

## Evaluations of Concretes Containing Mercury Sorbents

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### ABSTRACT

The substitution of fly ash for cement in concrete is one of America's biggest by-product usage successes. Unfortunately, however, if even a small amount of powdered activated carbon (PAC) is injected into power plant flue gases for mercury emission control, the resulting fly ash has been found to be unusable in concrete. The PAC adsorbs the air entraining admixtures (AEAs) which are added to the concrete mix to create the proper amount of air bubbles which are needed to impart workability and freeze/thaw capabilities. Consequently, upcoming mercury emission standards could threaten the market for fly ash use in concrete.

Over the past few years, Sorbent Technologies Corporation researchers have developed a brominated carbon-based mercury sorbent (B-PAC<sup>TM</sup>) with superior cost-effectiveness in power plant use. More recently, they discovered a processing method which allows the sorbents to retain high adsorption effectiveness for mercury, yet not interfere with AEAs in concrete slurries. Concretes made with fly ash incorporating representative amounts of the mercury sorbents appear to entrain the same the amount of air and to have the same strength as control samples without any sorbents. This "concrete-friendly<sup>TM</sup>" version of B-PAC offers important promise for use by power plants which can sell their fly ash for concrete use.

### INTRODUCTION

Over 15% of the fly ash generated by U.S. power plants, over 10 million tons per year, is currently sold for concrete use, rather than being disposed of in landfills. This is equivalent to about 85 pounds of utility fly ash being used in concrete for every person in the U.S. every year. And efforts are underway to increase this amount.<sup>1</sup> This fly ash substitutes for a portion of the costly manufactured portland cement in the concrete mix.

There are significant benefits in using fly ash in concrete. Economic benefits include reduced costs for fly ash disposal, increased revenue from the sale of the ash, and savings from using the ash in place of the more costly cement. Concrete performance benefits include greater resistance to chemical attack, increased strength, and improved workability.<sup>2</sup> Environmental benefits include reduced greenhouse gas emissions, reduced land disposal, and reduced virgin resource use.<sup>3</sup>

In late 2000, the U.S. Environmental Protection Agency announced in an official Regulatory Finding that it will regulate all coal-fired electric utility steam generating units for mercury emissions. With this Maximum Achievable Control Technology (MACT) rulemaking, mercury reduction regulations for all U.S. coal-fired power plants will be proposed by the end of 2003, with national enforcement in 2008.<sup>4</sup> For the majority of the coal-fired power plants, those without scrubbers, the lowest-cost, leading-candidate technology to comply with the new mercury emission regulations is the injection of powdered activated carbon (PAC) into the flue gas in front of the plant's particulate controls.<sup>5</sup> In this process, the PAC gets mixed in with the plant's collected fly ash.



The first full-scale mercury-emission-control testing using PAC injection technology with an electrostatic precipitator (ESP) was conducted under Department of Energy sponsorship at the Pleasant Prairie Power Plant of We Energies, near Kenosha, Wisconsin, in late 2001 by ADA-ES. The mercury test results indicated 40% to 70% mercury reductions when the PAC (Norit Darco FGD) was injected into the ductwork at rates of from 1 to 10 lbs/Million acf.<sup>6</sup> Unfortunately, however, it was simultaneously discovered that the powdered activated carbon sorbents badly contaminated the fly ash for concrete purposes. In fact, the sorbent effects were so harsh that no fly ash could be sold from the ESP that was used for over a month after the testing stopped due to residual PAC in the system.<sup>7</sup>

The following table of Pleasant Prairie results indicates that even at the lowest PAC injection rate of 1 lb/MMacf, the resulting fly ash failed the plant's contractual Foam-Index (FI) test limits and could not be used for concrete.<sup>7</sup> The highly-adsorbent carbon sorbents competitively adsorb the air-entraining admixtures (AEAs) which are added to concrete for air entrainment and stabilization. Unfortunately, the majority of concrete in the U.S. is air-entrained, with organic AEA chemicals added to the mix to provide the proper amount of fine air bubbles, usually 4 to 6 vol%, specified for the concrete.

Pleasant Prairie Fly Ash Foam-Index Tests <sup>7</sup>				
Inj. Rate (lbs PAC/MMacf)	Hg Removal Effic. (%)	Carbon in Ash	Foam Index <sup>+</sup> (Drops)	Comment
0	-	0.6%	15	Normal
1	40 – 50%	1.1%	>72	Maxed out
3	50 – 60%	1.6%	>72	Maxed out
10	60 – 70%	3.6%	>72	Maxed out

+ drops of 1wt% of AEA solution for a stable foam

The Foam Index test is a method to determine the degree of interference that fly ash components, primarily carbon, interfere with the action of AEAs to form stable bubbles. Lower values are better. Increasing the foam indexes is bad not only because more AEA is required, but more importantly, because it introduces dramatic variability into the concrete-making process. Due to power plant operation variations, the ready-mix concrete plant will not know from batch to batch the proper amount of AEA to add to impart the contractually-required degree of air entrainment.

The Pleasant Prairie plant situation illustrates the extent of the problem. This plant produces about 200,000 tons of fly ash annually. All of this ash is currently sold and the plant made about \$3 million in revenue from the ash in 2000. PAC mercury emission control would cause all of these coal combustion product (CCP) revenues to be lost. Just as important, there would be an additional annual cost of about \$7 million to landfill the fly ash that had been previously sold. The total difference would be about \$10 million annually for this one plant and these costs do not include the cost of mercury control itself.<sup>7</sup> In contrast, total mercury control costs for such a plant with sorbent injection would likely be less than about \$4 million annually (e.g. 2,500 tpy of brominated sorbent \* \$1,500/ton).

To insure that the fly ash can still be sold for use in concrete, there are a number of possible alternatives:

- One alternative is to add a whole new second particulate collector to the plant and inject the mercury sorbent between the old and new collectors. If the second collector is a baghouse, this configuration is EPRI's patented Toxecon® design.<sup>8</sup> Fly ash without sorbent would be recovered from the first unit and sold. Retrofitting a whole new baghouse, with additional fans and ductwork, of course, is an extremely expensive proposition. And the added pressure drop is a significant, additional continuous operating cost.
- A second alternative is to separate the carbon from the inorganic fly ash or to chemically pacify it in a post-processing step. This can be accomplished, for example, with a carbon burnout or ozone treatment system. These operations, too, however, have very high capital requirements and operating costs. Moreover, they must operate with a very high degree of success, because the slightest PAC that remains in the ash can have significant AEA effects.
- Rather than treat the entire gas stream, as with Toxecon®, or the entire fly ash stream, as with post-processing, it makes more sense to concentrate on just the offending 1-wt% of the ash load that is sorbent. The easiest and least expensive option is to simply use a mercury sorbent material that does not affect AEAs in a concrete mix. That is the route that was explored in this work.

## BACKGROUND

### Sorbent Technologies' Brominated Mercury Sorbents

Sorbent Technologies Corporation has been studying mercury removal from flue gas streams with sorbents for over eight years.<sup>9,10</sup> The company has developed and is commercializing a number of brominated powdered activated carbon sorbent materials, called 'B-PAC™', specifically for power plant use. These materials have demonstrated superior mercury-removal performance in duct-injection applications.

The injection of B-PAC into power-plant flue gases for mercury removal has now been tested at seven different power plants. These plants have burned bituminous, subbituminous, lignite coals, and blends and include testing with cold-side ESPs, hot-side ESPs, spray dryers, and fabric filters. Mercury-removal performance at these sites has varied between 70% and 98% at sorbent consumption costs of approximately \$2,000 to \$20,000 per-lb-of-mercury-removed, considerably less than previous technologies. See a summary of results below.

**Table 1.** B-PAC results to date indicate applicability across all coals and plant configurations

<u>Coal</u>	<u>PM Unit</u>	<u>Hg Removal</u>	<u>@lb/MMacf</u>	<u>@ Plant</u>	<u>Scale</u>	<u>Data</u>
Bitum. Low-S	FF	94%	0.5	Valley	Slipstream	Apogee
Bitum. High-S	CS-ESP	70%	4.0	Lausche	Full-Scale	SorbTech
Bitum. Low-S	HS ESP	>80%*	6.4	Cliffside	Full-Scale	SorbTech
Subbitum.Blend	CS-ESP	90%***	3.0	St. Clair	Full-Scale	SorbTech
Subbituminous	CS-ESP	90+%	3.0	St. Clair	Full-Scale	SorbTech
Subbituminous	CS-ESP	89%	4.9	Pleasant Prairie	Slipstream	Apogee
Subbituminous	FF	87%	0.5	Pleasant Prairie	Slipstream	Apogee
Subbituminous	SD/FF	82%**	<1.8	Holcomb	Slipstream	ADA-ES
Lignite	SD/FF	95%	1.5	Stanton 10	Full-Scale	EERC
Lignite	CS-ESP+	70%+	1.5	Stanton 10	Full-Scale	EERC

\* when under low-load conditions. STC will return in the fall for improved runs.

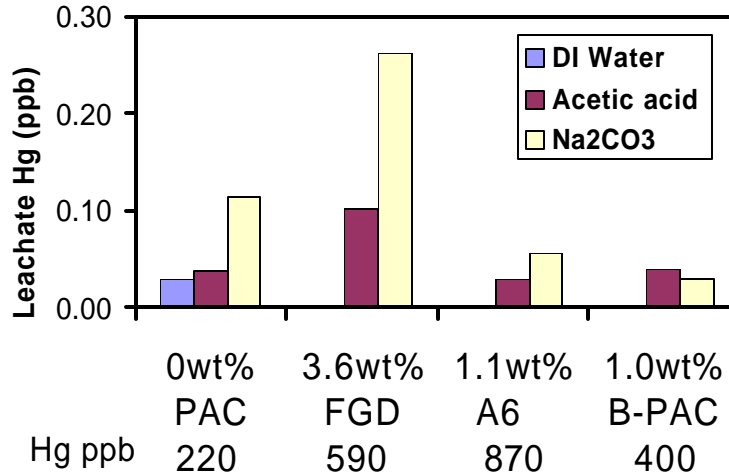
\*\* on-fabric removal only, with no in-flight opportunity. The effective "injection rate" could have been significantly lower.

\*\*\* data from only the first two weeks of parametric testing; more extensive data to come.

+ actually the in-flight Hg removal across the spray dryer, with an injection rate of only 1.5 lb/MMacf.

TCLP and SGLP tests done on fly ashes containing B-PAC indicate that the captured mercury does not leach or revolatilize from the sorbents. See the leachate data on the following page. For perspective, the U.S. EPA drinking water standard for mercury is 2.00 ppb, about 100 times higher than the mercury in B-PAC/fly ash leachates. Also, B-PAC contains a minimum amount of bromine. Even if all of its bromine was released as HBr, it would still amount to less than 1 ppm in the flue gas, which may already have 100 ppm HCl. And while HCl is considered a hazardous air pollutant under the Clean Air Act, bromine and HBr are not. Nor is HBr one of the 600 substances in the Toxic Release Inventory. For perspective, seawater contains about 75 ppm bromine.

## Mercury Leachates (TCLP & SGLP) from St. Clair Fly Ashes

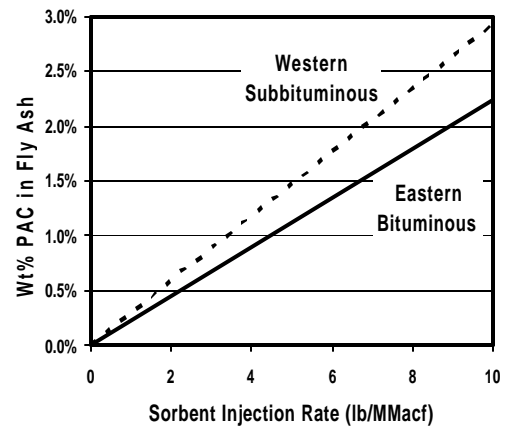


Using these brominated materials as a base, Sorbent Technologies recently sought out additional inexpensive processing methods that would lower the effect on AEAs in concrete.

## EXPERIMENTAL METHODS

Foam Index tests were used extensively in this effort. This is a shortcut method for gauging the degree to which the air content of a concrete will be affected by a fly ash. It is similar to a chemical titration. Fly ash, optionally with a representative amount of sorbent, is added to distilled water in a jar and shaken up. Then drops of an AEA solution, in this case usually Darex II®, are sequentially pipetted into the jar and the jar is reshaken and examined. This is repeated until a stable foam forms on the surface. This point, denoting the quantity of AEA surfactant required to saturate the adsorbing carbon, is the Foam Index (FI) value. Dividing the FI by the mass of carbon or PAC in the sample yields the Specific Foam Index (SFI).

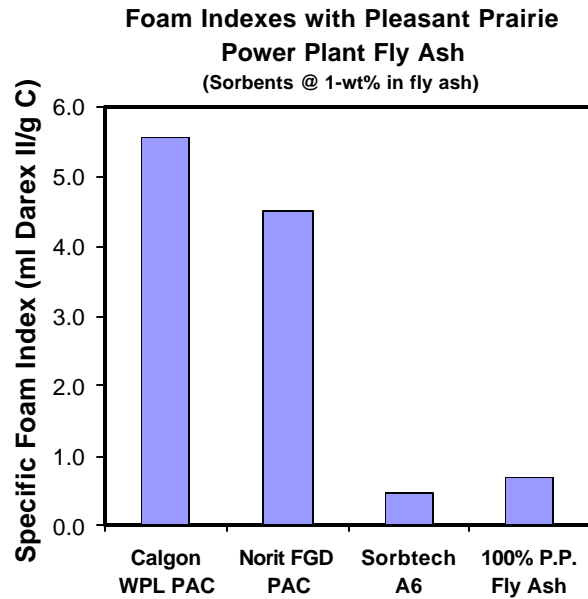
A 1-wt% sorbent loading level in the fly ash was chosen for most of the testing. For brominated sorbents, this is approximately the amount of sorbent to be injected to achieve a high degree of mercury control, relative to the amount of fly ash typically generated by a pulverized-coal-fired power plant. For example, the DOE's 300-MW bituminous-coal Reference Plant for Clean Coal Retrofits produces 463 lbs of fly ash and 962,000 actual cubic feet of flue gas per minute. If it takes a sorbent injection rate of 5 lbs per million acf to achieve a high rate of mercury removal, the resulting fly ash would thus contain about 1-wt% PAC. Subbituminous coal generally has lower ash levels, so for a given sorbent injection rate, the ash contains slightly more sorbent.



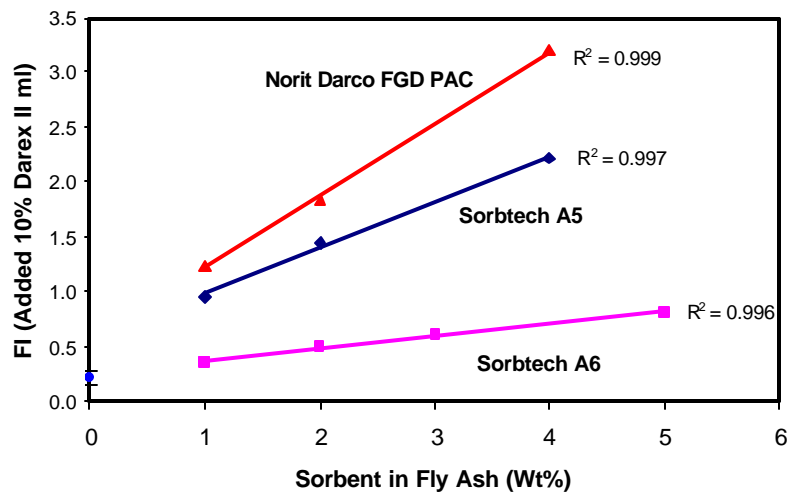
## RESULTS AND DISCUSSION

### Development of a Concrete-Friendly Mercury Sorbent

Sorbent Technologies researchers were successful in developing a processing method to lower AEA effects and two U.S. patents are pending. An example of foam index data appears below. The new “concrete-friendly” mercury sorbent is denoted “A6.”

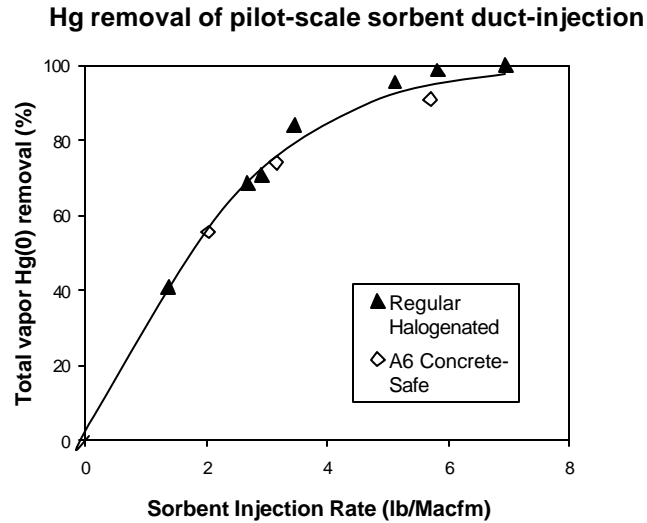


The two commercial PACs from Calgon and Norit have extremely high SFIs, indicating that a large amount of AEA needs to be added to their mixes before their AEA adsorption is satisfied and some is left over to stabilize the foam. In contrast, the A6 mercury sorbent has less of an effect on the AEA than the unburned carbon in the plain fly ash itself. As with other sorbents, its effect on AEAs is directly proportional to the amount added to the fly ash. Below is graph of the foam indexes of A6, along with that of A5, a regular brominated sorbent, and plain FGD PAC, when they are added to Pleasant Prairie fly ash in varying amounts, as would happen at different injection rates. The lines converge at the foam index of the plain fly ash in this example.



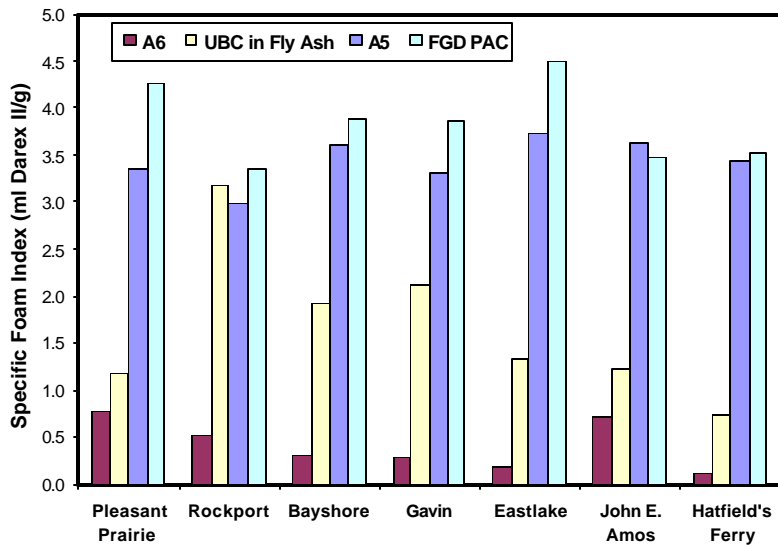
## Mercury Adsorption

Does the new concrete-friendly sorbent still adsorb mercury well? Fortunately, yes. The mercury adsorption abilities of the special low-AEA-adsorbing sorbent were tested in Sorbent Technologies' 40-acfm duct-injection pilot plant, which has been described in detail elsewhere.<sup>9</sup> Tested at three different injection levels under the system's standard conditions, it exhibited mercury performance just as high as the company's regular brominated sorbents.



## Effects with Different Fly Ashes

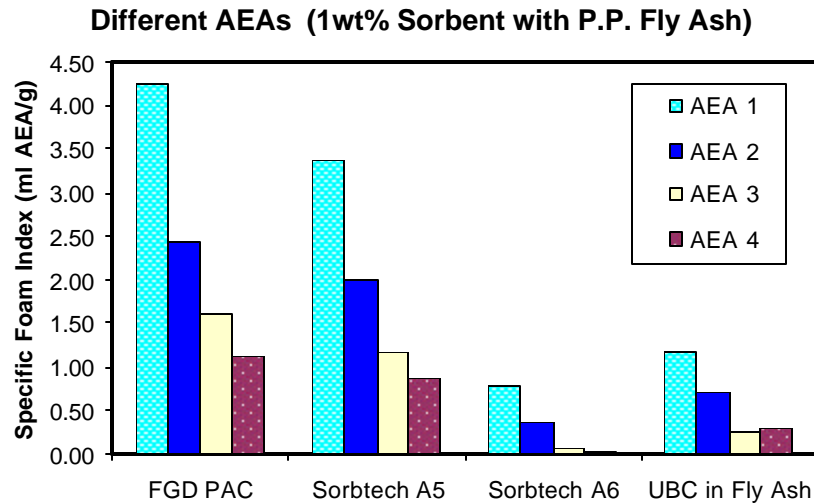
Do the results vary with the particular coal burned and its resulting fly ash composition? No. Fly ash samples, both Type C and Type F, were obtained from seven diverse power plants that sell their ash. The fly ash samples were mixed with 1-wt% of FGD PAC, Sorbent Technologies' regular A5 brominated sorbent, and the new "concrete-friendly" A6. Multiple foam index tests with Darex II were performed on each sample, as well as on the fly ashes without sorbents, and the SFIs area averaged. The new A6 sorbent exhibited a very low SFI with every fly ash tested.



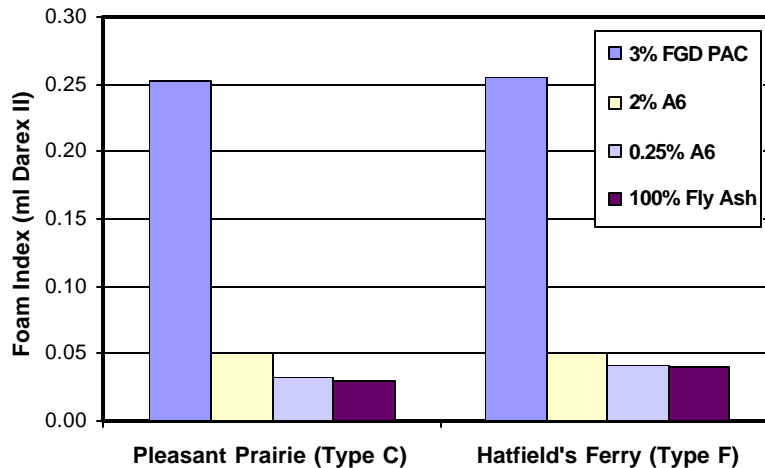
## Effects with Different Air Entraining Admixtures

Do the results vary with the particular AEA used in the concrete?

No. Foam index tests were performed on the A6, A5, and FGD PAC sorbents with three other commercial AEAs, in addition to the Darex II. Pleasant Prairie fly ash loaded with 1-wt% sorbent was used in each case.



As seen above, the AEA adsorption of the A6 sorbent was dramatically lower than that of the other sorbents, no matter which AEA was used in the mix.



For equivalent mercury removal, only a fraction as much brominated sorbent is required compared to regular PAC. Consequently, the amount of sorbent that ends up in the fly ash is proportionally lower. In actual practice, the concentration of PAC in fly ash can be expected to be 3-wt% or more. The concentration of A6 can be anywhere from 0.25% to 2%. The resulting foam indexes with a Type C and a Type F fly ash are shown above.

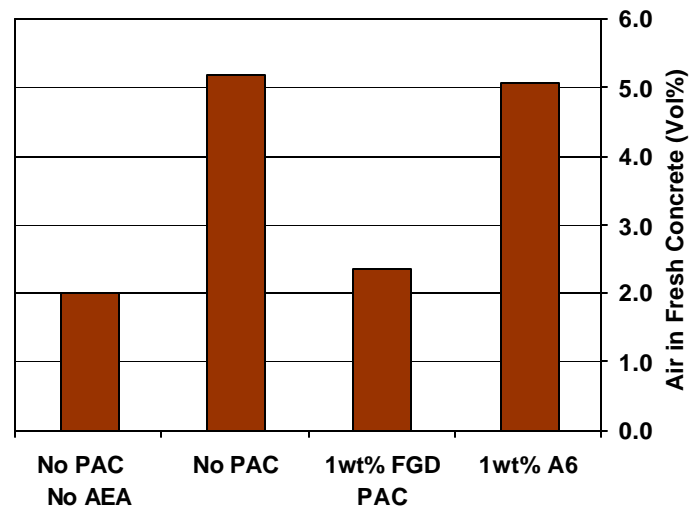
## Performance in Concrete

Foam Index tests reasonably simulate AEA interference effects and are frequently written into fly ash supply contracts. However, the best way to examine air entrainment effects in concrete is to make concrete samples containing the PACs and measure their actual air entrainment. Did the foam index data carry over to the actual cement samples? This was tested using fly ash from American Electric Power's giant Rockport station in representative concrete samples which included sand, aggregate, portland cement, water, and additives, with, in this case, a typical 20% of the cement being replaced by sorbent-containing fly ash.

The concrete samples were prepared according to ASTM C-192 and multiple samples from each batch were tested for their wet air entrainment according to ASTM Method C-231. The air-entrainment specification for concrete is usually selected at a point within the range of 4-to-6-vol%. With too little air, the concrete is difficult to work and has no freeze-thaw capability; with too much air, the concrete does not have adequate strength. The higher the specified air entrainment, the more AEA is added to the blend. In these tests entrained air of 5-vol% was targeted. The results appear below.



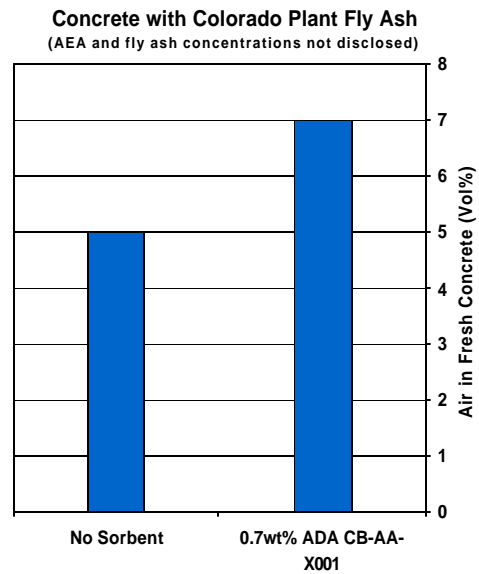
**AEP's Rockport Station Type C Fly Ash  
with 50 ml Darex II AEA/100 kg of (cement+ash)**



With no AEA (or PAC), the standard-method concrete naturally has only 2-vol% air entrained, not enough for workability or freeze-thaw capability. With no sorbent, but with the proper amount of AEA, it achieves the specified 5-vol%.

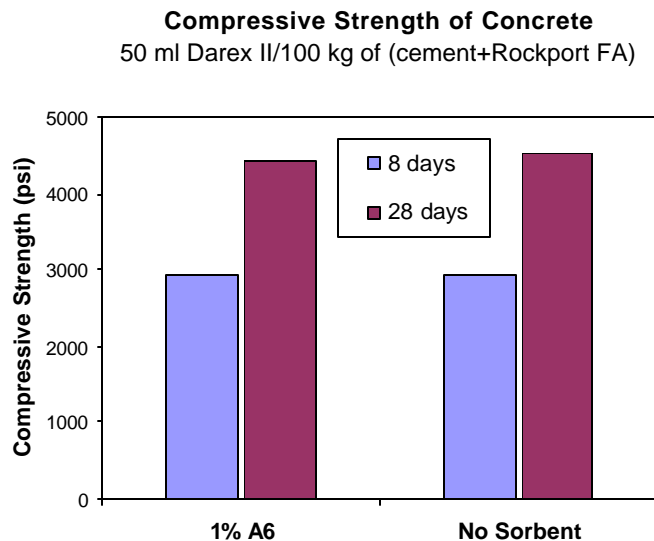
If only 1-wt% of the commercial Norit Darco FGD PAC is added to the fly ash portion, however, the AEA in the mix is made useless, adsorbed by the PAC, and the resulting air is hardly more than the 2-vol% natural level. However, if 1-wt% A6 sorbent is used as the mercury sorbent instead, then the proper amount of air is entrained in the concrete and the fly ash can be sold commercially.

Just because a mercury sorbent is made without carbon, it can still render the fly ash incapable of use in concrete. Butz et al.,<sup>11</sup> for example, recently reported on air entrainment tests by Boral Material Technologies on ADA Technologies' mercury sorbents. Concrete made with Colorado bituminous fly ash containing 0.66-wt% of "Amended Silicates®" mercury sorbent was compared against samples that did not contain this sorbent. See the results on the right. This small amount of Amended Silicates® severely impacted air entrainment, increasing it by 40%. Higher air significantly weakens the concrete. If air entrainment is so sensitive to the chemicals added with these sorbents, then the ready mix plant has no way of knowing how much AEA to add to particular concrete batches. As with traditional PACs, such fly ash cannot be used for concrete.



### Concrete Strength

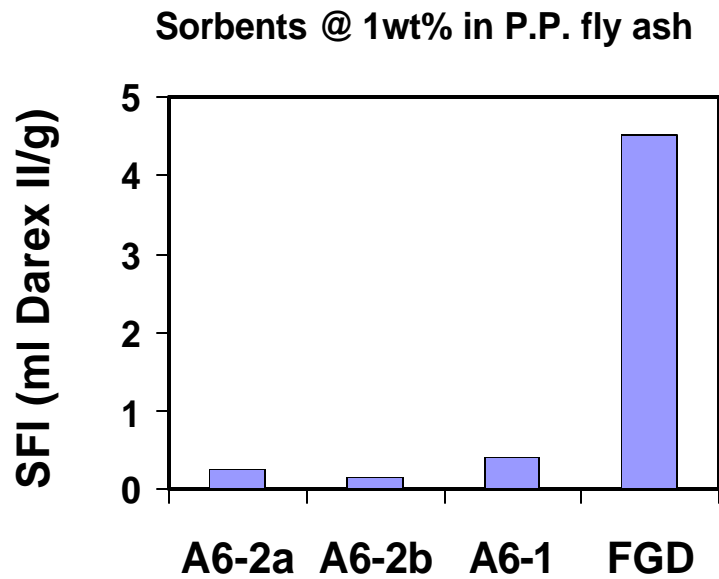
Compression tests were performed by Sorbent Technologies on various samples of concrete made according to ASTM C-192 that were cured for 8 and 28 days. When test according to ASTM C-39, the concretes with A6 sorbent at 1-wt% with respect to the fly ash exhibited compressive strengths equivalent to that of the control samples without sorbents.



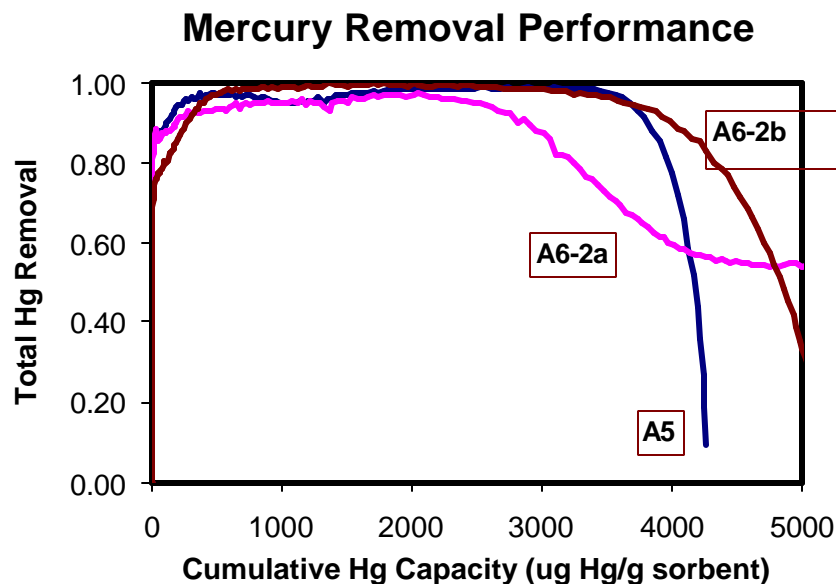
## SECOND-GENERATION “CONCRETE-FRIENDLY™,” B-PAC

Sorbent technologies is now working on a second generation of “concrete-friendly” B-PAC with even lower AEA interference and, importantly, even lower production costs.

The specific foam indexes of these materials, “A6-2,” is even lower than the previous “A6-1” B-PAC. The data below is with Pleasant Prairie fly ash and sorbents at 1 wt%



The second-generation B-PAC materials have mercury adsorption capacities similar to the first-generation materials. Efforts are now underway to produce these new materials in tonnage quantities for large-scale testing.

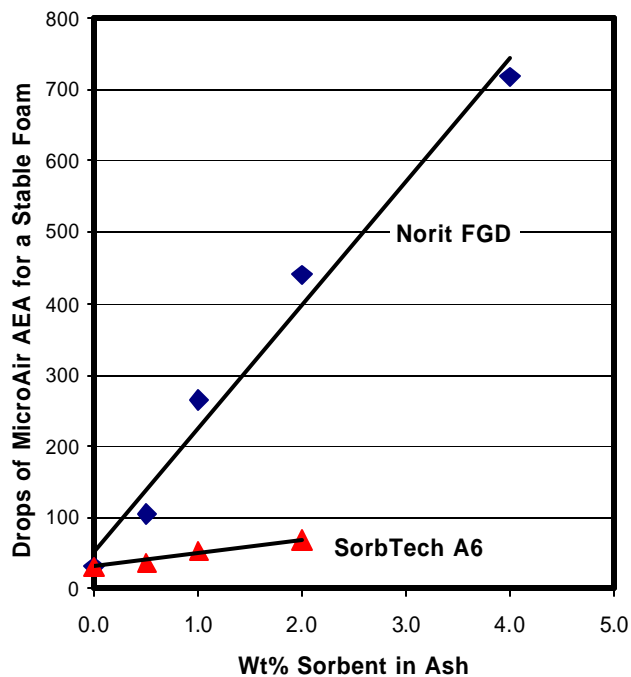


## HEADWATERS/ISG RESOURCES' CONCRETES

To independently confirm the low AEA interference of the “concrete friendly” first-generation A6 version of B-PAC, samples of the mercury sorbent were submitted to Headwaters/ISG Resources for analysis. Headwaters is the world’s largest utility fly ash marketer and largest producer of preformed fly-ash-containing construction products.

Using a different fly ash, a high-quality commercial fly ash from a lignite-burning client, and a different AEA, MicroAir<sup>®</sup> from Masterbuilders, Headwaters measured the foam indexes of the A6, plain Norit FGD PAC, and control samples. The results again indicated very low AEA absorption for A6, but unacceptably high interference from the plain carbon.

Foam Indexes of B-PAC and Plain PAC Sorbents in Fly Ash



Concrete test cylinders were prepared with the materials substituting fly ash for 25% of the cement. For the samples containing A6 (at 1 wt% relative to the fly ash), Headwaters chose to increase the AEA dosage to compensate for the added carbon content. They found that the target concrete slump and wet-mix entrained-air targets could easily be met. See the table on the following page.

Table 1. Concrete test cylinders prepared by Headwaters.

Concrete Cylinder	AEA (g)	Slump Target=6in.	Air (vol%) Target=5%
100% Cement Control	6	5.75	5.0
25% Ash Control	8	6.75	4.0
25% Ash with 1wt% A6-1	20	6.50	4.8

## CONCLUSIONS

Sorbent injection for utility mercury control and the sale of fly ash for concrete applications need not be mutually exclusive. By properly processing the mercury sorbents that are injected into the power plant ductwork, it is possible to produce materials with both a high affinity for gaseous mercury species and a low affinity for air entraining admixtures in concrete mixes.

The “A6” materials of Sorbent Technologies, for example, have miniscule specific foam index values when mixed with a variety of fly ashes and when used with a variety of AEAs. Standard concretes incorporating these sorbents appear to entrain the same amount of air as do samples without the sorbents and to have the same strengths.

For those power plants that sell their fly ash into concrete markets, use of these new “concrete-friendly” mercury sorbents may save millions of dollars annually relative to their next best alternatives.

## ACKNOWLEDGEMENTS

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