Overlook of carbonaceous adsorbents and processing methods for elemental mercury removal

Kyong-Min Bae, Byung-Joo Kim and Soo-Jin Park

1Department of Chemistry, Inha University, 253 Nam-gu, Incheon 402-751, Korea
2R&D Division, Korea Institute of Carbon Convergence Technology, 817 Duckjin-gu, Jeonju 561-844, Korea

Abstract
People have been concerned about mercury emissions for decades because of the extreme toxicity, persistence, and bioaccumulation of methyl Hg transformed from emitted Hg. This paper presents an overview of research related to mercury control technology and identifies areas requiring additional research and development. It critically reviews measured mercury emissions progress in the development of promising control technologies. This review provides useful information to scientists and engineers in this field.

Key words: mercury vapor removal, carbonaceous adsorbents, catalytic oxidation, selective catalytic reduction

1. Introduction

Mercury is considered one of the most toxic metals due to its volatility, persistence, bioaccumulation and health impacts on human beings [1-8]. On April 19, 2012, the US Environment Protection Agency (EPA) issued the national standard Final Mercury and Air Toxics Standards for the control of mercury, acid gases, and other toxic pollution from coal-fired power plants. On Dec. 20, 2012, the US EPA finalized a specific set of adjustments to Clean Air Act standards. The mercury emission limitation in the 2012 final standards is 2.0−3.0 tons/year for the boilers that need to meet emission limits in the 2012 final standards [9-12].

There are three forms of mercury in the flue gas from coal-fired power plants: elemental mercury (Hg⁰), oxidized mercury (Hg⁰²) and particle bound mercury (Hg⁰). Particulate-bound mercury refers to the mercury adsorbed onto residential particulate, it can be collected using current air pollution control devices (APCD) 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 [13-25].

As one of the most important materials, carbon materials have attracted a lot of attention for their potential applications as automobiles, aerospace, defense, sports, gas storage, electrodes, filler, and catalyst supports [26-41]. Especially, porous materials (including activated carbons, zeolites, and alumina powders) are useful materials for gas adsorption and storage [42-49]. Adsorption, especially using activated carbon (AC) as adsorbent, is currently the most widely used technology for hazardous gas removal from the incineration flue gases [50-61]. As for the sorbent injection technique, activated carbons are injected into the flue gas right before it enters the electrostatic precipitators or bag house filters. In a fixed-bed type system, the flue gas passes through a packed tower with a specified depth of the AC particles. The system is designed to increase the contact time between mercury and the sorbents (AC) without causing a pressure drop.
Overlook of carbonaceous adsorbents elemental mercury removal

2. Adsorbents

2.1. Chemically treated carbon sorbents

Sasmaz et al. [69] studied the speciation of Hg adsorbed on brominated activated carbon sorbents in the presence of air. It was found that Hg⁰ is oxidized at the brominated carbon surfaces at both 30°C and 140°C. The oxidation state of adsorbed Hg is found to be Hg²⁺, and coordinated to two Br atoms with no detectable bonding between Hg and O.

Yao et al. [70] investigated the sulfur treated activated carbon fibers (ACF) for gas phase elemental mercury removal. The incorporation of sulfur groups appears to facilitate the oxidation process of Hg and subsequent bonded with oxidized Hg, resulting in higher Hg capacities. Sulfide groups appear to be more effective for mercury removal than sulfate groups since the lone pairs of electrons of sulfide groups are responsible for interaction with mercury, or at least as a point of initial attachment. Additionally, physical properties associated with sorbent properties such as surface area, pore volume and pore size also affect mercury adsorption performance. For example, as stated earlier micropores are responsible for Hg adsorption while mesopores serve as transport route. Authors best results for mercury uptake is 11–15 mg/g C with sulfur content between 6 and 7 wt.% for NaSH–ACF and S(v)–ACF (Fig. 1).

Tian et al. [71] studied elemental mercury removal by activated carbon impregnated with CeO₂. The influencing factors researched include loading values changing from 1 wt.% to 10 wt.% and adsorption temperature changing from 30 to 200°C. The results show that CeO₂ impregnation particularly with 3 wt.% CeO₂-impregnated greatly enhanced the AC adsorption ability for elemental mercury. The experiment under a wide range of temperature implied that both chemisorption and physisorption played an important role in the removal of Hg⁰. 3% CeO₂/AC showed the best performance at 100°C (Fig. 2).
elemental mercury adsorption of all metal/ACs occurred at a level higher than that of the as-received sample. It is thus concluded metal plating (Cu and Ni) on carbon surfaces can be a good method for enhance elemental mercury adsorption [67].

2.2. Petroleum coke

Tao et al. [72] reported activated coke impregnated with cerium chloride used for elemental mercury removal from simulated flue gas. The effects of CeCl3 loading values, reaction temperatures and individual flue gas components including O2, NO, SO2 and H2O (g) on Hg0 removal efficiency of AICC samples were investigated. Results showed that Hg0 removal efficiency of AC was significantly enhanced by CeCl3. The optimal CeCl3 loading value and reaction temperature was around 6% and 170°C, respectively. Additionally, the experiment results of effects of flue gas components on Hg0 removal efficiencies showed that when O2 was present in the flue gas, NO and SO2 were observed to promote Hg0 oxidation. However, in the absence of O2, SO2 showed an insignificant inhibition on Hg0 removal. Furthermore, when H2O was added into the flue gas, the Hg0 removal capacity had a slight declination (Figs. 5 and 6).

Fig. 4. Elemental mercury adsorption of metal/activated carbon hybrid materials as a function of plating time. [67].

Fig. 5. SEM micrographs of (A) virgin AC, (B) AICC2, (C) AICC4, (D) AICC6, and (E) AICC10 [72].

Fig. 6. Effects of individual flue gas components on Hg0 oxidation and capture efficiency of AICC6 (all gases balanced with N2) [72].

elemental mercury adsorption of all metal/ACs occurred at a level higher than that of the as-received sample. It is thus concluded metal plating (Cu and Ni) on carbon surfaces can be a good method for enhance elemental mercury adsorption [67].
Overlook of carbonaceous adsorbents elemental mercury removal

2.3. Zeolites

Kim et al. [73] studied elemental mercury removal for some kinds of porous materials (MCM-41, SBA-15, AC). AC showed high elemental mercury adsorption of 295.2 μg/m³. However, comparing to two types of mesopore materials (SBA-15 and MCM-41), the mercury vapor adsorption was higher in SBA-15 as SBA-15 has a higher micropore volume fraction than MCM-41. We can conclude this work by stating that mercury vapor adsorptions rates can be optimized in terms of the specific surface area and micropore fraction (Fig. 7).

2.4. Fly ash

Xu et al. [74] reported mercury removal from coal combustion flue gas by modified fly ash. Fly ash shows unique adsorption activity for mercury removal. Incompletely burned carbon is an important factor for improving mercury removal efficiency. In particular, the C–M bond, which is formed via the reaction of C and Ti, Si and other elements, may improve the oxidation of mercury. High specific surface areas and small pore diameters are beneficial for mercury removal efficiency.

3. Processing technologies

The control of mercury emissions from coal-fired boilers is achieved via existing controls used to remove particulate matter (PM), sulfur dioxide (SO₂), and nitrogen oxides (NOx). This includes capture of particulate-bound mercury in PM control equipments such as electrostatic precipitator (ESP), fabric filter (FF), and soluble mercury compounds in wet FGD systems. The use of selective catalytic reduction (SCR) of NOX control enhances the concentration of soluble mercury compounds in flue gas and results in increased mercury removal in the downstream wet FGD system [75-81].

ESP is significantly less effective than FF, because there is less contact between gaseous mercury and fly ash in ESPs. A FF can be very effective for mercury removal from coals, which is one of the reasons that more and more FF units are being installed recently. However, this FF-only configuration only represents small percentage of (5–10% of the U.S.) coal burning capacity. Mercury in its oxidized state (Hg²⁺) is highly water-soluble and thus would be expected to be captured efficiently in wet FGD systems. However, over 80% of total mercury stays in elemental form, and easily escapes from wet FGD system [77].

3.1. Catalytic oxidation

It is well-known that the elemental form Hg⁰, which is the main component of mercury in gas phase, is very hard to be removed due to their high volatility and low solubility in water. However, the oxidized mercury Hg²⁺ has much higher solubility in water, and thus the oxidation of Hg⁰ to Hg²⁺ followed by the ESP and/or wet scrubbing processes became a promising method for mercury removal [77].

Kong et al. [82] studied catalytic oxidation of gas-phase elemental mercury by nano-Fe₂O₃. The results showed that Hg⁰ could be oxidized by active oxygen atom on the surface of nano-Fe₂O₃ as well as lattice oxygen in nano-Fe₂O₃. Among the factors that affect Hg⁰ oxidation by nano-Fe₂O₃, bed temperature plays an important role. More than 40% of total mercury was oxidized at 300°C, however, the test temperature at 400°C could cause sintering of nano-catalyst, which led to a lower efficiency of Hg⁰ oxidation (Figs. 8 and 9).

Liu et al. [83] investigated catalytic oxidation of gas-phase mercury over Co/TiO₂ catalysts prepared by sol–gel method. Experi-
mental results revealed that the optimal loading of Co was 7.5%, which yielded more than 90% oxidation efficiency within the temperature range of 120–330°C. The high activity was mainly attributed to the enrichment of well dispersed Co$_3$O$_4$ (Fig. 10).

Xu et al. [84] reported elemental mercury oxidation and adsorption on magnesite powder modified by Mn at low temperature. The results show that removal efficiency of Hg$_0$ is obviously improved due to the activity of Mn, and 10 wt.% Mn/MgO adsorbent exhibits high removal efficiency of Hg$_0$, which reached about 82% at 120°C. The results show amorphous MnO$_2$ and O$_2$ play a crucial role in the removal of Hg$_0$ from the simulated gas (Figs. 11 and 12).

### 3.2 Selective catalytic reduction

The selective catalytic reduction (SCR) of NOx with NH$_3$ has been an efficient and widely used technology to control NOx emissions in coal-fired flue gas. The recent investigations have demonstrated that the catalyst used in the SCR process, especially V$_2$O$_5$–WO$_3$/TiO$_2$ catalyst, showed the highest catalytic activity in Hg$_0$ oxidation reaction [85]. In addition, the activity component V$_2$O$_5$ played an important role in promoting Hg$_0$ oxidation efficiency on the surface of catalyst [86].

---

**Fig. 10.** Co-oxidation of NO and mercury oxidation under experiment condition; [Hg0]=180 μg/m$^3$, balanced gas = N$_2$, flow rate=700 mL/min, GHSV=105,000 h$^{-1}$, O$_2$=3%, HCl=29 ppm, NO=300 ppm. [83].

**Fig. 11.** Removal efficiency of elemental mercury by Mn/MgO with different Mn loading at temperature range (80-150°C) in air; carrier and balance gas N$_2$; O$_2$ vol% about 8%; inlet elemental mercury concentration=30-60 ppb; GHSV=27,000 h$^{-1}$ [84].

**Fig. 12.** Effect of O$_2$ (O$_2$ vol% about 6%) on elemental removal efficiency at 120°C; carrier and balance gas N$_2$; inlet elemental mercury concentration=30-60 ppb; GHSV=27,000 h$^{-1}$ [84].

**Fig. 13.** The conception of the SCR-Plus and its integration with the typical SCR catalyst [85].

**Fig. 14.** A comparison of the Hg0 catalytic oxidation with various catalysts and with 5 ppm HCl and 500 ppm SO$_2$. The compositions in the gas were 4% O$_2$ and N$_2$; the Hg$_0$ concentration in the gas was approximately 200 (±10) μg/m$^3$. The space velocity (SV) was approximately 5.9×10$^5$ h$^{-1}$. The temperature was 623K [85].
Chen et al. [85] studied elemental mercury oxidation and slip ammonia abatement with SCR-Plus catalysts. Authors reported that the SO$_2$ and NH$_3$ tolerance in the coal-fired flue with low levels of HCl was excellent. The Ru/SCR that was doped with Mo facilitated the activation of HCl. In addition, this treatment also achieved high NOx removal and NH$_3$ decomposition efficiency with excellent N$_2$ selectivity. Therefore, the Mo-Ru/SCR catalyst appears to have potential for synchronously removing Hg$^0$ and slip ammonia from industrial coal-fired flue gas (Figs. 13 and 14).

Rallo et al. [87] investigate the SCR effects in terms of mercury oxidation and the impact of acid gases on mercury oxidation in a SCR system. It was found that the mercury oxidation across the plate type catalyst investigated can vary from 0% to 70%. Results showed that by increasing the temperature above 320°C, the mercury oxidation rates decreased and reached zero for 420°C. In contrast, the reaction rate of NOx-reduction by NH$_3$ and SO$_2$-formation by SO$_2$-oxidation are strongly accelerated by increase in temperature (Fig. 15).

### 4. Conclusions

In this study, we reviewed the adsorbers and processing methods for elemental mercury control. Several factors potentially affect the efficiency of a sorbent to remove mercury from flue gas. These include the mercury speciation in flue gas; the flue gas composition; process conditions; sorbent characteristics; and the presence of other active additives.

Additional research is needed to identify the mercury compounds that are formed and to verify capture mechanisms. Engineering development is also needed to improve sorbent dispersion and optimize gas–solid contact time.

### Acknowledgement

This subject is supported by INHA UNIVERSITY Research Grant and the Carbon Valley Project of the Ministry of Knowledge Economy, Korea.

### References


[15] Ie IR, Hung CH, Jen YS, Yuan CS, Chen WH. Adsorption of vapor-phase elemental mercury (Hg$^0$) and mercury chloride (HgCl$_2$) with innovative composite activated carbons impregnated with Na$_2$S and S$^2$O in different sequences. Chem Eng J, 229, 469 (2013). http://


Overlook of carbonaceous adsorbents elemental mercury removal


