DEVELOPMENT OF CARBON-BASED CONCRETE-FRIENDLY MERCURY SORBENT

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Abstract

In 2005, the U.S. Environmental Protection Agency (U.S. EPA) promulgated its Clean Air Mercury Rule (CAMR), requiring coal-fired power plants to reduce their mercury emissions for the first time. Moreover, numerous states are already requiring swifter and higher mercury reduction levels than federally required. For the majority of the coal-fired power plants, the leading candidate technology to comply with the new mercury regulations is the injection of powdered activated carbon-based mercury sorbents into the flue gas in front of the plant's existing particulate control devices. However, when conventional carbon-based mercury sorbents used for mercury emission control become mixed in with the fly ash from coal-fired power plants, the ash can no longer be sold for its highest-value use, as a replacement for cement in concretes. The use of fly ash to replace a portion of the cement in concrete is a major market for fly ash. A new carbon-based mercury sorbent, C-PAC™, was recently developed by Sorbent Technologies that allows fly ash to continue to be used in concrete applications. This novel C-PAC™ was recently tested in a full-scale coal-fired power plant, Midwest Generation's Crawford Station, in a month-long trial. Mercury removal and concrete test data from the Crawford test is presented in this paper.

Introduction

The use of fly ash generated by U.S. power plants in concrete has economic and environmental benefits to both the utility and concrete industries. Currently, over 20% fly ash, about 15 million tons per year, is used as a substitute for a portion of the costly manufactured Portland cement in the concrete mix, rather than being disposed of in landfills. Efforts are underway to increase this amount (ACAA 2005). However, with the promulgation of the new federal Clear Air Mercury Rule (CAMR), this successful practice is threatened. In 2005, the U.S. Environmental Protection Agency (U.S. EPA) promulgated its CAMR, requiring coal-fired power plants to reduce their mercury emissions for the first time. Moreover, numerous states are requiring swifter and higher mercury reduction levels than federally required. For the majority of the coal-fired power plants, the leading candidate technology to comply with the new mercury regulations is the injection of powdered activated carbon (PAC) based mercury sorbents into the flue gas in front of the plant's existing particulate control devices. However, when carbon-based mercury sorbents used for mercury emission control become mixed in with the fly ash from coal-fired power plants, the ash can no longer be sold for its highest-value use, as a replacement for cement in concretes.

The typical PAC used for mercury emission control has high surface area and high adsorption capacity for air-entraining admixture (AEA) chemicals added to the concrete slurry to generate the air bubbles required for workability and freeze-thaw capability. Even small amounts of PAC get mixed in with fly ash, the fly ash can no longer be used in concrete. 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.

One of the solutions to this challenge is to develop a concrete-friendly mercury sorbent which has significantly lower AEA effects, but still retains high mercury performance. One direction to work on is to develop a mercury sorbent from mineral-base materials which naturally have low AEA adsorption. Another path was to process carbon-based mercury sorbents to have significantly lower AEA effects. Sorbent Technologies Corporation's researchers have been working on the second approach and successfully developed C-PAC™, which allows fly ash to continue to be used in concrete applications. This novel sorbent was tested month-long in a full-scale trail at Midwest Generation's Crawford Station. Mercury removal and concrete test data from the Crawford test is presented here.

Development of a concrete-friendly mercury sorbent

The interference of AEA by various mercury carbon sorbents has been correlated with the adsorption of Acid Blue 80 (AB80), which can be defined as Acid Blue Index (ABI). Detailed information about this test method has been given elsewhere (Zhang 2007). Generally, the lower ABI the carbon sorbent has, the more "concrete-friendly" the carbon sorbent is. The mercury performance of sorbent has been tested in a pilot duct-injection system with simulated flue gas containing typical amount of Hg, SO_2, NO_x, HCl and steam, the system has been detailed introduced elsewhere (Nelson 2003).

The mercury performance and the concrete-friendly character of the C-PAC™ are shown in Figure 1. For comparison, two other commercially available mercury sorbents, B-PAC™ from Sorbent Technologies and Darco Hg™ from Norit, are also listed in Figure 1.

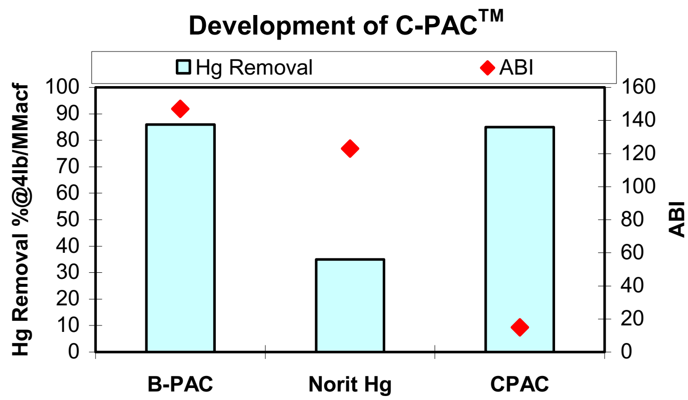

Figure 1. The Development of C-PAC™

Both B-PAC™, Sorbent Technologies' standard brominated powdered activated carbon, and Norit Hg™, a yardstick sorbent for mercury emission control, have extremely high ABIs, indicating that large amounts of AEA are needed before their AEA adsorption is satisfied and some is left over to foam and stabilize the desired bubbles. In contrast, the C-PAC™ 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 in with the concrete slurry.

Full-scale C-PAC™ trial at the Crawford Station

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 content is low enough, this plant sells 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 the duct configuration appear in Figure 2.

Figure 2. Overview and Duct Configuration of Midwest Generation's Crawford Generation

The sorbents were simply injected into the plant flue gas from lances ahead of the existing particulate collector. There, in a second or so before being captured by the ESP, they adsorb and sequester the gas-phase elemental and oxidized mercury from the flue gas. The test program included parametric sorbent injection tests of C-PAC™ and B-PAC™ and a 30-day continuous sorbent injection test. The mercury removal and concrete test results are discussed below.

C-PAC™ Injection Test Mercury Removal Results

The test program began with parametric tests of C-PAC™ at different injection rates. An example of the inlet and outlet mercury concentration appears in Figure 3. Before the sorbent was turned on, there was little difference between the mercury levels before and after the ESP. Measurement of mercury concentration in the fly ash confirmed this. Immediately after the sorbent was turned on at only 1 lb per million cubic feet of gas (lb/MMacf), the mercury emission level dropped dramatically. Raising the injection rate to 3 lb/MMacf lowered emissions even further.

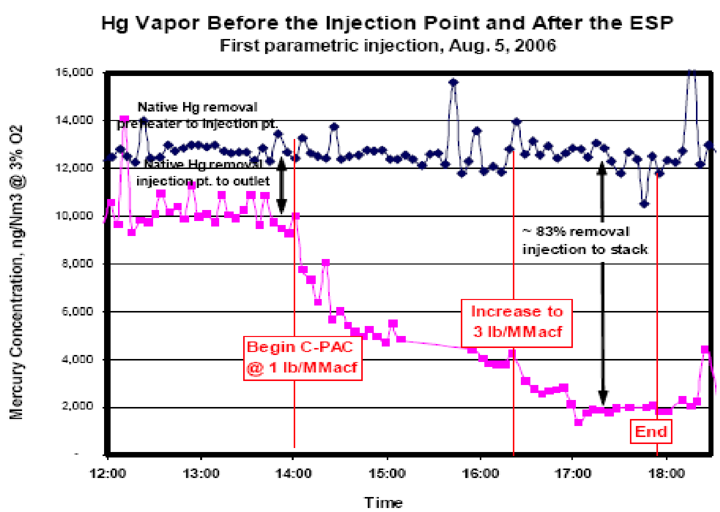

Figure 3. Hg Vapor Concentration before Injection Point and After ESP

A long-term, continuous, month-long trial of C-PAC™ injection was included in the program. The mercury removal rates over the month appear in Figure 4. 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 which were then tested for the variations in AEA effects. Some experimental "non-concrete-friendly" sorbents were tested for a few days near the end of the month-long trial and then 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.

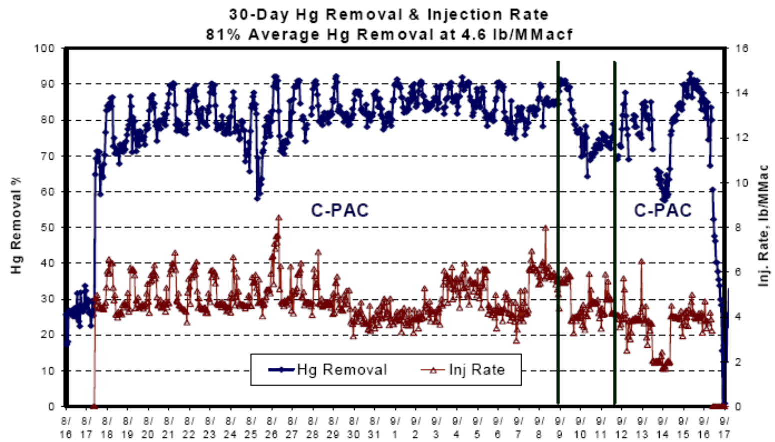

Figure 4. Hg Removal of 30-day Continuous Sorbent Inject Test in Crawford

C-PAC™ Injection Test Concrete Test Results

During the month-long trial, adequate fly ash samples were collected for extensive concrete testing. The materials used in Sorbent Technologies' laboratory to make test concretes included Portland cement (type I), gravel, sand, and Crawford fly ash with and without C-PAC™. The ratio of water to cement, W/C, for the 100% Portland cement (No Ash) was 0.52. For the 20 wt% fly ash control (Ash) and the C-PAC-fly ash (C-PAC™) concretes, which require less water, 0.50 W/C was used. 20% of the cement was replaced by fly ash in ash control and C-PAC concretes. Four commercially-available AEAs were used. The properties of fresh concretes are listed in Table 1.

Table 1. The Properties of Fresh Concrete

Concrete	AEA (ml/100 kg Cement-ash)*	Slump (inch)	Air (vol%)	FI (µl)
No Ash	41	6.0	6.7	32
Ash	43	6.1	6.0	37
C-PAC™	87	6.3	6.4	58
PAC**	349	6.0	5.5	190

* A dosage of 30 to 320 ml/100 kg of cement material is mentioned in the MSDS of the AEA.
** An equal weight of brominated PAC (Norit Darco Hg-LH) mixing with baseline fly ash. An extra 40 ml/100 kg of Darex II was required to increase air to 6%.

The concrete with the blank Crawford fly ash needs AEA additions of about 87 ml/100kg cement-ash to provide 6.0% air voids in the fresh concrete. With the fly ash collected during mercury emission control trial with C-PAC™ injection, about double the amount of AEA was required to make a 6% air in the concrete. Approximately ten times the amount of AEA (or 349 ml/100kg cement-ash) was needed for a concrete with a commercial available PAC (Norit Darco Hg-LH™) containing fly ash.

Even though more AEA was used in C-PAC™ concrete than in the control to achieve the same air, the dosage still satisfied contractor specifications, while the standard PAC ash was out of the range. The Unconfined Compression Strength (UCS) tests on the cured above concrete shows that UCS of the concrete with C-PAC™ fly ashes is comparable with that of the ash control.

ECONOMICS

Brominated carbons, such as Sorbent Technologies Corporation's B-PAC™, have significantly reduced the cost of mercury reductions at power plants, particularly those burning Western coals, as indicated in Figure 5, from U.S. Department of Energy, National Energy Technologies Laboratory (Feeley 2005). If fly ash sales for concrete use are affected, however, the net costs will be significantly higher. To preserve these sales, "concrete-friendly" mercury sorbents like C-PAC™ are required.

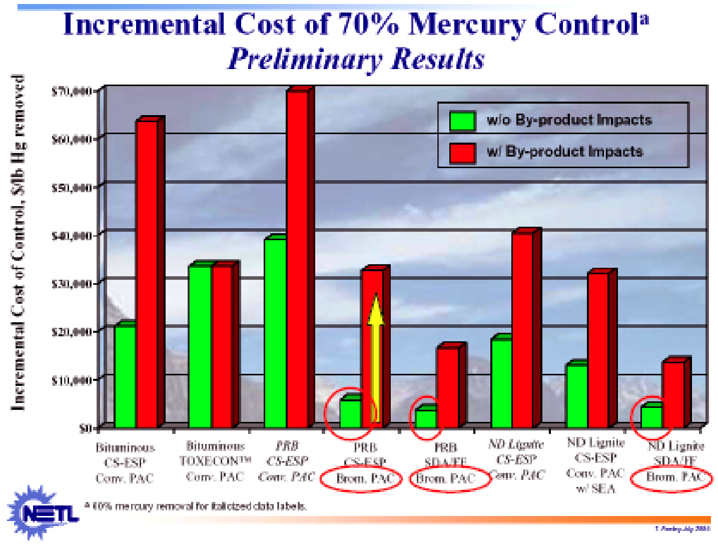

Figure 5. Incremental Cost of 70% Mercury Control (from DOE-NETL)

Conclusion

It is possible for carbon-based mercury sorbent to achieve high mercury removal rates and preserve the ability of fly ash to be used in concrete. 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 AEA interference.

References

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