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# Elemental mercury reaction chemistry on brominated petroleum cokes

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ABSTRACT

Activated carbon injection is a proven technology to capture mercury from flue gases. Due to the high cost and environmental concerns related to its disposal, high efficiency and low-cost sorbents have been studied to replace activated carbon. In this study, the petroleum coke obtained from two Canadian petroleum refineries, with high inherent sulfur content and impregnated with bromine, was compared to investigate elemental mercury capture mechanisms. These carbon-based sorbents showed excellent mercury removal efficiency at 100 and 200 °C. Elemental analysis, Brunauer–Emmett–Teller surface area, pore volume and thermogravimetric analysis were used to characterize the sorbents. X-ray photoelectron spectroscopy was used to examine the significant changes in chemistry and oxidation states of Br, S and Hg on the sorbent surface. More active mercury binding sites were created on brominated petroleum cokes after the chemical-mechanical bromination process. The inherent thiophene and organic sulfide in petroleum coke played a dominant role in mercury capture.

## 1. Introduction

Although at trace amount, mercury emitted into the atmosphere from fossil fuel combustion for power generation and heating purposes is an environmental threat [1–3]. Mercury emissions not only affect equipment and processes in the facilities but also present potential human health hazards. Mercury can be transformed into highly toxic methyl-mercury, which bio-accumulates in living organisms. Exposure to mercury can affect the human nerve system and harm the brain, heart, kidneys, lungs, and immune system [4]. To reduce anthropogenic mercury emission from coal combustion, strict emission standards have been set by many countries. In United States for example, the mercury emission reductions of 20 tons from the power sector have been estimated in year 2016. Chinese State Environmental Protection Administration (SEPA) has also established emission standards of air pollutants for various industries (GB13223-2011). These standards set the mercury emission limit for coal-fired power plants to 0.03 mg/m$^3$ [5].

Mercury in combustion flue gas is emitted in three major forms: elemental, oxidized and particulate. Due to its reactivity and volatility in the operating temperature range of flue gases from the combustion sources, capturing elemental mercury is rather difficult. The most widely used technique for capturing mercury from flue gas is sorbent injection, mainly using activated carbon. Carbon-based sorbents have been developed extensively [6,7]. Some have been reported to impregnate with sulfur and halides to capture mercury from flue gas [8]. The cost associated with sorbent injection is high; thus alternative low-cost sorbents have been investigated. Petroleum coke, with high inherent sulfur content, a by-product of heavy crude oil refining, is used as a low-cost material for mercury capture [9–11]. Petroleum coke containing around 7 wt% sulfur pyrolyzed at 1100 °C for 10 min showed great potential for removing mercury from flue gas. One possible reason for this improved efficiency was that the sulfur migrated to the surface during pyrolysis at high temperatures [9]. Morris et al. [10] showed that $SO_2$-activated petroleum coke, which could be thermally regenerated with a minimal loss of active surface sulfur sites, has the potential for mercury capture. Hong et al. [11] reported that when petroleum coke was activated by $Na_2S$ and then treated with $NH_4Br$,

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it became highly efficient at removing elemental mercury. These studies revealed petroleum coke as a potential low-cost material to capture elemental mercury from flue gas. However, all of these activation methods are energy intensive and produce secondary harmful pollutants. Thus, a novel activation method is required to overcome these shortcomings. In our previous study, petroleum coke brominated by the chemical-mechanical bromination process showed promising mercury removal efficiency [12]. To optimize the design of the sorbent for safe disposal, it is important to study the mechanism of mercury binding in the modified petroleum coke and the fate of the spent sorbent disposed to the environment.

The mechanisms of elemental mercury removal by brominated carbon-based sorbents are complex and depend on various factors, including the bromine-impregnation methods [13]. Several bromine-impregnation technologies, including direct $Br_2$, have been reported [14–17]. Several studies reported a mercury-binding mechanism on brominated carbon-based sorbent by analyzing the surface and bulk chemical compositions using X-ray photoelectron spectroscopy (XPS) and extended X-ray absorption fine structure (EXAFS) spectroscopy. Hutson et al. [18] concluded that elemental mercury was oxidized by surface-bound bromine species. In some cases mercury-sulfate species were expected to form due to the presence of $SO_2$ in the flue gas. Olson et al. [19] suggested that acidic sites on the surface are responsible for elemental mercury capture on activated carbon. For the brominated biomass ash, Bisson et al. [13] proposed a mechanism of Hg capture by oxidizing elemental mercury followed by binding of the oxidized mercury with the sulfur near Br on the surface of the sorbent. Huggins et al. [20] showed that elemental mercury was oxidized and bound to anionic species on the surface of brominated activated carbons. Sasmaz et al. [21] found that elemental mercury was oxidized on the brominated carbon surface, the oxidation state of adsorbed mercury was $Hg^{2+}$, and the oxidized mercury was coordinated to two Br atoms with no detectable binding between Hg and O. These studies indicated that the acidic sites, anionic species and Br atoms on the surface of the sorbents play an important role on $Hg^0$ capture by brominated activated carbons.

In addition to brominated sorbents, sulfur-impregnated carbon-based sorbents have been reported to be highly efficient at removing mercury. A number of sulfur-impregnation technologies including $H_2S$, $SO_2$ and $S^o$ have been reported [22–26]. The efficiency of mercury removal depends mainly on the physical or chemical nature of the sorbents while the mercury capture capacity depends mainly on the conditions of the sulfur-impregnation process [27]. Analyzed by mercury X-ray absorption spectra (XAS), Bisson et al. [22] found a mixed Hg-Br, Hg-S and Hg-C binding environment on biomass ash co-impregnated with bromine and sulfur. Feng et al. [28] used XPS and XAFS analysis to show that elemental sulfur, thiophene, and sulfate were likely responsible for mercury uptake, with elemental sulfur species being the most effective. Morris et al. [24] also reported that activated carbon treated with $SO_2$ at 700 °C exhibited a much faster rate of mercury uptake, which was attributed to the presence of sulfur functional groups. From XPS analysis, Saha et al. [29] found that the amount of surface-bound Br and reduced sulfur groups decreased Hg capture, while the level of a weaker Hg-binding surface S(VI) increased significantly for the brominated and sulfur-treated activated carbon pellet samples. His et al. [23] found that the presence of elemental sulfur on the sorbent and microporous structure both are important for improving the performance of carbon-based sorbents to remove elemental mercury from coal combustion flue gases. The forms of sulfur on these sulfur-impregnation sorbents are mainly elemental sulfur ($S_1$-$S_8$), $S^0$ and $S^{2-}$ bound on the surface of carbon-based sorbents which are known to be effective in elemental mercury capture.

Although many studies have investigated the adsorption mechanism of mercury on bromine- or sulfur-impregnated carbon-based sorbents, very few have explored the adsorption mechanism of mercury on brominated petroleum coke which contains both Br and S. Similarly, many studies have mentioned that organic sulfur could enhance the capture of elemental mercury from flue gases, but few have investigated the role of thiophene and organic sulfide on mercury removal. To the best of our knowledge, no previous studies have investigated the synergistic effects of bromine and organic sulfur on $Hg^0$ removal using brominated petroleum coke and mercury reaction chemistry on petroleum coke. In our previous paper [12], we developed petroleum coke as a sorbent for mercury capture by bromination. Compared with commercial brominated activated carbon, the novel sorbent showed better mercury capture efficiency, a negligible leachability of bromine and mercury from the spent sorbent which is safe for disposal after its use. In this study, the petroleum coke obtained from two Canadian refineries was brominated by the novel chemical-mechanical bromination process. The surface of resulting sorbents was characterized while mercury breakthrough, mercury loading capacity and the thermal stability of bromine-loaded samples were determined. The synergistic effect of mercury capture by brominated high-sulfur petroleum coke and the mercury reaction chemistry were studied using XPS, adding more insight into mercury reaction chemistry and the mechanism.

## 2. Experimental section

### 2.1. Sample preparation and mercury saturation procedure

Two raw petroleum cokes (named as PC1 and PC2), mainly with different mineral matter and S contents, obtained from two different sources: PC1 from upgrading of oil sands deposits in Alberta, Canada and PC2 from refining of conventional crude oil in Saskatchewan, Canada. The received materials were ground and screened with a 100 mesh sieve. These were then dried in a vacuum oven at 110 °C for 24 h. The elemental analyses of the petroleum coke were carried out with a EuroEA Elemental Analyzer (EuroVector, Italy) and the results are given in Table 1.

The brominated petroleum coke (Br-PC) was prepared by a novel chemical-mechanical bromination process [30]. In this process, 20 mg of liquid bromine (99.5% purity) were added to 2 g of petroleum coke in a sealed container. Proper glass beads were added in the sealed container. The container was tumbled on a mechanical tumbler for 30 min and then kept in the fume hood for 30 min to release unbounded bromine. The brominated petroleum coke obtained as such was treated in a vacuum oven at 200 °C for 30 min to further remove unbound bromine, and cooled to room temperature in a fume hood. The petroleum coke samples prepared as such were named Br-PC1 and Br-PC2.

The brominated petroleum cokes were saturated with mercury in order to determine mercury loading capacity and the chemistry and oxidation states of Br, S and Hg on the sorbent. Br-PC1 and Br-PC2 were spread over the bottom of a glass vessel. A smaller glass container with elemental mercury was then placed in the center of the vessel and the whole glass vessel was sealed. The setup was placed in the fume hood at room temperature for a week for

**Table 1**
Elemental analysis of petroleum cokes (wt. %).

| | C | H | O | N | S | Ash |
|---|---|---|---|---|---|---|
| PC1 | 83.31 | 3.67 | 2.36 | 0.7 | 5.85 | 4.11 |
| PC2 | 91.24 | 3.84 | 1.37 | 0.49 | 2.14 | 0.92 |