



Short communication

Mercury chemistry of brominated activated carbons – Packed-bed breakthrough experiments



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HIGHLIGHTS

- The impact of SO₂ and NO_x on Hg capture and oxidation on activated carbon is tested.
- NO and NO₂ promote the oxidation of Hg on brominated AC fiber.
- SO₂ prevents adsorption and oxidation on brominated AC fiber.
- Interaction of SO₂ and NO_x with surface Br leads to sorbent deactivation.

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ABSTRACT

Coal-fired power plants provided between 45% and 50% of the United States net energy generation in the years between 1999 and 2010 and will continue to be a primary source of electricity into the future. Among the major environmental concerns of coal utilization is the release of mercury (Hg), which was recently regulated by the US EPA in the Mercury and Air Toxics Standards (MATS) ruling in December 2011. Among the variety of potential methods for Hg capture, activated carbon injection (ACI) is viewed by the EPA as a viable, ready technology available to energy utilities to comply with MATS. However, there remain significant questions regarding the complicated interaction between the carbon sorbent, Hg, and contaminants present in combustion flue gas, such as SO₂ and NO_x (NO and NO₂). In this study, bromine-impregnated carbon fiber (Br-ACF) was tested for Hg capture and oxidation in a controlled flue gas environment to elucidate trends in the interaction of the flue gas components. These results are compared with prior surface analysis results from this group to provide additional support to prior conclusions. Compared to baseline capture rates in a clean environment, results indicate that NO_x promotes the oxidation of Hg, while SO₂ prevents the adsorption or oxidation of Hg on the Br-ACF.

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1. Introduction

The control of Hg emissions is a top priority for the U.S. Environmental Protection Agency (EPA) due to human and environmental health effects related to bioaccumulation due to anthropogenic emissions. The primary source of anthropogenic Hg emissions in the United States, and worldwide, is coal combustion for electricity generation. The Mercury and Air Toxics Standards (MATS) were finalized by the EPA in December 2011, and further updated in April 2013, to reduce emission of toxic air pollutants by setting emission limits on power plants [1].

Only a portion of the Hg volatilized during the coal combustion process is captured through conventional pollution control technologies [2]. Particle-bound Hg can be captured in particulate

control devices and oxidized Hg (Hg²⁺) may be removed in wet flue gas desulfurization (FGD) units. However, the majority of Hg, primarily Hg⁰, that is not captured through conventional technologies escapes into the environment, resulting in a wide range of potential solutions being investigated [3]. The injection of sorbent upstream of air-pollution control devices appears to be an efficient and cost-effective process to oxidize and retain volatile Hg⁰ [4].

Recent efforts in Hg emission reduction have focused on capturing Hg from low-rank coals, and one method employed the addition of chlorine [5] or other oxidizing agents directly to the flue gas. Activated carbon surfaces functionalized with halogens and/or sulfur can also improve Hg capture performance [6]. The mechanism of Hg sorption with chemically modified ACs is not fully understood, but the beneficial role of Br in the capture of Hg species is well established [7].

In Sasmaz et al. [8], prior work by this group using mercury adsorption experiments carried out on brominated AC sorbents indicate that Hg–Br compounds form on the surface of the carbon.

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X-ray adsorption fine structure (XAFS) analysis of Br-ACF sorbents indicates that surface-bound Hg is in the oxidized form, Hg^{2+} . Furthermore, the results demonstrated that the form of sulfur on the AC surface affects the adsorption of Hg. SO_2 reacts with water vapor to form sulfate groups that then occupy the same active sites on the surface that bind oxidized Hg compounds. Surface nitrogen appears to be in the form of ammonium (NH_4^+) or bonded to carbon, rather than adsorbed NO or NO_2 .

The investigation reported here covers the interaction of Hg and flue gas components (SO_2 and NO_x) on brominated AC fibers to support the conclusions in Sasmaz et al. [8]. This interaction is analyzed by exposing packed beds of the AC sorbents to methane-combustion flue gases doped with Hg, SO_2 , and NO_x . Breakthrough curves were analyzed for both Hg^0 and Hg^{2+} using a commercial Hg analyzer in combination with a commercial Hg speciation unit. These breakthrough results are then compared to the X-ray photoelectron spectroscopy (XPS) and XAFS results from Sasmaz et al. [8].

2. Materials and methods

2.1. Activated carbon

The AC used in this study is an AC fiber material impregnated with liquid Br_2 at 25 °C with a BET surface area [9] of $790 \text{ m}^2 \text{ g}^{-1}$, as measured using N_2 adsorption at 77 K with a Quantachrome Autosorb iQ2. This material was chosen, and extensively analyzed, in the previous work [8] for XAS purposes, where a pure carbon sample, free of Si, was needed. The AC fiber material is used as a model compound for brominated activated carbons and would not be used in an injection-based Hg removal process.

2.2. Breakthrough experiments

A packed-bed reactor (PBR) system was configured to investigate Hg adsorption on sorbents in a realistic flue gas environment. Coal-fired flue gas is simulated through methane (99%) combustion with air (Medical Grade), which produces a stable flame and a laminar flow regime. Stoichiometric ratios of CO_2 (8%) and H_2O vapor (16%) are formed from the flame with an O_2 content of approximately 3%. Desired amounts of NO (300 ppmv), NO_2 (5 ppmv), and SO_2 (300 ppmv) were mixed downstream of the flame, but upstream of the packed bed. All concentrations are provided at $T = 298 \text{ K}$ and $P = 1 \text{ atm}$. All gases were obtained through Praxair and controlled with Brooks Instrument 5850E mass flow controllers, except for air, which was controlled by the PS Analytical 10.534 Mercury Calibration System. Mercury was added pre-combustion, also through the 10.534 Mercury Calibration System.

Breakthrough curves on the Br-ACF were performed in order to analyze the impact of flue gas components (NO, NO_2 , and SO_2) on Hg adsorption and oxidation and to verify results observed in the XPS and XAFS analyses in previous work [8]. The inlet Hg^0 concentration was maintained at 25 ppbv to allow the experiments to be performed in a reasonable time frame (i.e., 120 min). The mercury concentration measurement variability of the system is ± 2.5 ppbv, is based on conservative estimates of potential error introduced through the experimental flow system, including flow controllers, temperature controllers, speciation instrumentation, and the detector response. A packed bed of $10 \text{ mg} \pm 0.2 \text{ mg}$ is supported in a 7-mm OD quartz reactor held at 140 °C by a Carbolite tube furnace on a plug of quartz wool. Baseline calibration experiments were performed, indicating that there was no loss (through adsorption or oxidation) across the quartz plug. While an extended calibration was performed to verify a linear response in the detector, a two-point calibration (0 ppbv and 25 ppbv) was performed before each experiment with a sorbent-free reactor to ensure the

validity of each individual experiment. Each set of conditions was performed twice, one analyzing elemental Hg (Hg^0) and the other total Hg ($\text{Hg}^T = \text{Hg}^0 + \text{Hg}^{2+}$, where Hg^{2+} is defined as oxidized Hg, independent of speciation), each time with a new packed bed of Br-ACF. The mercury speciation was determined using a commercial dilution/cracker probe (S123P200 Cracker Probe, PS Analytical, England). The experimental set up did not allow for analysis of both Hg^0 and Hg^T with the required time resolution (changing Hg species requires about 30 min) for concurrent detection, so each experiment was performed under the same conditions and compared to each other. In this manner, the concentration of Hg^{2+} ($= \text{Hg}^T - \text{Hg}^0$) can be calculated. The actual Hg^{2+} species is not identified in this study.

3. Results and discussion

As expected, based on the surface analysis results from Sasmaz et al. [8], the Br-ACF readily captured Hg in a “clean” flue gas (CO_2 , H_2O , N_2 , and O_2), devoid of other contaminants (SO_2 or NO_x). The packed bed was exposed to 25 ppbv Hg^0 for 120 min and captured >97% of the inlet Hg over the course of the experiment. Due to detection limitations of 0.6 ppbv, >97% is the confidence limit for the capture of Hg. There was no indication that Hg^0 left the surface as Hg^{2+} . Complete results for every experiment after 120 min are shown in Table 1.

As indicated by the surface analysis results, NO_x compounds are not expected to have a significant impact on Hg^0 adsorption, although, due to the presence of a potential ammonia compound on several of the sorbents, there is indication that there is interaction with the surface [8]. Minimal Hg^0 was observed downstream of the Br-ACF bed in the situation where NO, NO_2 , or both were present. There may be a slight increase in Hg^0 after 120 min (as compared to $t = 0$), but this is within the range of experimental error, and is, therefore, not conclusive. While Hg^0 is not observed downstream of the AC bed, Hg^{2+} is observed, indicating that NO_x is not preventing Hg from interacting with the AC surface. Over the 120 min experiment, both 300 ppmv NO and 5 ppmv NO_2 (which is expected to be the more reactive NO_x compound) resulted in a slow breakthrough of Hg^{2+} to 50% of the inlet Hg^0 , as seen in Fig. 1. The combination of NO and NO_2 resulted in a near doubling of the individual results, with near complete breakthrough at the end of 120 min. These results are consistent with previous XPS results [8], where N-compounds did not interact with surface Br, and would not be expected to prevent oxidation. However, they were shown to interact with the surface, and could serve to prevent Hg^{2+} from remaining bound to the surface. However, a significant question remains regarding the form of the Hg^{2+} seen downstream of the bed. Based on previous results, it is expected to be a Hg–halogen molecule (HgBr_2) [8].

A more significant concern for Hg capture and oxidation on brominated AC fibers is competition with SO_2 . The XPS results from

Table 1

Outlet mercury concentration (ppbv) after 120 min for each experiment. Hg^0 and Hg^T are direct measurements, while $\text{Hg}^{2+} = \text{Hg}^T - \text{Hg}^0$. Inlet Hg concentration is 25 ppbv. Experimental errors in the system mean all values are ± 2.5 ppbv.

Flue gas composition	Hg^0 ppbv	Hg^{2+} ppbv	Hg^T ppbv
Clean	1	0	1
NO	2	12	14
NO_2	1	12	13
NO_x	1	24	25
SO_2	12	0	12
$\text{SO}_2 + \text{NO}$	23	0	23
$\text{SO}_2 + \text{NO}_2$	23	0	23
$\text{SO}_2 + \text{NO}_x$	25	0	25

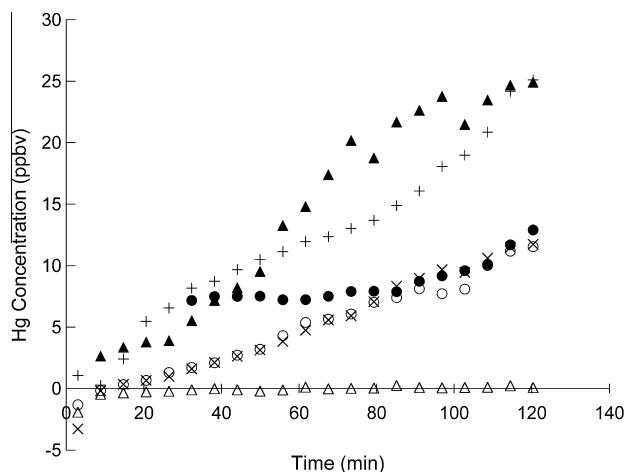


Fig. 1. Selected breakthrough curves on Br-ACF for: oxidized: \triangle – Hg^{2+} and clean; \circ – Hg^{2+} and NO ; \times – Hg^{2+} and NO_2 ; $+$ – Hg^{2+} and NO_x ; elemental: \bullet – Hg^0 and SO_2 ; \blacktriangle – Hg^0 and $\text{SO}_2 + \text{NO}_x$.

Sasmaz et al. [8] indicate that, when comparing the Br-ACF before and after exposure to flue gas, the Br species is removed from the surface in the presence of SO_2 , and Hg peaks are no longer observed. This conclusion is further supported in the results seen in Fig. 1, which displays the breakthrough curves for Hg^0 when SO_2 is present in the simulated flue gas, either by itself or in combination with the NO_x compounds. Apart from the baseline experiment, Hg^0 has completely broken through within the 120 min experimental time for all SO_2 – NO_x combinations. The Br-ACF experiment performed with only 300 ppmv SO_2 indicates a slightly better performance, which is a sign that there is interaction between the SO_2 and NO_x compounds, as previously reported by Miller et al [10].

The breakthrough experiments on Br-ACF confirmed and expanded upon the results presented using surface characterization techniques, as well as past results in the literature [7,8,10,11]. As expected, SO_2 has significant effects on both Hg capture and catalytic Hg oxidation. The fact that no Hg^{2+} is observed downstream of the bed when SO_2 is present is a strong indication that SO_2 may be scavenging the surface bromine species. The presence of NO or NO_2 in the flue gas stream does prevent Hg^0 from adsorbing on the AC

surface, but it does not prevent oxidation, a positive outcome since Hg^{2+} is easier to capture using standard techniques than Hg^0 .

There remain questions unanswered by this research, including: the speciation of Hg^{2+} downstream of the AC bed; the impact of the presence of a halogen (Cl, Br) and whether it can negate the affect of SO_2 on surface halogens; and the impact of virgin and sulfated AC on Hg speciation. Further research can elucidate the answers to these questions, and allow for more efficient and effective Hg capture in coal-fired power plants.

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