Mercury Reduction Performance of Concrete-Friendly™ C-PAC™ Sorbent

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ABSTRACT

When traditional powdered activated carbon (PAC) mercury sorbents become mixed in with fly ash, the power plant can no longer sell the ash for its highest-value use, as a replacement for cement in concretes. The primary problem is that the PAC strongly adsorbs the special air-entraining admixture (AEA) chemicals added to the concrete slurry to generate the air bubbles required for workability and freeze-thaw capabilities.

This paper presents full-scale power plant results for a unique brominated PAC called C-PAC™, which has been made to have extremely low AEA adsorption. A DOE-sponsored full-scale thirty-day trial with this concrete-friendly™ C-PAC™ was performed at Midwest Generation’s Crawford Station last summer. The mercury reduction performance results of that trial are detailed. Data on stack opacity is also presented for the unit’s very small, 120-SCA electrostatic precipitator.

See also the companion paper by Zhou, Q. et al. on the concrete performance of the fly ashes containing C-PAC™ from the Crawford Station trial.[1]

BACKGROUND

Over 20% of the fly ash generated by U.S. power plants, over 12 million tons per year, is currently sold for concrete use, rather than being disposed of in landfills. And efforts are underway to increase this amount. This fly ash substitutes for a portion of the costly manufactured portland cement in the concrete mix, lowering its cost, making the concrete more durable, and lowering greenhouse gas emissions.

The ability to recycle fly ash into this high-value use, however, is now threatened. The federal Clean Air Mercury Rule soon requires coal-fired power plants to reduce their mercury emissions for the first time. In addition, numerous states have jumped in and are already requiring swifter and higher mercury reduction levels.
Many coal-fired power plants will comply with the new mercury regulations by injecting powdered activated carbon (PAC) into the flue gas in front of their existing particulate controls. In this process, however, the PAC gets mixed in with the plant’s fly ash. Because of the high surface area of typical PACs, if even the smallest amount gets mixed in with fly ash, the fly ash can no longer be used in concrete. The PAC adsorbs the air-entraining admixture (AEA) chemicals later added to the concrete slurry to generate the air bubbles required for workability and freeze-thaw capabilities. Additional AEA can easily be added, but because of inevitable variations in the amount of the highly-adsorbent PAC in each batch, some concretes would end up with too much void space and some with too little. What is needed is a mercury sorbent with low intrinsic AEA adsorption, so that inevitable variations in its proportions have little to no effect.

DEVELOPMENT OF A CONCRETE-FRIENDLY MERCURY SORBENT

Sorbent Technologies researchers have developed a way of making carbon sorbents that significantly lowers AEA effects. An example of the resulting foam index data appears below.

The two commercial PACs from Calgon and Norit have extremely high specific foam indexes, 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 desired bubbles. B-PAC™, Sorbent Technologies’ standard brominated powdered activated carbon, has a lower foam index, but it is still far too high to be usable in concretes. In contrast, the C-PACTM sorbents have an extremely low adsorption of the AEA. Consequently, truck to truck variations in its concentration in the fly ash will have little effect on the amount of void space created by AEAs mixed with it in the concrete slurry.
FULL-SCALE C-PAC™ TRIAL AT THE CRAWFORD STATION

But is the sorbent that does not adsorb AEAs a good sorbent for flue gas mercury?

With support from the U.S. Department of Energy’s National Energy Technology Laboratory, Sorbent Technologies recently demonstrated C-PAC™ concrete-friendly mercury sorbent in full-scale trials at Midwest Generation’s Crawford Station. When the unburned carbon is low enough, this plant can sell its fly ash as a substitute for cement in concrete. The plant burns subbituminous coal and has a challenging, very small cold-side ESP for particulate control. A photograph of the plant, located within the city limits of Chicago, Illinois, and schematic appear below.

The sorbents were simply injected into the plant flue gas from lances ahead of the existing particulate collector. There, in the second of two that they have before being captured by the ESP, they adsorb and sequester the gas-phase elemental and oxidized mercury from the flue gas. To insure good duct coverage and mixing with the flue gas, an iterative design process for optimal lance placement was used at Crawford utilizing computational fluid dynamic modeling.

Right: The sorbent particle distribution at the ESP entrance plenum from the CFD model with an optimized injection design of 10 lances.
C-PAC™ INJECTION RESULTS

An independent group, Western Kentucky University, was responsible for the mercury semi-continuous mercury emission monitors, one before injection and one at the ESP outlet. Baseline measurements without sorbent, shown below, indicate relatively high total vapor mercury emissions at Crawford and little to no native capture by fly ash.

The test program began with parametric tests of C-PAC™ at different injection rates. An example of the inlet and outlet mercury monitor traces appears below. Before the sorbent was turned on, there was little difference between the mercury levels before and after the ESP, as measurements of mercury in the fly ash confirmed. Immediately after the sorbent was turned on at only 1 lb per million cubic feet of gas, the mercury emission level dropped dramatically. Raising the injection rate to 3 lb/MMacf lowered emissions even further.
A long-term, continuous, month-long trial of C-PAC™ injection was included in the program. The mercury removal rates over the month appear below. For the first twelve days, the injection rate varied from about 4 lb/MMacf during most of the day, to about 6 lb at night. This produced fly ash samples with considerably varying carbon levels that could be tested for the degree of variation in AEA effects. Some experimental non-concrete-friendly sorbents were tested for a few days near the end of the month before the injection of C-PAC™ was resumed. Over the thirty days, the C-PAC™ averaged about 81% mercury removal at an average injection rate of about 4.6 lb/MMacf.

In addition to the PS Analytical continuous mercury monitors, sorbent traps (Method 324/Appendix K) were also continuously drawn to double-check mercury removal rates. The removal rates calculated from their measurements, plotted in the following graph, closely matched those of the monitors. The tubes use a special brominated carbon manufactured by Sorbent Technologies which makes analyzing them less expensive and more accurate. They are now being supplied to others for mercury monitoring as well. Mercury mass balance calculations based on the mercury levels found in the fly ash and originating in the coal suggested that even higher mercury removal rates may have been achieved.
Once the month-long trial was completed and adequate fly ash samples were collected for extensive concrete testing, further parametric injection tests were run with non-concrete-friendly sorbents. Results with two variations of Sorbent Technologies’ B-PAC™ sorbents and Norit’s Darco® Hg-LH appear below. In these tests significantly more of the Hg-LH sorbent was required to meet the same mercury removal rate as the B-PAC™.
Operation of the electrostatic precipitator was closely observed during the month-long trial. Crawford has a very small ESP with a specific collection area of only 120 ft$^2$/kacf and stack opacity at high load was in the neighborhood of 20% in the baseline period before injection began. In a previous trial by others with different sorbents on a small ESP, degraded particulate performance was observed. At Crawford, the particulate load to the ESP increased about 2.5% with sorbent injection.

Fortunately, injection of C-PAC™ appeared to improve ESP performance, rather than degrade it, offering a particulate removal co-benefit. This has been observed before with B-PAC™ sorbent, most recently in a month-long trial with bituminous coal at Progress Energy’s Lee Station Unit 1,[2] where the plant was able to operate without its flue gas conditioning system for the first time. At Crawford, with subbituminous coal, the average opacity at high load continued to drop over the course of the trial. See the graphic above. The degree of any change should be doubled, because only half of the gas going to the stack was being treated by the sorbent.

**RESULTING FLY ASHES**

The resulting fly ashes were all usable in concrete, most, and possibly all, usable in premium concrete. Using Lafarge’s method and the AEA Vinsol®, 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.
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.

For details on the resulting fly ashes and concretes made from them, see the companion paper by Zhou, Q., et al., “Concretes and Fly Ashes from a Full-Scale, Concrete-Friendly™ C-PAC™ Mercury Control Trial.”

**ECONOMICS**

Brominated carbons such as B-PAC™ have significantly reduced the cost of mercury reductions at power plants, particularly those burning Western coals. See the DOE NETL graphic below.

If a plant loses its ability to sell its fly ash for concrete, however, mercury control is much more expensive, as indicated in the following DOE graphic.
CONCLUSIONS

It is possible to achieve both high mercury removal rates while retaining the ability to sell fly ash into concrete markets if the proper sorbent is chosen. A month-long trial at Midwest Generation’s Crawford Station with C-PAC™ sorbent demonstrated mercury reductions of over 80% while yielding a fly ash with low foam index values.

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REFERENCES

