Commercial Experience with Concrete-Friendly Mercury Sorbents

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ABSTRACT

When traditional carbon mercury sorbents become mixed with power plant fly ash, the fly ash can no longer be used as a cement replacement in concrete. For most plants selling into concrete markets, this can have tremendous financial repercussions. At the last World of Coal Ash meeting, the results of full scale trials of C-PAC™, a concrere-friendly carbon-based mercury sorbent were reported.[1] This product has now been commercialized and millions of pounds per year are being sold.

This paper presents the results of two full-scale trials performed using C-PAC™. It focuses on the mercury removal achieved (> 80%) with C-PAC™, while continuing to maintain the marketability of the fly ash as a replacement for cement in concrete.

1. BACKGROUND

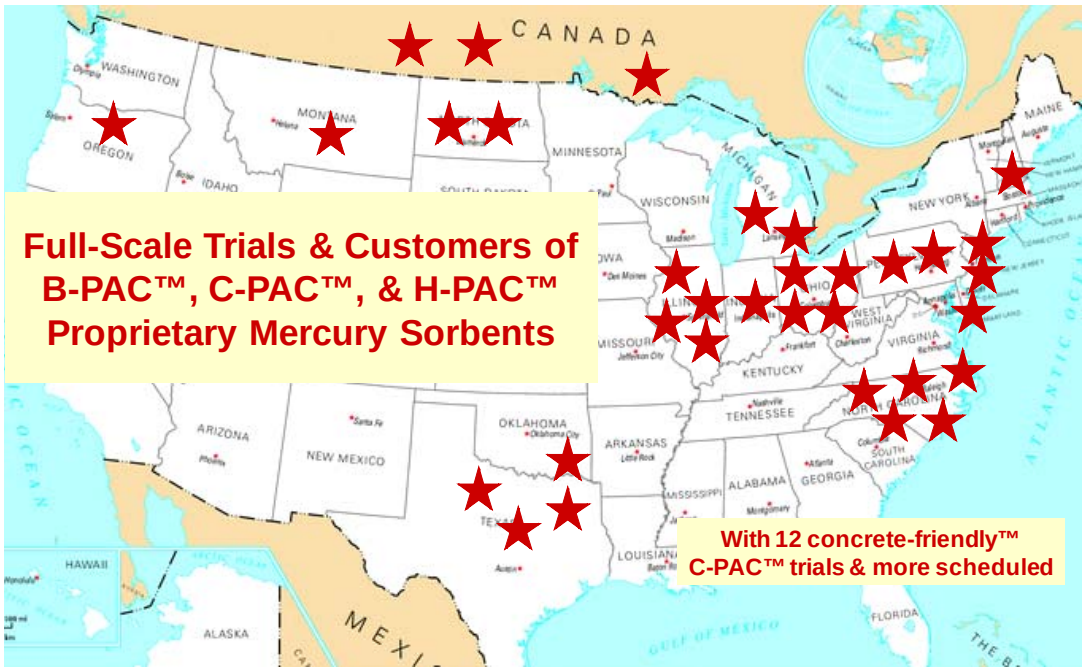
An important use of fly ash is as a replacement for cement in concrete. Commonly, cement in a concrete mix is replaced by fly ash at about 20% by weight.[2] Fly ash enhances the workability, durability, and ultimate strength of concrete at a lower cost than cement. Additionally, substituting one ton of fly ash for Portland cement eliminates about one ton of CO2 emissions.[3] In 2006 over 12 million tons of fly ash was sold for concrete use and efforts are underway to increase this amount.

As mercury emission reductions become implemented, however, the ability to substitute by-product fly ash may be threatened as many coal-fired utilities adopt powdered activated carbon (PAC) based sorbents. Duct injection of PAC sorbents is leading technology for power plants mercury mitigation control. In this process, the PAC get mixed in with the plant's fly ash causing the fly ash not to be saleable in concrete. This is because the standard PACs strongly adsorb the air-entraining admixtures (AEAs) that are added to the concrete slurry to create the air bubbles needed required for workability and freeze-thaw capabilities of the concrete.

To solve this problem Albemarle Sorbent Technologies developed a new activated carbon-based mercury sorbent - C-PAC™ that is "concrete-friendly." This particular mercury sorbent effectively removes mercury from the flue gas, while having minimal adsorption of AEA, thereby allowing plants to continue to sale its fly ash. Albemarle has a patent pending on carbon-based, concrete-friendly mercury sorbents.

During the development of C-PAC™, a standardized and repeatable method for measuring the effect of fly ash carbon or mercury sorbent carbon on AEAs, Acid Blue Index (ABI) was developed to replace foam index test. It uses a standard reagent, Acid Blue 80, tests at an equilibrium condition, and eliminates operator discretion in determining when a sample begins to "foam" by utilizing instrumental measurements. The method was reported in the last World Coal Ash Conference two years ago.[4] In contrast to other sorbents, C-PAC™ has an ABI less than 15.

Albemarle Sorbent Technologies Corporation's C-PAC™ sorbent is now commercially available and is being shipped from our Twinsburg, OH manufacturing plant on a daily basis. Albemarle Sorbent Technologies has now conducted many full-scale trials with C-PAC™.



This paper includes full-scale test results performed with C-PAC™ at Midwest Generation's Crawford Station, a DOE supported trial, and at PPL's Montana's Corette Station. These focused on the effectiveness of mercury removal using C-PAC™ and the effect of the sorbent on the resultant fly ash. The results of a utility trial not conduct by Albemarle Sorbent Technologies is also presented. That trial focused on the effectiveness of mercury removal by injecting the C-PAC™ before the air preheater. Finally, data from a fourth, confidential site will be presented focusing on relative ESP performance with C-PAC™.

2. FULL-SCALE C-PAC™ TRIAL AT THE CRAWFORD STATION

The goal of the full-scale C-PAC™ injection for mercury control at the Crawford plant was to determine if greater than 70% reduction could be achieved while maintaining the quality of the fly ash for concrete sales.

TRIAL RESULTS

Albemarle Sorbent Technologies developed the concept of C-PAC™ concrete-friendly brominated carbonaceous mercury sorbents with funding from the National Science Foundation. The first long-term, full-scale, demonstration trial of C-PAC™ was conducted at Midwest Generation's Crawford Station Unit 7 in Chicago in the summer of 2006 with the financial support from Department of Energy NETL (Project DE-FC26-05NT42308). The Crawford Station Unit 7 fires PRB coal and has an ESP with a specific collection area of only 120. Much of this plant's fly ash has historically been sold for concrete use. During the month-long continuous test, C-PAC™ was injected at an average rate of 4.6 pounds of sorbent per million actual cubic feet of flue gas (lb/MMacf). An average total mercury removal rate of over 80% was achieved, as indicated in Figure 1 below.

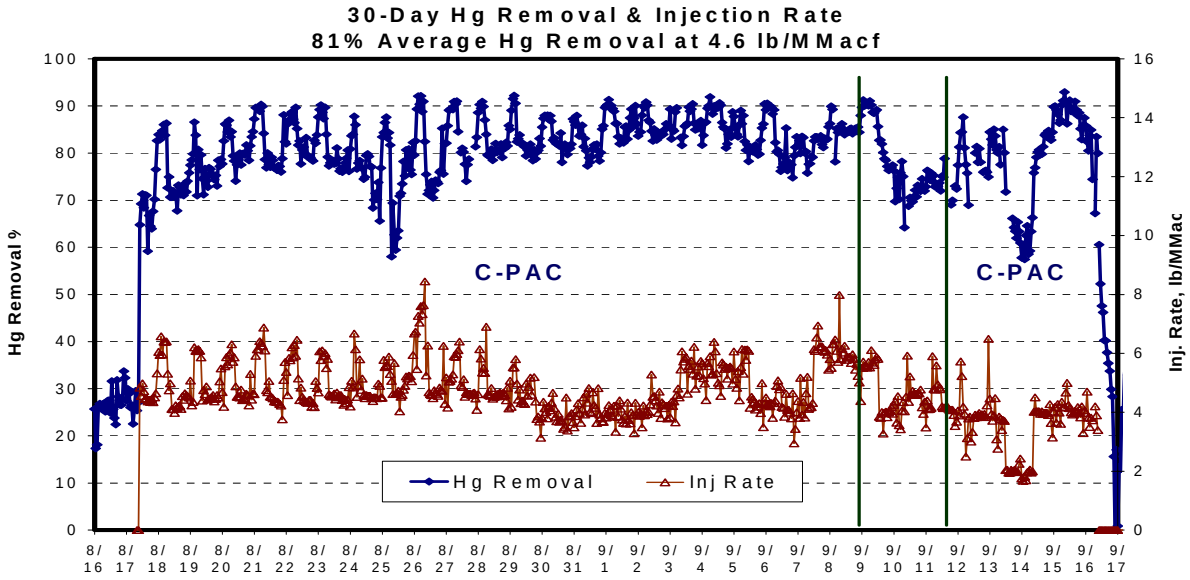


Figure 1. Crawford Unit 7 Mercury Removal & Injection Rates Over 30 Days.

The sorbent injection rate varied over the course of the trial, as it might in commercial practice, putting varying amounts of the sorbent into the fly ash and challenging the consistency of the fly ash for concrete use. Despite this, the resulting AEA adsorption of the ashes held to a tight band.

During the trial, the stack opacity improved, rather than degraded. It was observed that C-PAC™ injection had the co-benefit of improving the particulate collection performance of the electrostatic precipitator.

RESULTING FLY ASH

The resulting fly ash was usable in concrete, most from the front hoppers was usable in premium concrete. Using Lafarge's method and Vinsol® AEA, if the foam index is less than 40 drops, Crawford's fly ash is considered acceptable for cement replacement in premium concrete. At 99 drops or less, it can be used in standard concrete. See the Figure 2 results below.

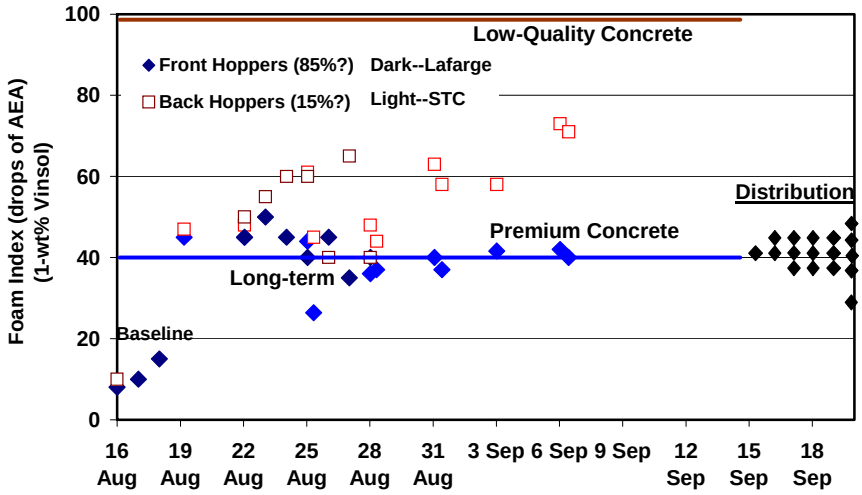


Figure 2. Foam Index of Crawford Fly Ash During a 30-Day C-PAC Injection Trial

The 40-drop cut off for premium concrete is a somewhat arbitrary value, based on the foam index of the unburned carbon and, particularly, on the variation observed in this value. The standard deviation of the C-PAC™-containing ash was only 4 drops, while that of the baseline control ash was even higher, at 5 drops.

3. FULL-SCALE C-PAC™ TRIAL AT THE PPL MONTANA CORETTE STATION

The purpose of the trial conducted at the Corette Steam Generating Station of PPL Montana was to determine whether the injection of C-PAC™ could reduce the mercury emissions by 80% while maintaining the ability to sell the fly ash for use in concrete. Two different mercury monitors and an Appendix K sorbent trap sampler were all used to make the mercury measurements at this site. There was baseline period before the parametric testing with C-PAC™ began. The injection trial was around the clock beginning at an injection rate of 3 lb/MMacf, based on an ESP inlet (cold-side) flow basis. The object was to identify the injection rate that would maintain a mercury removal rate at minimum 80%, the pending mercury standard, and then stay at this injection rate to insure the representative fly ash samples could be obtained.

TEST RESULTS

The mercury removal results were impressive. In the first phase of the parametric testing, mercury removal rates of >80% were achieved at an injection rate of 3 lb/MMacf and > 90% at an injection rate of 5 lb/MMacf. It did not appear that the mercury levels had reached a stable level in these short trials and would have possibly achieved higher mercury removal rates if the injection had been maintained at each rate longer. In the subsequent testing, this position was confirmed by the extended run at an injection rate of 4.3 lb/MMacf and the second phase of the parametric trials.

The average mercury removal rate in the 4.3 lb/MMacf run was 92%. Based upon the results of this testing, it appeared that a C-PAC™ injection rate of 3 lb/MMacf would be sufficient to reduce the mercury emissions below the required mercury limit.

The test period consisted of two 18 hour trials. A C-PAC™ injection rate of 3 lb/MMacf was used in the first 18 hours and 5 lb/MMacf in the last 18 hours. These tests would insure that good fly ash would be collected for the concrete testing and would confirm the mercury removal data from the first test period. The mercury monitor data for the second test period is presented in Figure 3.

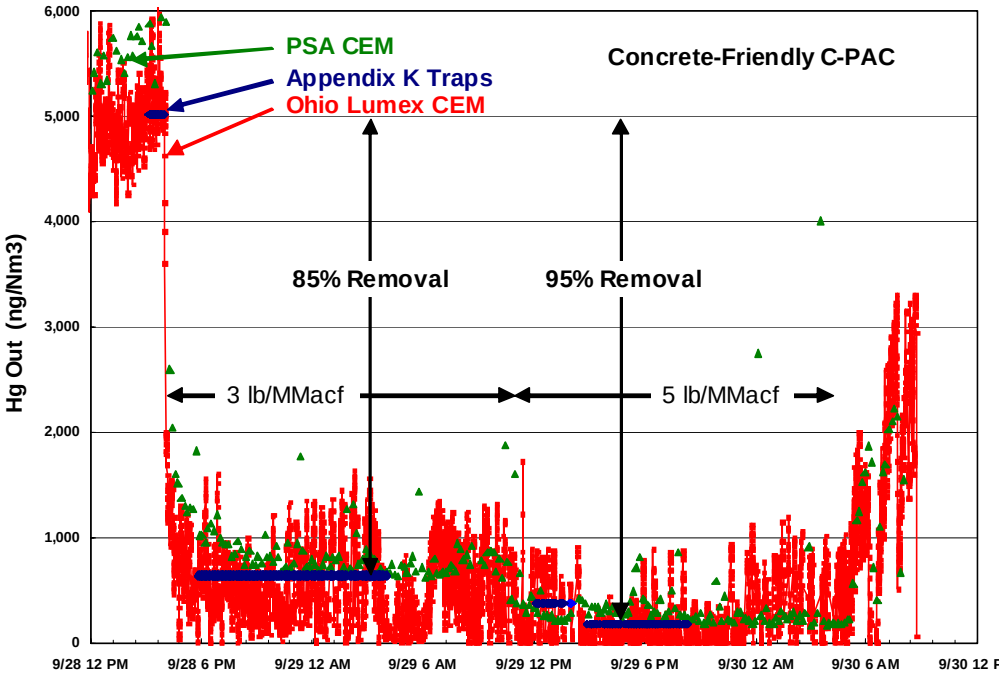


Figure 3. Mercury Removal & C-PAC Injection rate at Corette.

At injection rate of 3 lb/MMacf, mercury removal was about 85% and it increased to 95% when the injection rate increased to 5 lb/MMacf, as shown in the below Table 1.

Table 1. Mercury removal and C-PAC™ injection rate at Corette

Injection Rate	3 lb/MMacf	5 lb/MMacf
Appendix K Traps	87%	96%
PSA CEM	85%	93%
Ohio Lumex CEM	85%	96%

COAL AND FLY ASH DATA

PPL Corette burned a Powder River Basin (PRB) subbituminous coal. The coal samples contained about 30% moisture, less than 5% ash, and 0.3% sulfur. The coal heat content was slightly below 8,500 Btu/lb. The average mercury content of the coal was approximately 0.080 ppm on a dry basis.

Analysis of the fly ash samples collected during the test confirmed that the proper amount of mercury was being removed from the flue gas and collected in the fly ash.

The foam index testing conducted by Headwaters Resources of the resulting fly ash indicated that the fly ash maintained its ability to be used in cement. All of the fly ash generated during the C-PAC™ injection period was transferred into PPL's storage silos and sold by Headwaters Resources for concrete use.

4. C-PAC^{TM} INJECTION BEFORE THE AIR PREHEATER

In another trial in Illinois, Albemarle's C-PAC^{TM} sorbent was injected before the air preheater at Midwest Generation's Waukegan Station. This plant burns PRB coal and has a cold-side ESP for particulate control. The testing was performed by URS Corporation.

The test results are indicated in Figure 4. At an injection rate of 3 lb/MMacf, the sorbent removed over 85% of the mercury. At 4 lb/MMacf it removed over 90%. Injecting on the hot side of the ESP lowered the amount of sorbent required. A significant amount of turbulent mixing occurs through the air preheater and the sorbents have longer residence time. The C-PACTM was not negatively affected by the increased temperature ahead of the air preheater. The data presented are averages of measurements from continuous mercury monitors and Appendix K sampling at full load.

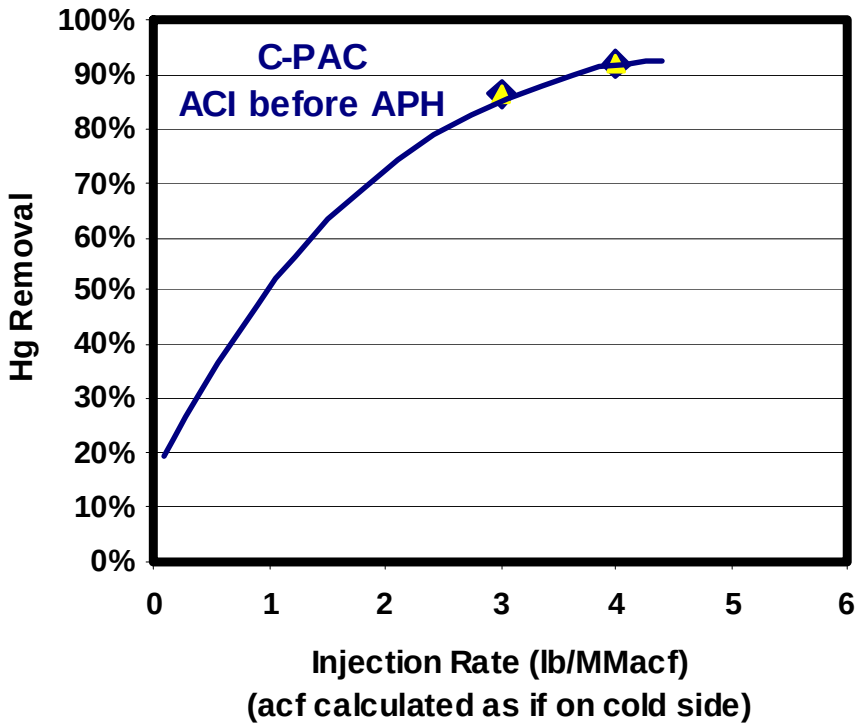


Figure 4. Mercury Removal Rate of C-PAC at Waukegan.

5. C-PAC™ EFFECTS ON ELECTROSTATIC PRECIPITATORS

Previously, Albemarle Sorbent Technologies has reported in two Department of Energy trials that injection of its gas-phase brominated sorbents significantly lowered the electrostatic precipitator opacity as a co-benefit of mercury reductions. This occurred at Progress Energy's Lee Station with bituminous coal and at Midwest Generation's Crawford Station Unit 7 with subbituminous coal. This has not been reported with competitive salt-phase brominated carbons, so it has been an open question whether the two types of brominated sorbents are fundamentally different in this respect.

This year an unnamed utility site started up permanent operation using a salt-phase brominated carbon for mercury control with subbituminous coal. Immediately, however, it began having opacity problems, exceeding its 30% opacity limit. Consequently, it then loaded up its silo with C-PAC™, to see if a gas-phase brominated sorbent would lead to better opacity results under the same conditions. The results are displayed on the following page.

Even injected at 1 lb/MMacf, the salt-phase carbon caused opacity to average about 27%, with significant exceedances over 30%. With the C-PAC™, however, even at a higher full-load and with 3 and 4 lb/MMacf injected, the opacity averaged about 22%.

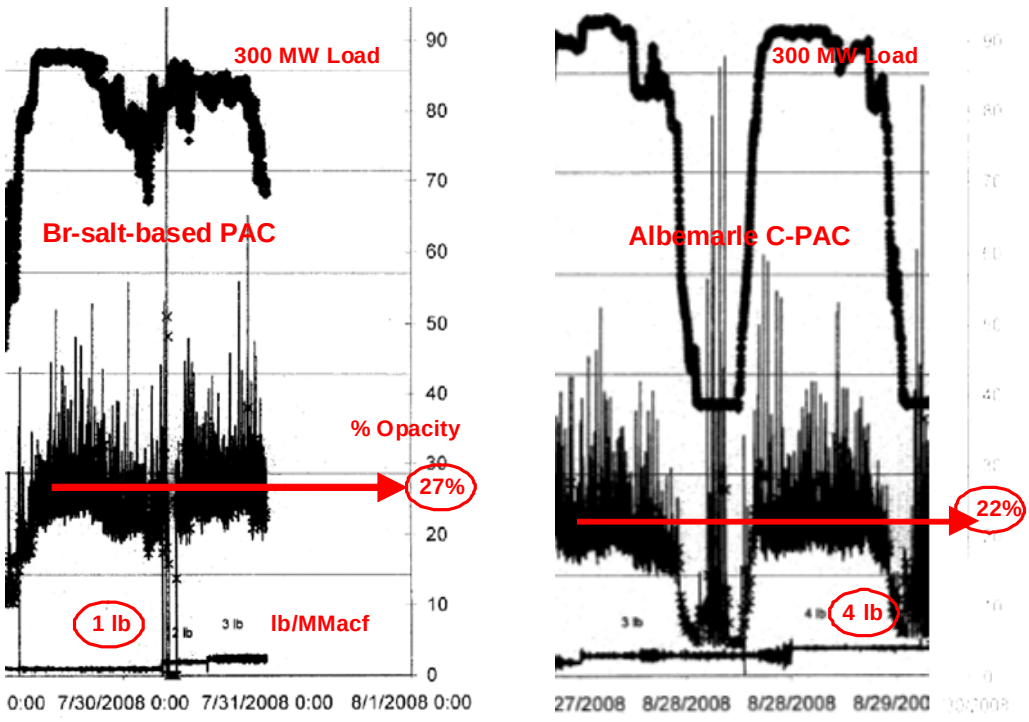


Figure 5. Stack opacity with load with the injection of different sorbents.

6. SUMMARY

Albemarle Sorbent Technologies' carbon-based concrete-friendly mercury sorbents, on which a patent is pending, continue to demonstrate high mercury reduction performance at an expanding number of power plants. C-PAC™ is now fully commercially available and millions of pounds have been shipped. Requirements for high levels of mercury emission reduction no longer mean sacrificing fly ash sales for use in concrete.

REFERENCES

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