies and DOE, under a Clean Coal Power Initiative (CCPI) program, have been working together since 2004 to design, install, evaluate, and demonstrate the EPRI-patented TOXECON™ air pollution control process. The primary goal of this project was to reduce mercury emissions from three 90-MW units that burn Powder River Basin coal at the We Energies Presque Isle Power Plant in Marquette, Michigan. This goal was accomplished by injecting powdered activated carbon (PAC) upstream of the TOXECON™ baghouse, resulting in a very high LOI PAC/fly ash mixture. A secondary goal was to evaluate methods to utilize 100% of their fly ash.

Fly ash has long been used as an admixture for concrete. Utilization of fly ash material in concrete turns a coal combustion by-product into a useful material reducing energy needed to produce concrete, reducing the use of portland cement in the mix, and improving the workability of concrete without dramatic changes to the rate of set and/or early strength. During the CCPI project, different options for utilizing concrete made with PAC-laden ash were evaluated. Results will be presented from concrete made with the TOXECON™ PAC/ash mixture using Miracon Technologies' proprietary foam air entrainment chemical.

INTRODUCTION

Fly ash is commonly used in numerous applications, primarily as a substitute for portland cement in concrete manufacturing. In 2007, 31.6 million tons of fly ash were beneficially used, and of that amount 13.6 million tons were used in concrete, concrete products, and/or grout manufacturing. The remainder was used to make flowable fills/embankments, raw feed for clinker, mining applications, waste stabilization, and other applications.

Two classifications of fly ash are produced, depending on the type of coal used. Anthracite and bituminous coal produce Class F ash. Class C fly ash is produced from lignite or subbituminous coal. Fly ash can be cementitious or pozzolanic, or both. Class F fly ash is pozzolanic while Class C ash is cementitious and pozzolanic. Cementitious fly ash hardens when wetted while pozzolanic ash requires a reaction with alkali (lime) before hardening. This is why Class C fly ash is used as a partial cement replacement in making concrete.

Fly ash also affects the plastic properties of concrete by improving workability, reducing water demand, reducing segregation and bleeding, and lowering the heat of hydration. Fly ash also increases strength, reduces permeability, reduces corrosion of reinforcing steel, increases sulfate resistance, and reduces alkali-aggregate reaction.

Full-scale activated carbon injection for mercury control is becoming more common in the utility industry, but this can have a significant impact on ash sales for concrete due to the carbon content. In order to create structural concrete suitable for exterior applications, concrete must be able to withstand multiple freeze-thaw cycles. This freeze-thaw durability is obtained by the introduction of numerous small air bubbles in the concrete. The carbon content of fly ash has a negative effect on most air entrainment additives (AEA), resulting in increased cost for additional chemical and, more importantly, unreliable batching operations, which generates significant material and labor cost increases.

Under the CCPI project at Presque Isle Power Plant (PIPP) ADA-ES led an effort to develop new approach to using PAC-containing ash for concrete manufacturing. This method utilizes the combination of a specific batch design (developed by ADA-ES) with a foam-based AEA that was modified specifically for this application (developed by Miracon™ Technologies, Inc.). This combined technology was tested on concrete mixtures with ash containing <1% to as much as 30% Loss on Ignition (LOI) from PAC. A successful field demonstration using 30% LOI ash to make a large concrete pad at the Presque Isle plant was completed in June 2009.

EXPERIMENTAL

Concrete batches were prepared in the laboratory using a variable speed mixer (Fig. 1) to evaluate the affect of different formulations on key concrete properties. Variables included the amount of cement, fly ash, LOI in ash, water/cement ratio (w/c ratio), and commercial admixtures. The coarse and fine aggregate were from a local supplier and were kept constant for all of the tests except for those in preparation for the Presque Isle field demonstration, which used aggregate from the Marquette, Michigan, area. Each batch was 1.3 ft^3.and preparation included a mixing phase at 20 rpm until the , simulating the mixing speed in a truck, followed by 60 to 90 minutes at “transit speed,” or 4–5 rpm, simulating the speed used during transit to the job site. Cylinders from successful batches were tested at independent laboratories for compressive strength. Hardened Air Void (HAV) tests were performed on select batches to determine the size and spacing of the air bubbles, which is a predictor of freeze/thaw durability.

Fig. 1. ADA-ES variable-speed concrete mixer.

RESULTS AND DISCUSSION

Laboratory Testing

Fig. 2 shows a comparison of compressive strength results using Micro-Air® (liquid) AEA and Miracon™ (foam) AEA. Three ash LOI values were tested at a 20% cement replacement; 0.7% (control), 5%, and 30% LOI. The unit amount of AEA was normalized to the amount used in control batches, which varied for each AEA. The 5% LOI ash tests show high strength (> 6000 psi after 21 days) for both the Micro-Air® and Miracon™ AEAs. The main difference between the two AEAs was that usage varied significantly. Miracon™ required no increase in dosage with increased LOI compared to the control, while the Micro-Air® required six times the amount needed for the control batch. The 30% LOI tests with Miracon™ required 7–12 times more AEA than the control, compared to a test with Micro-Air® that required up to 250 times more (not shown) and was considered a failed batch. The air content was stable for 90 minutes, which is sufficient for most field applications. The w/c ratio varied in the tests, shown in the Fig. 2 legend, and was the major factor in strength variability between the batches. The same strength data from Fig. 2 is provided in Fig. 3, but with the w/c ratio on the x-axis to demonstrate the effect of w/c ratio. In general, higher air content results in lower strength concrete. Hardened Air Void (HAV) tests on batches at 5% and 30% LOI showed good air void size and spacing, passing the criteria for freeze/thaw durability.

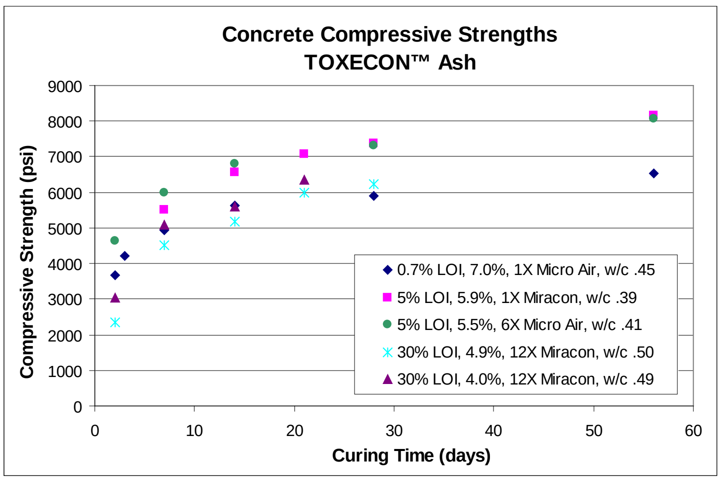

Fig. 2. Concrete compressive strength results.

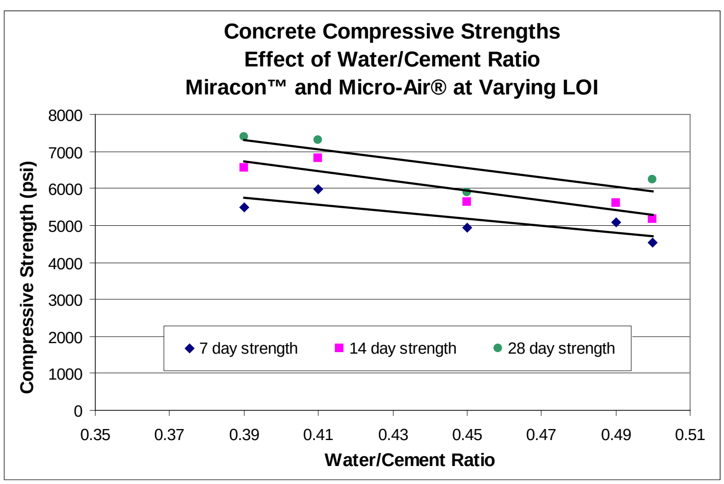

Fig. 3. Effect of water/cement ratio on compressive strength.

Field Testing—Sky Ute Sand & Gravel

The first field test using the new foam and batch design was performed in the first week of January 2009 at Sky Ute Sand & Gravel in Farmington, New Mexico. Two drums of TOXECON™ ash were shipped to the site for testing. The ash was blended with water in order to minimize dusting and to allow exact additions of the ash to the truck (Fig. 4). The batch size for these field tests was 4 cubic yards each. This was considered the minimum amount that could be used in a truck and still have representative mixing.

Fig. 4. TOXECON™ ash added during concrete mixing.

There were water dosage issues with the first two batches so they were discarded (i.e., either too wet or too dry). Either condition results in poor air retention. A 2% LOI blend on the second day had sufficient air content (5.6%) and slump (6") so cylinders were made for compressive strength testing. Fig. 5 shows the strength data through 28 days. The strength at 28 days was very good and was well above the targeted level of 4500 psi. The HAV data showed a reduction in the air content (3.8%) indicating that the air may not have been stable during curing. This issue was addressed with a new admixture formulation that was used in the second field test at Presque Isle.

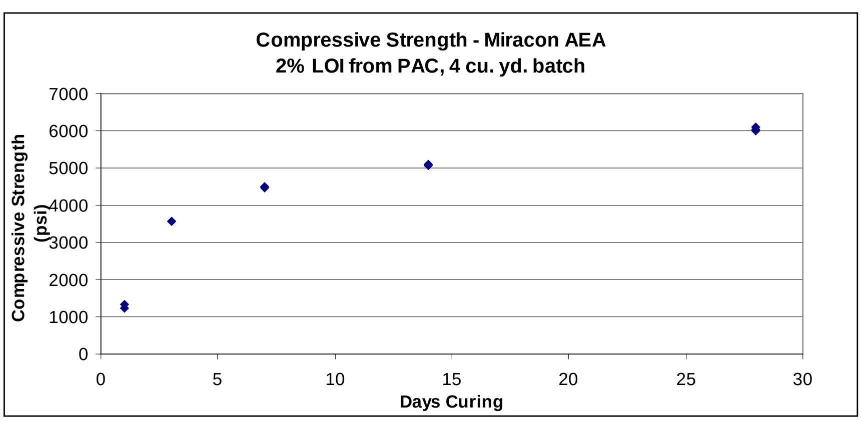

Fig. 5. Compressive strength data—field test at Sky Ute Sand &Gravel.

Field Testing – Presque Isle Power Plant

A new batch design was tested and finalized before the second field test, which was conducted at PIPP. This batch design addressed some of the issues observed during the first field test. The second field test was a full-scale demonstration of the combined technology to generate high-strength, durable concrete using a 30% LOI ash at 18% cement replacement. The TOXECON™ ash was used in the concrete blend to make a 30' x 50' x 1' concrete pad for bottom ash dewatering. The pad was designed for freeze/thaw durability and high strength (6000 psi) so that it could withstand heavy equipment use.

A push wall and footer were installed in May 2009 using standard low-carbon concrete. This was installed early so that both footer and push wall would have sufficient time to cure before the high-carbon concrete was placed. Excavation and subsequent backfilling around the footer and wall were needed before the supporting steel for the pad could be installed. Fig. 6 shows the completed push wall and steel for support of the pad.

Fig. 6. Completed push wall and support steel for high-carbon concrete pad.

Once the push wall and steel installation was complete, the high-carbon concrete pad was placed in June 2009. Ash from the TOXECON™ silo was loaded into a 1550-gallon poly tank using the dry unloader (Fig. 7). The ash was then transported to Fraco Concrete Products, Inc., the ready mix plant in Marquette where the concrete batching was taking place.

Fig. 7. Unloading dry TOXECON™ ash for concrete.

Because of the dusty nature of the ash, possible variability in LOI, and difficulty delivering the exact amount of ash into each truckload, water was added to the tank and a slurry formed. The dry ash was tested for LOI and moisture so that an exact amount of ash equivalent to a 30% LOI dry ash blend could be dispensed into each truck. The dry ash from the silo was 42% LOI, so low-carbon ash from the ESP was added to each truckload of concrete to “dilute” the high-carbon slurry to form the equivalent of a 30% LOI ash. The final combined ash at 30% LOI replaced 18% of the cement in each truckload. The actual cementitious replacement value was 10% due to the fact that only a little over half of the final ash blend had cementitious and pozzolanic properties. The other 8% by weight was PAC.

After the water was added to the dry TOXECON ™ ash at Fraco, a TM 2000 series pneumatic mixer from Pulsair Systems Inc. was used to mix the material into a slurry. The Pulsair mixer sends pulses of high-pressure air into the liquid to break up solids and keep them in suspension.

Test batches of 4 cubic yards each were made to test the batch design and Miracon™ AEA at full-scale conditions. The first batch was too dry and would not hold the air so it was discarded. The second batch was within specifications so it was transported to PIPP and placed in the drainage area between the pad and the settling pond (Fig. 8). The wet concrete had good workability and showed no unusual properties compared to low-carbon concrete.

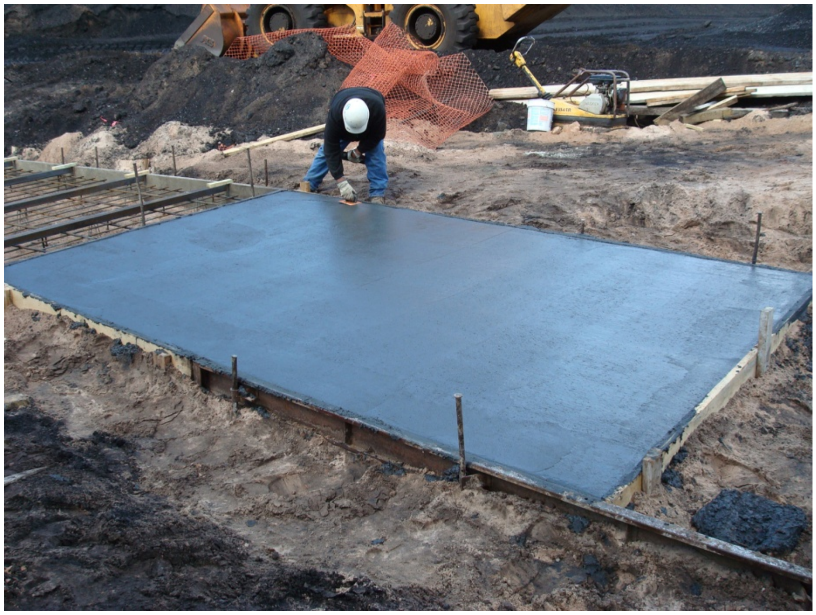

Fig. 8. First successful high-carbon concrete placement.

The following day, a third 4-yard batch was generated then placed in the drainage area. Two nine-yard batches were then generated to complete the drainage area (Fig. 9). All batches for the drainage area after the first one were successful.

Fig. 9. Completion of the drainage area with high-carbon concrete.

On Thursday, June 4, the large pad was placed using 7 9-yard truckloads of concrete. Batch #2 showed high slump, which resulted in high air due to entrapment. This may have been due to residual water in the truck. All other truckloads showed air and slump within specifications. The pad was completed by 6:00 p.m. Thursday and covered with plastic to prevent shrinkage cracking. Fig. 10 shows the pad the next morning after the forms had been removed.

Fig. 10. Completed high-carbon concrete pad after the forms were removed.

Cylinders from each truckload were taken for testing compressive strength, air void characteristics, and rapid chloride permeability. Fig. 11 shows the results from compressive strength testing through 56 days. The average compressive strength for the pad was 6646 psi at 28 days, which exceeded the design specification of 6000 psi. One batch (#2) showed air content above specifications, resulting in lower strength for that truckload of material. The average compressive strength for the pad was 6690 psi at 56 days, indicating that there was not significant strength increase after 28 days.

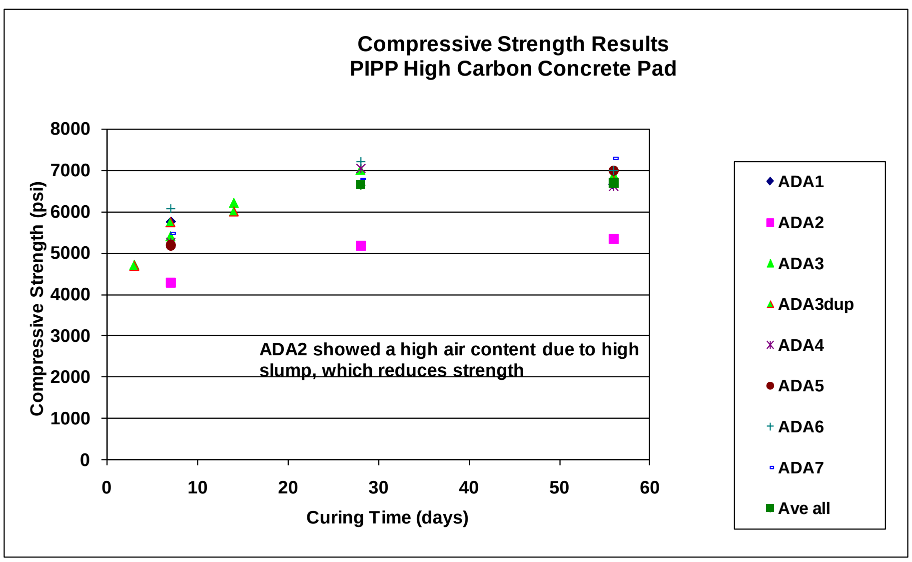

Fig. 11. Compressive strength results for high-carbon concrete pad.

Once the compressive strength results showed that the pad was above design specifications, the plant began to use it for bottom ash dewatering. Fig. 12 is a picture from September 2009 showing the ash pile and drainage area. There were no visual indications of problems with the pad.

Fig. 12. High-carbon concrete pad used for bottom ash dewatering.

Two cylinders were sent for HAV analysis and two for Rapid Chloride Permeability testing. One cylinder sent for HAV testing was from the high air batch (#2) and the other was from batch #3, which had the lowest air content. **Table 1** outlines the result of these tests. The HAV air content was significantly lower in batch #3 than the value from the field. The HAV value from batch #2 was also lower but not as significantly. The average air content measured in the field was 4.8%, which was within the target range. The spacing factor measurement was excellent for batch #2, but was out of range for batch #3. The larger air bubbles seen in batch #3 were not typical compared to previous HAV results from laboratory batches.

Table 1. Hardened air void results from field test.

Parameter	**Batch #2**	**Batch #3**	**Target**
Air Content – field (%)	10.3	4.6	4–8%
Air Content – HAV (%)	9.9	3.2	4–8%
Spacing Factor (inch)	0.004	0.010	<0.008
Specific Surface (in^2/in^3)	702	639	>600

Rapid chloride permeability testing was performed on two cylinders (batches #5 and #7) from the field test at PIPP. This test is used to determine the resistivity of concrete, which is then correlated to permeability. Low permeability is preferred for most applications. The cylinders were cured in a temperature and humidity controlled fog room (as were the cylinders for HAV). The cylinders were tested in general conformation with ASTM C1202 “Electrical Indication of Concrete’s Ability to Resist Chloride Ion Penetration.” The results showed high chloride ion penetrability at 6280 and 6890 coulombs. This result was not surprising due to the conductive nature of activated carbon particles. Tests conducted in the ADA-ES laboratory in 2008 on high-carbon concrete showed an increase in electrical conductivity compared to low-carbon concrete. This characteristic of high-carbon concrete has been investigated for many years at We Energies and other institutions. What is unknown at this time is the actual effect of the increased conductivity on the life of the concrete. It is accepted in the industry that the presence of ionic species and other additives can affect the test while not affecting the actual permeability of the concrete. Also, these particular samples represent the extreme end of PAC-containing ash in concrete applications. More typical ash with 1–2% LOI would likely not see this effect.

Concrete and Ash Leaching Results

Fly ash and concrete samples were tested using Method 1311 Toxicity Characteristic Leaching Procedure (TCLP) and Method 1312 Synthetic Precipitation Leaching Procedure (SPLP). Four concrete samples were crushed and sieved to Number 6 aggregate size (3/4" to 3/8" diameter) according to ASTM C33 "Standard Specifications for Concrete Aggregates." This size was chosen because it is common for concrete reused as an aggregate. A low-carbon concrete made using ESP ash from PIPP was used as the control. A low-PAC concrete at 1.5% LOI was tested to represent the most typical concrete that would result from utilities injecting PAC upstream of the primary particulate control device. Two high-carbon samples at 30% LOI at 18% (pad) and 36% ash replacement (lab sample) were also tested. As described previously, the 18% ash replacement consisted of 10% cementitious ash replacement and the additional 8% was PAC. ADA-ES had performed several successful tests in the lab at twice this ash replacement level (20% cementitious, 16% PAC), so one of these samples was also chosen for testing.

The leachate from the concrete tests was analyzed for the following: arsenic, barium, beryllium, boron, cadmium, total and hexavalent chromium, lead, manganese, mercury, molybdenum, selenium, silver, vanadium, fluoride, bromide, and sulfate. In addition to those just listed, the ash leachate was also tested for aluminum, antimony, cobalt, copper, iron, magnesium, nickel, strontium, thallium, titanium, and zinc. Many of these were part of a suite of tests and not targeted specifically. Table 2 shows the results for mercury, total chromium, and bromide. For all samples tested, mercury and chromium were well below the TCLP criteria for a hazardous waste. Also, the concrete samples containing high levels of PAC showed no detectable leaching of mercury while the low-carbon control showed a very small amount of leachable mercury. PAC-containing ash and concrete seemed to exhibit a similar behavior regarding chromium, showing a reduction in leachable chromium when compared to the low-carbon controls. Hexavalent chromium showed the same trend as total chromium (not shown). Because the PAC used in the TOXECON™ baghouse was brominated, the bromide levels in the leachate were tested. All concrete samples showed very little bromide in the leachate. The TOXECON™ ash at 42% LOI showed an increase in bromide in the leachate compared to the ESP ash.

Table 2. Concrete and ash leaching results.

Sample		Mercury (ng/L)	Total Chromium (ug/l)	Bromide (mg/l)
TCLP Criteria		200,000	5,000	
0.7% LOI concrete – 20% ash replacement (Control)	SPLP	9.8	46.5	0.92
	TCLP	ND	75.0	ND
1.5% LOI concrete – 20% ash replacement	SPLP	ND	23.0	1.2
	TCLP	9.7	42.0	ND
30% LOI concrete – 20% ash replacement (Lab sample)	SPLP	ND	ND	0.66
	TCLP	ND	ND	1.40
30% LOI concrete – 10% ash replacement (Pad sample)	SPLP	ND	ND	0.36
	TCLP	ND	ND	ND
TOXECON™ Ash (42% LOI)	SPLP	19.9	1.5	63.0
	TCLP	43.7	4.8	69.6
PIPP ESP Ash (0.7% LOI)	SPLP	18.5	177.0	ND
	TCLP	8.7	628.0	ND

CONCLUSIONS

In collaboration with DOE in a Clean Coal Program, We Energies and team members successfully completed the design, construction, installation, and demonstration of the first commercial mercury control system, EPRI's TOXECON™ process, on a coal-fired utility power plant. One of the objectives of this project was to utilize 100% of the fly ash from the three boilers at PIPP. ADA-ES, in collaboration with Miracon™ Technologies, Inc., developed a process that utilizes a combination of a specific batch design approach with the modified Miracon™ foam-based AEA developed for this application. The process was used to create high-strength, durable (stable air) concrete containing high-carbon ash. This combined technology was tested in the laboratory on concrete mixtures with ash containing <1% to 30% LOI from PAC, and showed stable air even after mixing for 90 minutes.

A successful field demonstration of producing concrete using 30% LOI ash was completed in June 2009. A 30' x 50' x 1' pad was poured at PIPP to be used for bottom ash dewatering. This concrete used high-carbon ash from the TOXECON™ baghouse and low-carbon ash from the ESP to generate an ash containing 30% LOI from PAC. This was used in the concrete at a 10% cementitious replacement, but due to the high level of PAC, the replacement was 18% by weight of cementitious material. The average compressive strength for the pad was 6646 psi at 28 days, which exceeded the design specification of 6000 psi.

The average air content measured in the field was 4.8%, which was within the target range. HAV results on the highest and lowest air batches showed that the spacing factor measurement was excellent for batch #2, but was high for batch #3. Rapid chloride permeability testing was performed on two cylinders (batches #5 and #7) and showed high chloride ion penetrability at 6280 and 6890 coulombs. This result was not surprising due to the conductive nature of activated carbon particles. More typical ash with 1–2% LOI would likely not see this effect.

Fly ash and concrete samples were tested using TCLP and SPLP Methods. For all samples tested, mercury and chromium were well below the TCLP criteria for a hazardous waste. The concrete samples containing high levels of PAC showed no detectable leaching of mercury, while the low-carbon control showed a very small amount of leachable mercury. PAC-containing ash and concrete seemed to exhibit a similar behavior regarding chromium, showing a reduction in leachable chromium when compared to the low-carbon controls. Hexavalent chromium showed the same removal trend as total chromium. All concrete samples showed very little bromide in the leachate. As expected, the TOXECON™ ash at 42% LOI showed an increase in bromide in the leachate compared to the ESP ash.

One challenge to widespread implementation of ACI for mercury control at plants that sell their fly ash is the resulting presence of activated carbon in the fly ash. Increased levels of activated carbon have been problematic when using the fly ash as a cement replacement in concrete production. Through several bench-scale and field tests, ADA-ES has shown that fly ash with even high levels of PAC can be used in concrete production. Although more development will be required before batch uniformity can be assured, this work has shown promise in addressing one challenge to widespread implementation of ACI for mercury control.