BROMINATED ACTIVATED CARBON FOR COAL-FIRED POWER PLANT MERCURY EMISSION CONTROL

Sid Nelson Jr., Ronald R. Landreth, Yinzhi Zhang, Quihui Zhou, Zhong Tang and Xin Liu
Sorbent Technologies Corporation, Twinsburg, Ohio, USA

Abastract

Coal-burning power plants have been the largest unregulated source of mercury emissions in the United States, sending 48 tons of mercury into the air annually. In 2005, the U.S. Environmental Protection Agency promulgated its Clean Air Mercury Rule (CAMR), requiring coal-fired power plants to reduce their mercury emissions by approximately 20% beginning in 2010. Numerous states are already requiring swifter and higher mercury reduction levels than what is 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) mercury sorbents into the flue gas in front of the plant's existing particulate control devices. This opens a potential U.S. market for activated carbon that could exceed $500 M per year. Flue gas conditions, including very short contact times, about 1-2 seconds, very low Hg concentrations, about 10μg/m^3, and high flue gas temperatures, about 160-200°C, make the mercury adsorption of activated carbon far below its equilibrium capacity. Our studies indicate that a bromination pretreatment can significantly increase the mercury adsorption of activated carbon. A family of PAC based brominated mercury sorbents have been developed and are conmmercially manufactured. The characterization of the brominated carbon sorbent and its mercury performance compared to plain activated carbon, including the results from the full-scale power plant trials, is presented in this paper.

Introduction

Historically activated carbon has been widely used in environmental pollution control due to its high adsorption performance of various pollutants. The continuing introduction of more stringent environmental legislation ensures the growth of the activated carbon market. Recently, a significant carbon market is being created to address coal-fired power plant mercury emission control. 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, 12 states have passed more stringent legislation than CAMR and other states are expected to follow.

Coal-burning power plants had been the largest unregulated source of mercury emissions in the United States, sending 48 tons of mercury into the air annually. 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 sorbent into the flue gas in front of the plant's existing particulate control devices. This opens a potential U.S. market for activated carbon of more than $500M per year.

Very short contact times, about 1-2 seconds, very low Hg concentrations in flue gas, about 10μg/m^3, and high flue gas temperatures, about 160-200°C, make the mercury adsorption of activated carbon far below its equilibrium capacity. Research by Sorbent Technologies and others have proven that a bromination pretreatment can significantly increase the mercury adsorption of activated carbon and decrease the mercury emission control cost for coal-fired power plants (Nelson 2004 and Feeley 2005). A family of PAC based brominated mercury sorbents have been developed and are being manufactured by Sorbent Technologies Corporation: B-PAC™ for standard use, H-PAC™ for hot-side ESPs, and C-PAC™ for the plants that sell their fly ash for concrete. The characterization of the brominated carbon sorbent and its mercury performance compared to plain activated carbon, including the results from the full-scale power plant trials, is presented in this paper.

XPS Study of B-PAC™

B-PACs are plain PACs treated with a small amount of gas-phase bromine following the techniques described in US patent 6,953,494 (Nelson 2005). Unlike chlorine, HCl, and HF, bromine and HBr are not

considered by the US EPA to be air toxics. Actually, bromine is the third-most-common anion found in the ocean. Seawater contains approximately 80ppm dissolved bromine.

XPS was used to study the chemical structure of bromine in B-PAC™. The XPS instrument used was a Kratos Analytical Axis Ultra with 280-watt X-rays and spot size of 700µm X 350µm. The sample powders were pressed into 3M double-sided tape with a mortar and pestle and each sample was subsequently examined under an optical microscope to ensure uniform coverage of the tape surface. Low resolution survey scans were acquired on all samples, followed by high-resolution scans for the elements of interest. Figure 1 displays a representative high resolution scan of a B-PAC™ which contained about 5wt% bromine.

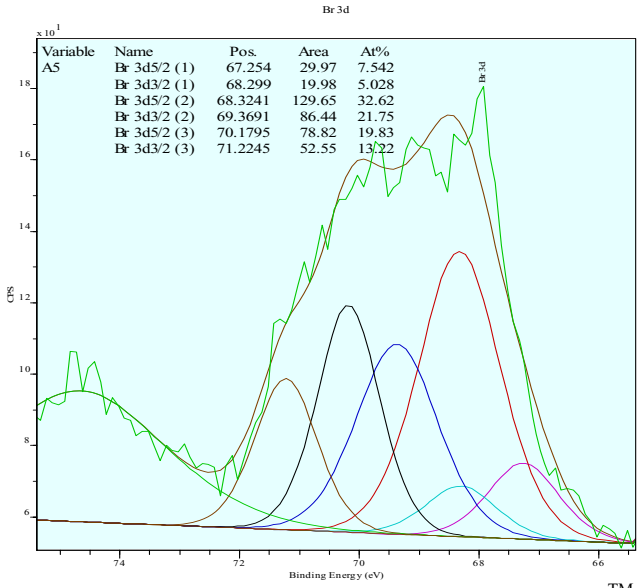

Figure 1. Br High-Resolution Scan of a Typical B-PAC™

There appear to be three bromine species in most of the brominated samples studied. The binding energies for these three species are about 67.2eV, 68.3eV, and 70.2eV, respectively. According to Papirer (1994), the bromine specie with the highest binding energy, ~70eV, labeled here as Br(3), is related to bromine covalently bonded to carbon, C-Br. Also according to Papirer, the bromine specie with the binding energy of ~68.5eV, labeled as Br(2), is related to physically adsorbed bromine. The bromine specie with the lowest binding energy of ~67.4eV, Br(1), is attributed to $Cn \rightarrow Br_2$ surface complexes, which are formed by charge transfer to the Br_2 molecule acting as an electron acceptor. However, Papirer did not provide much evidence to support the hypothesized chemical states of these three bromine species.

In order to investigate the chemical state of these three species, FTIR was applied to analyze the samples. Unfortunately, due to the low analytic concentration of Br, ~5wt%, coupled with the high adsorption index of carbonaceous material in the infrared region, the FTIR analysis was not able to provide insight into the nature of the carbon bromine interactions in B-PAC. Without further investigations, the present research was not able to reach any definitive conclusions on the various chemical states of these three bromine species.

Mercury Removal Performance of B-PAC™

B-PAC has been tested by Sorbent Technologies and other companies at a number of power plants. As an example, during the summer of 2004, B-PAC was tested by Sorbent Technologies at Detroit Edison's St. Clair Station, with the support from Department of Energy's National Energy Technology Laboratory. The four St. Clair Station 160MW boilers typically burn a blend of 85% subbituminous coal and 15% Eastern bituminous coal. In this project sorbent was injected into the ductwork ahead of an 80-MW cold-side ESP, as shown in Figure 2. Baseline mercury emissions range from about 3 to 8 $\mu m/Nm^3$ with about half in the elemental form.

Figure 2. Portion of Ductwork and ESP of St. Clair Plant

The test program includes parametric test, during which different sorbents were injected for short periods at different injection rates and a 30-day long-term test, during which B-PAC was continuously injected at the same injection rate. The parametric test results appear in Figure 3. In the St. Clair testing, injected at only 1 pound of sorbent-per-million-actual-cubic- feet-of- flue-gas (lb/MMacf), B-PAC appeared to lower mercury emissions at full load by about 70% with the 85% subbituminous coal blend. When the plant's 30% native mercury removal from unburned carbon under these conditions is also included, the net reduction observed was 80%. Injecting B-PAC at 3 lb/MMacf while burning the blend yielded 90% removal due to the sorbent and total removal of about 93%. With 100% subbituminous coal the performance was even higher, with over 75% and 94% removal due to the B-PAC sorbent alone when injected at 1 and 3 lb/MMacf respectively. In contrast, when plain powdered activated carbon Norit Darco FGD™ was injected, the mercury removal rates were 45% and 70% when injected at 2 lb/MMacf and 6 lb/MMacf, respectively, and stopped at 70% removal even injection rate increased to 12 lb/MMacf.

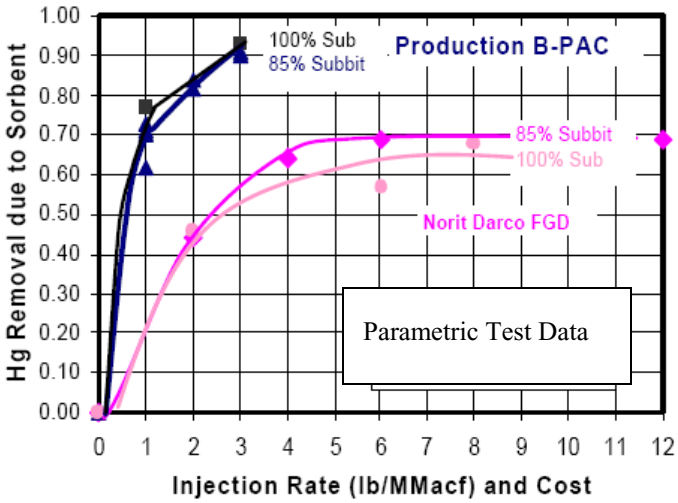

Figure 3. Mercury Removal due to Sorbent of St. Clair Test

This data suggest that 70% removal due to the B-PAC can be achieved at about $4,000 per- lb-of-Hg-removed and 90% removal for less than $9,000 per- lb. Costs are even lower when 100% subbituminous coal was burned. Such costs are over 85% to 90% less than baseline mercury-removal costs currently estimated by the DOE (Feeley 2005). The plain yardstick PAC (Norit Darco FGD) proved much less effective than B-PAC. Similar to the other tests, the performance of the plain PAC topped out at about 70% Hg removal (Durham 2004).

A continuous 30-day, 24-hours-per-day run was included in the DOE NETL demonstration. The mercury removal of this long-term test appears in Figure 4. B-PAC at 3 lb/MMacf was continuously injected as the plant naturally cycled between 100% subbituminous on the weekends and the blend on weekdays, operating usually at full power during the days and ramping down to less output at night.

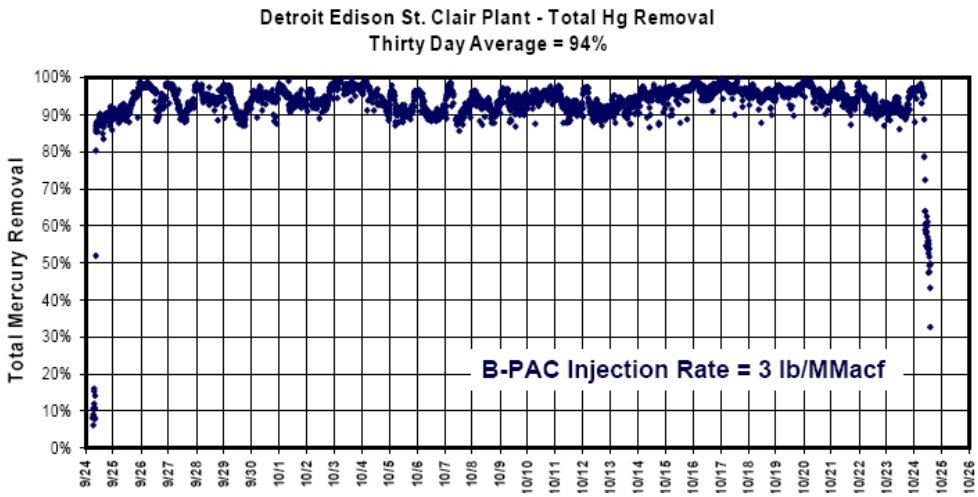

Figure 4. Total Mercury Removal of St. Clair 30-day Test

During the long term test, the mercury removal varied within ±5% during the high load and low load due to the changes in the flue gas conditions. But the mercury removal remained very high with the 3 lb/MMacf injection rate. Balance-of-plant effects were also closely monitored and none was observed. The total mercury removal across the ESP averaged 94% over the 30 day's test period. These test results remain one of the best full-scale mercury emission control trials ever published so far.

The resulting fly ash collected from the long-term test was collected and systematically analyzed. In the long-term test fly ashes, significantly higher LOI and mercury than those in baseline fly ashes were found. This confirms the high gas-phase mercury removal. In order to test if the mercury captured in the fly ash would cause any secondary pollution when the fly ash is disposed of in landfill, leaching tests were carried out using TCLP, SGLP and distilled water. The results show the mercury captured by B-PAC in fly ash is not leachable. Additionally, further test shows the mercury captured in fly ash is also not volatile at moderately high temperature.

Besides the St. Clair plant, B-PAC™ has been tested in a number of other plants, which have proven the material's applicability across a wide variety of coals and air pollution control equipment configurations. Table 1 is a summary of these test results.

Table 1. Major B-PAC™ Full-Scale Test Results

Coal	PM Unit	Hg Removal	Injection Rate @lb/MMacf	Plant	Utility	Data
Bitum. Low-S	CS ESP	**85%**	**5.0**	Allen	Duke	Apogee/ST
Bitum. High-S	CS-ESP	**70%**	**4.0**	Lausche	OhioU	Sorbtech
Bitum. Low-S	HS ESP	**80%***	**6.4**	Cliffside	Duke	Sorbtech
Bitum. Low-S	HS ESP	**50%**	**5.0**	Buck	Duke	Sorbtech
Bitum. Low-S	CS ESP	**85%**	**8.0**	Lee 1	Progress Energy	Sorbtech
Subbitum.Blend	CS-ESP	**90%**	**3.0**	St. Clair	Detroit Ed.	Sorbtech
Subbituminous	CS-ESP	**90+%**	**3.0**	St. Clair	Detroit Ed.	Sorbtech
Subbituminous	CS-ESP	**90%**	**3.2**	Stanton 1	Great River Energy	EERC/URS
Subbituminous	CS-ESP	**81%**	**4.6**	Crawford	Midwest Generation	Sorbtech
Lignite	SD/FF	**95%**	**1.5**	Stanton 10	Great River Energy	EERC/URS

* when under low-load conditions at this plant.

The full-scale test results summarized in table 1 indicate B-PAC™ performs well with different coals and different plant configurations and is applicable to mercury emission control for various coal-fired power plants. B-PAC™ now is commercially available.

Based on our accumulated experience on mercury sorbent development and mercury emission full-scale trials, the most relevant factors affecting the mercury control performance of the B-PAC™ sorbents are summarized in Table 2.

Table 2. The factors Affect Sorbent Mercury Performance

Properties of Sorbent	Flue Gas and APCD Configuration	Operation Parameters
1. bromine content 2. particle size 3. pore structure 4. surface chemistry	1. temperature 2. acid gas composition and concentration, especially SO_3 concentration 3. residence time of carbon before captured by PM device	1. injection rate 2. sorbent distribution in flue gas within ductwork

Some of the topics mentioned in Table 2 have been well studied, however, there are still topics being investigated.

Conclusions

1. Coal-fired power plant mercury emission control is a significant emerging market for activated carbon.
2. Bromination pretreatment can significantly improve the mercury performance of carbon-based mercury sorbents.
3. Sorbent Technologies' B-PAC™ has been tested in a wide variety of power plants and has demonstrated excellent mercury removal performance at relatively low injection rates.

Reference

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