



Design of sulfur treated activated carbon fibers for gas phase elemental mercury removal



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HIGHLIGHTS

- We introduce sulfur containing functional groups in activated carbon fibers.
- The sulfide groups appear to be more effective for mercury removal than sulfate.
- Pore properties associated with adsorbents can also affect Hg adsorption.

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ABSTRACT

Several methods have been used to introduce sulfur containing groups in glass fiber supported activated carbon fibers (ACFs). The chemical and physical properties of these sulfur treated ACFs have been evaluated to determine their mercury adsorption capacities. Although sulfur impregnations decreased surface area and pore volume of ACFs, Hg uptake capacities increased when compared to raw ACF samples. For our sulfur-treated samples, sulfur atoms were incorporated into the carbon matrix in the form of sulfide and sulfate. The sulfide groups appeared to be more effective for mercury removal than sulfate. A possible mechanism for mercury adsorption, which is likely to involve the oxidation process of Hg⁰, is also discussed. Besides the effects of chemical structure on mercury adsorption, the effects of pore properties associated with adsorbents have also been studied.

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1. Introduction

Mercury is considered one of the most toxic metals due to its volatility, persistence, bioaccumulation and health impacts on human beings [1,2]. In the USA alone, approximately 50 tons of mercury is released into the atmosphere annually from coal-fired power plants, and this contributes to nearly one third of the U.S. anthropogenic mercury emissions [3]. Therefore, mercury control from coal-fired power plants has become an issue of pressing need.

There are three main forms of mercury present in the flue gas: particulate-bound, oxidized (primarily mercuric chloride), and elemental mercury [4,5]. Particulate-bound mercury refers to the mercury adsorbed onto residential particulate (e.g. fly ash), it can be collected using current air pollution control devices such as electrostatic precipitator (ESP) and fabric filter (FF). Oxidized mercury can be captured efficiently using wet scrubbers since it is water-soluble. Conversely, elemental mercury is very difficult to be removed because of its high vapor pressure and low water solubility. Thus, control of elemental mercury should be the focus of

mercury emissions from coal-fired power plants since it is the most difficult species to be eliminated.

Many researchers have been studying mercury removal methods and technologies including the use of various adsorbents such as fly ash, activated carbon and precious metals and the use of current air pollution control devices installed in power plant such as selective catalytic reduction (SCR) and wet flue gas desulfurization (WFGD) [6]. Among these, one promising technology being studied is sorbent injection [5,7]. In sorbent injection technology, typically the sorbent is injected in a coal-fired power plant downstream of the heat exchanger and upstream of the particulate control devices such as ESP and FF. The injected sorbents such as sulfur-treated powdered activated carbon (SPAC) adsorb mercury from flue gas and then are captured along with fly ash using ESP or FF.

Sulfur-impregnated activated carbons have been studied extensively at the University of Pittsburgh [8–10]. By reacting with H₂S, several sulfur forms are introduced into activated carbons, including sulfide, sulfoxide, elemental sulfur, sulfone, thiophene and sulfate. By comparing the relationship between Hg uptake and different sulfur forms, Vidic concluded that elemental sulfur, thiophene, and sulfate groups were likely responsible for mercury uptake. Hsi et al. at the Geological Survey at UIUC have also studied

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mercury adsorption using an impregnated sulfur deposited on activated carbon fibers (ACFs) [11–13]. Although ACFs were used in this case, samples were ground from mat to powder form. They mixed sulfur powder with the resulting carbon powder and heated the mixture. By varying the sulfur impregnation temperature from 250 °C to 650 °C, the authors reported the equilibrium Hg⁰ adsorption capacity ranging from 2.2 mg/g C to 11.3 mg/g C.

Carbon injection technologies have been relatively successful; however, they suffer from potential problems [7]. For example, sorbent costs are relatively high and fresh sorbents are needed for each injection. Additionally, excessive loading of particulates may lead to filter bag failure. The sorbents tend to contaminate the fly ash and increase disposal costs.

To solve the problems of carbon injection technology, we sought to combine a bag house with carbonaceous material to remove Hg and fly ash simultaneously. Assuming the combined system could collect all the emitted mercury, costs would be comparable to that of carbon injection technology since bag houses only need to be replaced every two to three years which compares favorably to the large amounts of PAC continuously injected to insure removal of Hg. Fly ash would still be collected by shaking the fabric filter while Hg adsorbed on a carbon coating on the fabric filter would not be removed. Thus, the quality of the fly ash would not be affected. After usage, PPG baghouse experts proposed that the carbon coated fabric filter containing Hg would be sent back to a coal mine to be buried underground.

2. Materials and methods

2.1. Materials

Glass fibers were provided by PPG Industrial. Novolac resin 2074 was obtained from Georgia Pacific. CO₂, N₂, O₂ gases are lab grade from S.J. Smith Welding, Inc. Na₂S₄ (28–30 wt% solution) was supplied by Tessenderlo Kerley, Inc. Other chemicals used were all from Sigma–Aldrich unless indicated.

2.2. Preparation of activated carbon fibers (ACFs)

Based on previous work in the Economy group, ACFs were made from Novolac precursor coated on a glass fiber [14,15]. This synthetic process not only lowered the cost but also simplified the manufacture. Compared with activated carbon granules, ACF coated on a glass fiber substrate showed improved wear resistance and contact efficiency. The glass fibers were impregnated with a Novolac precursor (Novolac 4.17 g, hexamethylenetetramine 0.28 g, ethanol 100 ml) and placed in the hood overnight to be dried. The coated glass fibers were cured first by heating to 100 °C for 20 min to further remove solvent, then heated to 170 °C and kept at 170 °C for 3 h. The samples were activated in flowing N₂ by heating to 600 °C (~10 °C/min) and then switching to CO₂/H₂O and holding for 5 h. (The activation gas was generated by bubbling CO₂ through liquid water.) After activation, the ACFs were cooled in flowing N₂. The samples were washed with deionized water and dried under vacuum at 120 °C for at least 12 h before using.

2.3. Preparation of sulfur impregnated ACFs

Several sulfur impregnation methods were tried to introduce sulfur on ACFs. DMSO–ACF was made from DMSO (dimethyl sulfide) according to the Durante et al. approach [16], where ACF was soaked in DMSO for 30 min and placed in the hood to be dried. The sample was then heated to 200 °C for 30 min, and air was used to decompose a portion of the sulfur compound but not to decom-

pose it to elemental sulfur. The sample was washed with deionized water and dried in a vacuum oven at 80 °C overnight before use.

Na₂S₄ is also noted to be very effective for Hg capture [17]. In our method, sulfur was introduced to ACF by Na₂S₄ decomposition (Na₂S₄–ACF). Thus, ACF was soaked in 10 wt% Na₂S₄ in the sodium hydroxide (NaOH) aqueous solution (pH = 10–12) for 30 min and placed in the hood to be dried. Then the sample was heated to 400 °C for 6 h. N₂ was used to maintain an oxygen free condition. After the heating, the sample was washed with D. I. water and dried in the hood.

Another sulfur impregnation method developed by ourselves used NaSH. The samples were identified as NaSH–ACF. Thus, ACF was soaked in 10 wt% NaSH solution for 30 min and placed in the hood to dry. Then the sample was heated to 400 °C for 3 h. N₂ was used to maintain an oxygen free condition. After heating, the sample was washed with D. I. water and dried in the hood.

The samples made from sulfur vapor were labeled as S(v)–ACF. This method was inspired by Hsi et al. approach [11–13], in their papers carbon power is mixed with sulfur power and reacted at high temperatures (250–650 °C). In our process, a combustion boat containing approximately 6 g of sulfur was placed in the furnace, followed by three boats containing ACF (the weight of the three pieces of ACF with glass fibers totaled 12 g). The samples were heated to 400 °C for 5 h. N₂ was used to blow off the excess sulfur and maintain an oxygen free condition. After the heating, the samples were washed with D. I. water and dried in the hood.

Na₂S₄–HSO₃–ACF was made by two steps of sulfur impregnations; a method also developed by ourselves. ACFs were functionalized in concentrated sulfuric acid for 4 h at 140 °C. After sulfonation, the samples were rinsed with 0.1 M NaHCO₃ solution to neutralize any residual acid, then rinsed with distilled water, and dried in the hood. After the sulfonation process, the sulfonated samples were impregnated with 10 wt% Na₂S₄ in NaOH solution for 30 min and placed in the hood. Then the samples were heated to 200 °C for 30 min. N₂ was used to maintain an oxygen free condition. After the heating, the samples were washed with D. I. water and dried in the hood. The purpose was that Na ions would attach to the negatively charged sulfonated samples, leaving S ions being active.

2.4. Static mercury uptake test

Static mercury capacity test was run by PPG Inc. The sample (8 cm * 8 cm) was suspended in a saturated mercury vapor in air at room temperature (~21 ng/mL). After two weeks, the weight change was measured assuming all the increased weight attributed to Hg adsorption.

2.5. Characterization techniques

All the samples were heated at 120 °C in a vacuum oven overnight to remove moisture and other contaminants adsorbed.

The amount of the carbonaceous material coated on glass fiber mat was measured using a Hi-Res TA instrument 2950 thermogravimetric analyzer (TGA) by burning off the coating in air at 750 °C. The samples (10–20 mg) were heated at 10 °C/min to 750 °C, and then held at that temperature for 30 min.

A Model CE440 elemental analyzer (EA) was used to determine the C, H, S, and N weight percentages in the samples. The oxygen contents were calculated by mass difference after combining the results of TGA and assuming the glass weight remained unchanged after burn-off and that there were no other elements in the samples.

X-ray photoelectron spectroscopy (XPS) experiments were performed on a Kratos Axis ULTRA. XPS spectra were obtained using an X-ray source operated at 13 kV and 10 mA. Survey scans were

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