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Further Progress toward Concrete-Friendly™ Mercury Sorbents

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ABSTRACT

Nearly 20% of U.S. power plant fly ash is currently sold each year for use as a cement substitute in concrete. Unfortunately, if typical powdered activated carbon (PAC) for mercury emission control becomes mixed in with this ash, it can no longer be used in concrete. The PAC severely interferes with air entraining admixture chemicals (AEAs) added to the concrete mixes for workability and freeze-thaw capability.

This paper will report on continuing investigations on a specially formulated brominated PAC mercury sorbent that appears to be safe for concrete use. First, data on the mercury removal performance of the sorbents will be described. Next, concrete data will be presented for both regular and these concrete-friendly mercury sorbents, at multiple levels in the ash, with difference commercial AEAs, and with a variety of power-plant fly ashes. Wet-mix air-entrainment levels, concrete strength, slump, and bubble-size data will be presented. Finally, the relative economic implications of this data will be discussed.

INTRODUCTION

According to the American Coal Ash Association, production of fly ash in the United States in 2004 totaled 70.8 million tons. This represents a production increase of less than 1% from 2003. Of that 70.8 million tons, 14.1 million tons were used as a partial replacement for cement in the manufacture of ready mix concrete. This represents an increase of 12% from the 12.3 million tons used for the same purpose in 2003. The dramatic difference between the growth in utilization and the growth in supply points to both the increased demand for concrete based construction and the growing acceptance of fly ash as a viable, economical construction material.

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.¹ Environmental benefits include reduced greenhouse gas emissions, reduced land disposal, and reduced virgin resource use.²

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. Subsequently the Clean Air Mercury Rule (CAMR) was proposed where mercury emissions will be capped at 38 tons nationwide with allowance defined on a state by state basis.³ Each state must submit a plan under rule 111(d) that includes:

- A description of control measures to meet the statewide mercury budget
- Fully-adopted State rules for the mercury reduction strategy with compliance dates providing for control by 2010.



Each State must impose control requirements that demonstrate it will meet its assigned statewide Hg emissions budget.

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.⁴ 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.⁵ 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.⁶

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.⁷ 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 ⁷				
Inj. Rate (lbs PAC/MMacf)	Hg Removal Effic. (%)	Carbon in Ash	Foam Index ⁺ (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 index 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 can be used to illustrate the extent of the problem. This plant produces nearly 200,000 tons of fly ash annually, all of which is currently sold into the ready mix concrete industry. Based on national averages (\$10/Ton) the revenue generated from the sale of this ash would approach \$2 million annually. If the ash becomes contaminated through traditional PAC injection for mercury control, not only would the revenue be lost, but an additional expense of \$1.1 million would be incurred for landfill and disposal expense. This is based on the current national average of \$5.50/ton for disposal.

The total difference between selling ash and disposing of ash at this one plant is in excess of \$3.1 million annually and these costs do not include the cost of mercury control itself⁷. 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.⁷ Fly ash without sorbent would be recovered from the first unit and sold. While quite effective, retrofitting a whole new baghouse, with additional fans and ductwork 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, through carbon burnout (PMI), carbon/ash separation (STI) or ozone/chemical treatment processes. These operations, too, may have very high capital requirements and operating costs.

- Rather than treat the entire gas stream, as with Toxecon®, or the entire fly ash stream, as with post-processing, a third alternative is to 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 ten years.^{8,9} The company has developed and commercialized 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.

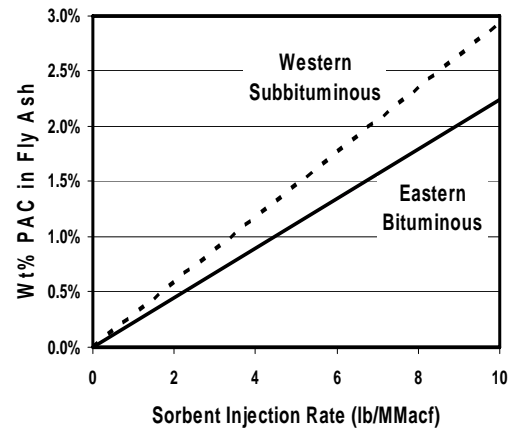
+ actually the in-flight Hg removal across the spray dryer, with an injection rate of only 1.5 lb/MMacf.

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 rapid, industry accepted, method for gauging the degree to which the air content of a concrete will be affected by a fly ash. 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).

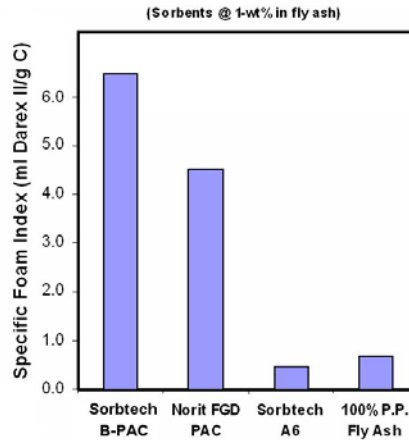
A 1-wt% sorbent loading level in the fly ash was chosen for most of the testing. For brominated sorbents, this is approximately the amount of sorbent to be injected to achieve a high degree of mercury control, relative to the amount of fly ash typically generated by a pulverized-coal-fired power plant. 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

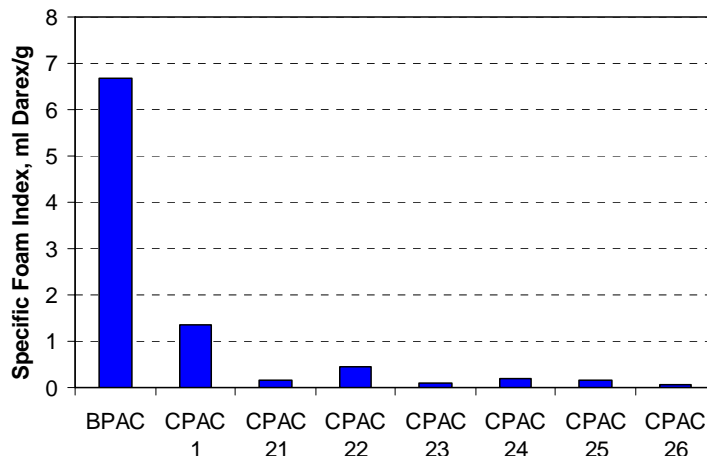
Development of a “Concrete-Friendly” Mercury Sorbent

Sorbent Technologies researchers were successful in developing a processing method to lower AEA effects and two U.S. patents are pending. The following chart show previously reported information on the relative SFIs of commercially available PACs, the original Sorbtech Concrete-Friendly C-PAC and untreated Pleasant Prairie fly ash (used as a reference point)

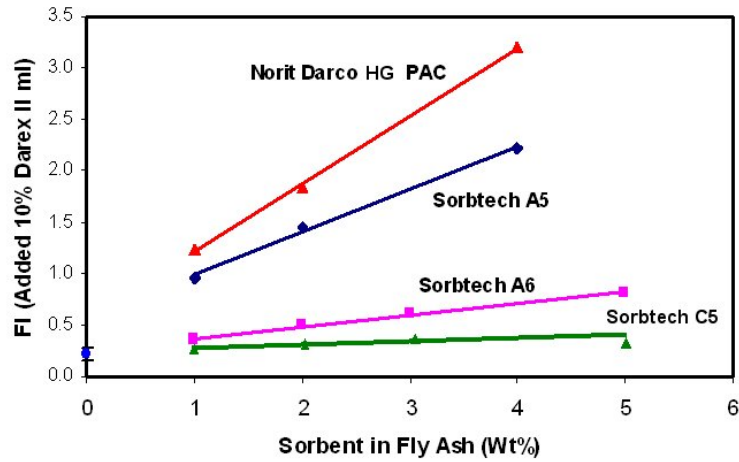


The two commercial PACs (Norit FGC and Sorbtech B-PAC) have extremely high SFIs, indicating that a large amount of AEA needs to be added to their mixes before their AEA adsorption is satisfied and some is left over to stabilize the foam. In contrast, the A6 mercury sorbent has less of an effect on the AEA than the unburned carbon in the plain fly ash itself.

Since that time, further work has been done toward establishing a “zero” foam index sorbent. The following chart show the relative SFI values of several second generation materials, maintaining B-PAC and C-PAC-1 (A6) as reference points. As can be seen, an order of magnitude increase has been achieved in reducing SFI against the first generation C-PAC.



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.

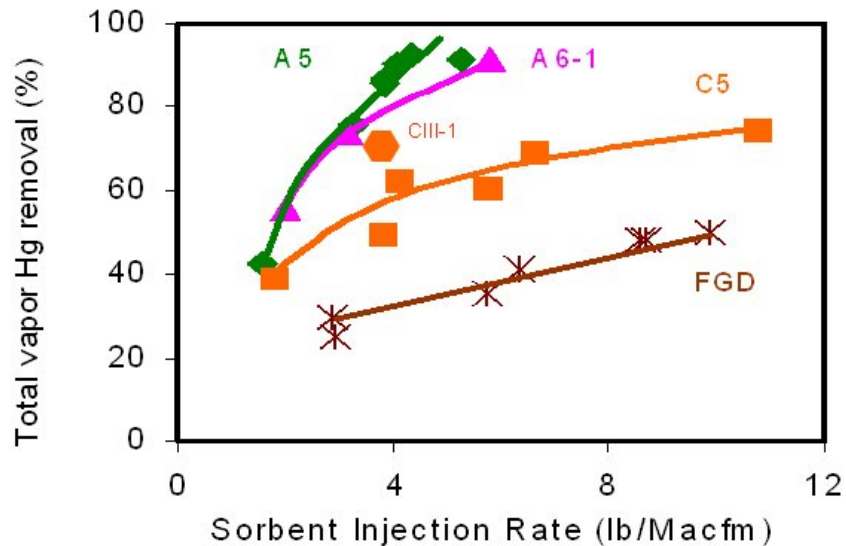


Note that second generation Sorbtech C5 is approaching a zero slope, indicating a virtual invisibility to Air Entrainment Admixtures.

Mercury Adsorption

The mercury adsorption abilities of the special low-AEA-adsorbing sorbents were tested in Sorbent Technologies' 40-acfm duct-injection pilot plant, which has been described in detail elsewhere.⁹ Tested at multiple injection levels under the system's standard conditions, The Concrete-Friendly™ sorbents exhibited varying levels of mercury performance when compared to the standard Sorbtech B-PAC (A5).

Fortunately, as the design and manufacturing tradeoffs between mercury performance and AEA tolerance were explored new information learned has resulted in a third generation C-PAC (C11-1) with mercury performance approach B-PAC, but extremely favorable results in tolerating AEAs.

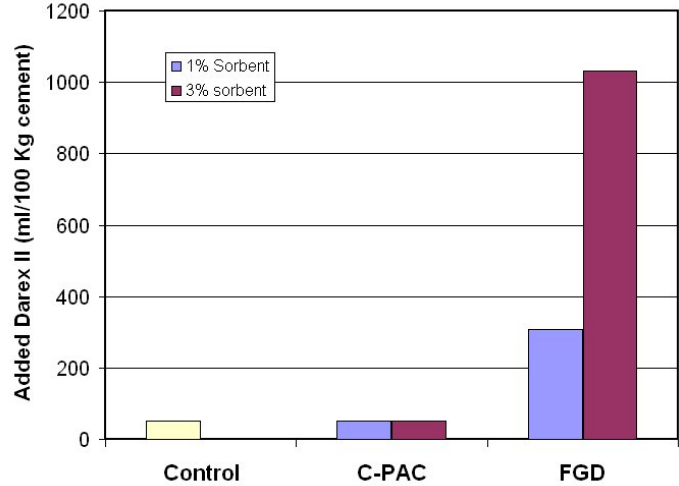


Performance in Concrete

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 and their compressive strengths, two key indicators of long term concrete performance.

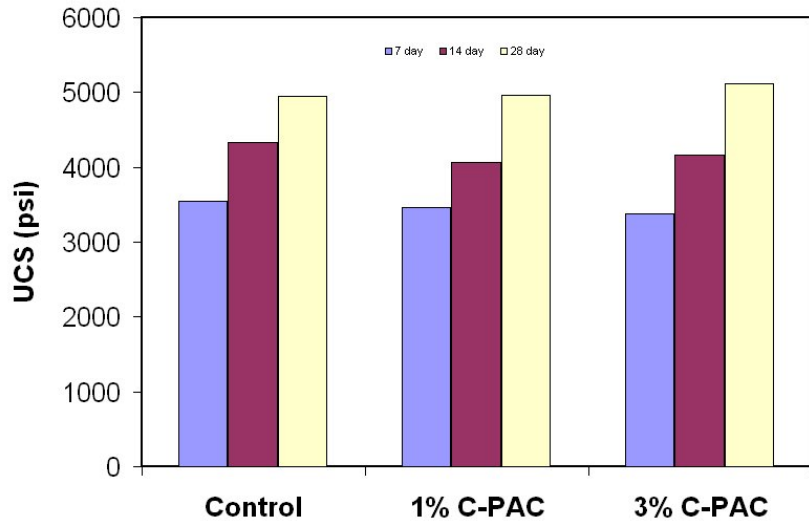
Several concrete samples were prepared according to ASTM C-192 and multiple samples from each batch were tested for their wet air entrainment according to ASTM Method C-231. The air-entrainment specification for concrete is usually selected at a point within the range of 4-to-6-vol%. With too little 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

6-vol% was targeted with the amount of AEA needed to achieve this result measured. The results appear below.



Using pure fly, with no added carbon, as a control it can be seen that Concrete-Friendly™ C-PAC, in both 1-wt% and 3-wt% levels had no measurable affect on AEA requirements. Standard PACs, however, required almost 10 times as much AEA to achieve the 6% air entrainment goal at 1-wt% and nearly 30 times as much at 3-wt%.

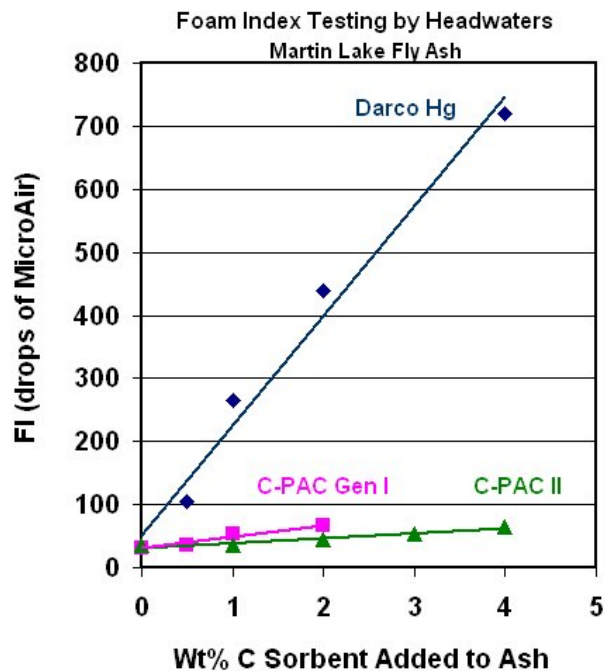
Lastly, as can be seen in the graph below, addition of C-PAC at both 1-wt% and 3-wt% concentrations had not measurable effect on 7 day, 14 day, or 28 day compressive strengths.



HEADWATERS/ISG RESOURCES' CONCRETES

To independently confirm the low AEA interference of the Concrete-Friendly™ first-generation A6 version of C-PAC and the second generation C-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® from Masterbuilders, Headwaters measured the foam indexes of the A6, plain Norit FGD PAC, and control samples. The results show the expected dramatic improvement of C-PAC-1 against Standard PAC, and the second generation C-PAC material exhibits an 80% improvement over the first generation C-PAC after the baseline carbon-in-ash is taken into account.



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

VALUE vs. PERFORMANCE

As was stated earlier, the national average for disposal of fly ash is \$5.50/ton. However, this number can run much higher depending on geographical location and the availability of low cost landfill sites. Also, the revenue generated by ash sales varies from site to site based on local supply/demand conditions and the royalty base in the ash marketing contract.

Based on this, the decision to continue selling ash vs. disposal is unique from site to site. The options available to plant management for effective mercury control vs. ash quality are clear. Add a secondary collection system at significant capital cost and operating cost increases, or utilize a concrete friendly sorbent.

While Concrete-Friendly™ sorbents are in the early stages of commercialization, it is possible that a price premium may be necessary to achieve the balance of mercury removal and AEA tolerance. For the simple sake of discussion let's assume a 50% premium over commercial brominated PACs.

Using the original Pleasant Prairie example, this would extend to an increase in sorbent cost of \$2 million/yr. Compared with the avoided loss of \$3.1 million in bottom line profit due to lost ash sales this is a clear benefit of over \$1.1 million per year, without any additional equipment, operating costs, or maintenance issues.

FURTHER WORK

As of this writing, Sorbent Technologies Corporation has been awarded DOE contracts to further this important work and will conduct full scale site work at two Midwest Generating sites in 2006. It is fully expected that the result of this effort will be commercial verification of C-PAC in mercury and AEA performance as well as a reduction, or elimination, of the price premium necessary.



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, C5 and C11-1” materials from Sorbent Technologies 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-FriendlyTM” mercury sorbents may save millions of dollars annually relative to their next best alternatives.

ACKNOWLEDGEMENTS

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REFERENCES

- 1 Dodson V.H. (1990) Concrete Admixtures. New York: Van Nordtand Reinhold.
- 2 Schwartz, K., "The Outlook for CCPs," Electric Perspectives, July/August 2003.
- 3 Wayland, Bob. (2005) Clean Air Mercury Rule (CAMR). Subbituminous Energy Coalition conference, September 7, 2005.
- 4 Brown, E., "Current Policy Developments Concerning Control of Mercury Air Emissions," Air Quality III, Arlington, Va., Sept. 10, 2002.
- 5 Starns, T., et al., "Full-Scale Test of Mercury Control with Sorbent Injection and an ESP at Wisconsin Electric's Pleasant Prairie Power Plant," Air & Waste Management Association Annual Meeting, Session AE1-C, 2002.
- 6 Coughlin, T., "Operational & Maintenance Impacts of Hg Control," Sciencetech Hg Emissions Workshop, Clearwater, Fl., Jan. 2002.
- 7 Bustard, C. J., et al., "Full-Scale Evaluation of Mercury Control with Sorbent Injection and COHPAC at Alabama Power E.C. Gaston," J. Air & Waste Manage. Assoc. 52:918-926, 2002.
- 8 Nelson, S., J. Miller, & D. Summanen, "Innovative Mercury Emission Control," Air & Waste Management Association Annual Meeting, Toronto, Canada, June 1997.
- 9 Nelson, S., Q. Zhou, & J. Miller, "Novel Duct-Injection Mercury Sorbents," Air Quality III Conference., Arlington, Va., Sept. 2002.