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Removal of gas-phase elemental mercury by iodine- and chlorine-impregnated activated carbons

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Abstract

Gas-phase Hg^0 adsorption experiments were carried out using iodine (I)- and chorine (Cl)-impregnated granular activated carbons in a laboratory-scale fixed-bed reactor. To verify the effect of chemical loading contents on removal of mercury, different concentrations of chemicals such as KI and HCl were applied. In addition, two types of impregnated activated carbons (ACs) were tested at different temperature conditions. The characteristics of impregnated ACs were analyzed using scanning electron microscopy/energy-dispersive spectroscopy for surface morphology and chemical contents. BET analysis for surface area and X- ray spectroscopy for identification of mercury compounds on the carbon surface were conducted.

Hg^0 removal efficiency increased with temperature in the case of I-impregnated ACs, while the removal efficiency decreased with temperature for Cl-impregnated ACs. According to increasing chemical content, the surface area decreased and the morphology of carbon became more complicated. Both types of impregnated ACs showed reasonable efficiency for gas-phase Hg^0 removal by adsorption.

Keywords: Elemental mercury; Removal technology; Adsorption; Chemical treatment Activated carbons

1. Introduction

Most of the heavy metals that are released to the atmosphere from combustion flue gas are in the form of bound particulate. However, depending upon the combustion conditions and flue gas chemistry, mercury compounds may be emitted as bound particulate (Hgp), as oxidized mercury (Hg^{2+}) or in the vapor state (Hg^0), due to their high volatility and vapor pressure. According to the previous studies (US EPA report, 1997; Pacyna et al., 2003; Pirrone et al., 2001), combustion facilities such as coal-fired power plant, municipal solid waste incinerator (MSWI), ferrous or non-ferrous smelter, hazardous waste combustor (HWC) and so on are considered the major anthropogenic sources of mercury to the atmospheric environment. Therefore, to reduce the global emission of mercury, a cost-effective mercury emission control technology is required. In general, however, Hg^0 is more difficult to remove than Hg^{2+} because it tends to be water insoluble and is thus unlikely to be removed in downstream scrubbers. The Hg^{2+} species, however, are water soluble and tend to be easily removed with wet type (e.g., scrubbers) air pollution control devices (APCDs).

In order to remove the mercury compounds from combustion flue gas, activated carbons (ACs) are

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available; however, virgin ACs show poor removal of mercury compounds. For this reason, chemically treated activated carbons are often employed for mercury control. Table 1 shows the previous studies of mercury removal technology.

Since Hg compounds react with impregnated chemicals, sulfur (Granite et al., 2000; Jurng et al., 2002; Krishnan et al., 1994; Liu et al., 1998), chlorine (Cl) (Ghorishi et al., 2002; Vidic and Siler, 2001) or iodine (I) (US DOE, 1998; Granite et al., 2000), chemically impregnated activated carbons are more expensive than the virgin precursors. Therefore, many researchers have studied ways to enhance the mercury adsorption ability of the activated carbons while reducing the cost for mercury removal. Some researchers applied a cheaper material such as pyrolysis wood char and fly ash (Jurng et al., 2002; Karatza et al., 1998; Serre and Silcox, 2000). However, the removal efficiency of fly ash is quite lower than that of activated carbons and in case of sulfur impregnation at high temperature the manufacturing cost is increased because a large amount of sulfur is required and high temperature condition is needed. Therefore, the cost-effective impregnation method and treatment technique are required to reduce the Hg removal cost. The objectives of this study are to evaluate the mercury removal efficiency of I- or Cl-impregnated granular ACs that have a varying chemical loading, and to compare the effects of adsorption temperature on the mercury uptake capacity using a laboratory-scale adsorption fixed-bed reactor. I and Cl are relatively cheap materials and easy to treat with water, which are the advantages of using these materials. These cost-effective mercury removal technologies can contribute to reducing total mercury emission to the global atmospheric environment. Additionally, to identify the characteristics of impregnated ACs, BET surface area analysis, (ion chromatography (IC)) and (thermogravimetric analysis (TGA)) were carried out. Finally, the resulting products, mercuric iodine and mercuric chloride compounds, were analyzed by (SEM/EDS) scanning electron microscopy/energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy (XPS), which can prove the chemisorption process between impregnated activated carbon and elemental mercury.

2. Experimental

2.1. Treatment of the carbon

Lignite coal-based ACs, Norit Darco® 4–12 US mesh size with granular type, were used as the virgin ACs in these experiments. The material was ground and sieved to 14–16 US mesh size, a geometric mean particle diameter of around 1.1 mm. After sieving, the carbon was washed with (de-ionized (DI)) water, then dried in an electric oven at 110°C for 24 h. The resulting material was stored in a desiccator prior to adsorption experiments. Chemical impregnations were implemented using hydrochloric acid (HCl) (35–37%, Kanto, Japan) for the Cl-impregnated ACs and potassium iodine (99%, Adrich, USA) for the I-impregnated ACs. In order to

Table 1
Summary of previous studies on the mercury removal technologies

Sorbents	Sorbent characteristics	Adsorption capacity (μg g^{-1})	Experiment temperature (°C)	Reference
I-AC	3.5 wt% iodine	3100–4800	162	Granite et al. (2000)
S-AC	5.9–7.6 sulfur	400–3500 wt%	123–162	Granite et al. (2000)
Cl-AC	6.0–6.7 wt%	2600–4000	123	Granite et al. (2000)
HNO$_3$-AC	Treatment with boiling HNO$_3$	1200	123	Granite et al. (2000)
Fly ash[a]	Coal combustion fly ash	~4870[b]	At room temp.	Hassett and Eylands (1999)
Wood char[c]	CS$_2$ treatment	588	110	Jurng et al. (2002)
Fly ash[d]	MSW fly ash	4200–1180	150	Karatza et al. (1998)
ACF Filter[e]	Activated carbon fiber	~53	25	Hayashi et al. (2000)
BPL-C	Chlorine impregnation[f]	25–332[g]	140	Vidic and Siler (2001)
BPL-S	Sulfur impregnation[h]	2200	140	Liu et al. (1998)
OC[i]	Oil-based carbon	1168–2267	120	Dombrowski et al. (2003)
TDAC	Tire-derived AC	444–2310	120	Dombrowski et al. (2003)

[a] Fly ash from coal combustion (lignite, subbituminous, bituminous).

[b] Post-loading mercury content.

[c] Derived from wood gasification process in Germany, after 24 h experiment results.

[d] Fly ash from municipal solid waste incinerator.

[e] Calculated up to 90% of effluent concentration.

[f] CuCl$_2$ dissolved in 6N HNO^3

[g] Calculated at 30% of total breakthrough.

[h] Elemental sulfur pyrolysis at high temperature in the electric oven.

[i] Mercury adsorption capacities increased after activation process.

identify the effect of chemical concentration on gas-phase Hg^0 adsorption capacity and physio-chemical properties, four different HCl aqueous solutions, 0.5, 1, 5, and 10 N, were prepared by dilution with DI water. In the same manner, KI solutions were prepared with different weight concentrations, 1, 5, 10, and 20 wt%, dissolved with DI water in a 100 ml volumetric flask.

Cl impregnation was carried out using 10 g of virgin AC sufficiently immerged into 20 ml of HCl solution in a glass bottle. In order to facilitate the impregnation process, the solution was heated at 70°C with constant stirring for 2 h. (Moreno-Castilla et al., 1998). After impregnation, the ACs were vacuum filtered and then dried in an electric oven at 110°C for 24 h. In the case of I impregnation, four samples of 10 g virgin ACs were immerged into 20 ml bottles containing four different concentrations of KI solution. The bottles were then stored for 24 h at room temperature and shaken periodically during the impregnation time to prevent the non-homogeneity before being filtered and dried using the same procedure as was used in Cl impregnation. Both types of impregnated ACs were stored in desiccators prior to Hg^0 adsorption experiments.

2.2. Experimental setup

Fig. 1 shows the experimental setup for the fixed-bed Hg^0 adsorption tests performed in this study. The permeation device (VICI Metronics) was used to provide a vapor-phase Hg^0 source. Ambient air was made to flow through the permeation oven at a total flow rate of 1.5 l min^{-1} to provide a Hg^0 vapor-phase concentration of approximately 300 μg m^{-3}. A quartz adsorption column of 0.77 cm i.d. and 10 cm length was placed in the temperature-controlled electric furnace. Approximately 100 mg of impregnated ACs was packed into the quartz column, with about 4 g of glass beads having a similar size as the ACs and glass wool was packed to avoid the channeling effect and to support the AC bed. The glass beads and wool were tested to ensure inert characteristics for gas-phase Hg^0 capture before the adsorption experiments. The vapor-phase Hg^0 concentrations were analyzed continuously using a VM-3000 (Mercury Instruments GmbH, Germany), cold vapor atomic absorption (CVAA) analyzer, which can analyze only elemental mercury upstream and downstream of the adsorption bed.

2.3. Adsorption test parameters

The adsorption temperature is the most important factor in the adsorption process; therefore, to evaluate the removal efficiency of gas-phase Hg^0, adsorption tests were carried out at different adsorption temperatures, from 80°C to 160°C in addition to the Hg^0 removal efficiency, compared to different chemical contents of impregnated ACs. All experiments were duplicated or triplicated in the same experiment conditions. During each 4 h experiment, only outlet Hg^0 concentrations were recorded to calculate the total amount of removed Hg^0 (μg g^{-1}) and breakthrough ratios ($C\,C_0^{-1}$). Of course, a few Hg^0 can oxidize in this experiment at flue gas conditions, however, in general, gas-phase chlorine is regarded as the major reactant because the reaction with elemental mercury is quite fast (Edwards et al., 2001); on the other hand, mercury–oxygen reaction is slow at the gas phase because the pre-exponential factor in the form of Arrhenius equation is extremely small (Hall et al., 1995). Ambient air is used as carrier gas in this study.

The early stage of breakthrough, about 4 h, was used as adsorption test time in this study because complete breakthrough ($C_{\text{in}} = C_{\text{out}}$) took considerable time ($\gg$4 h).

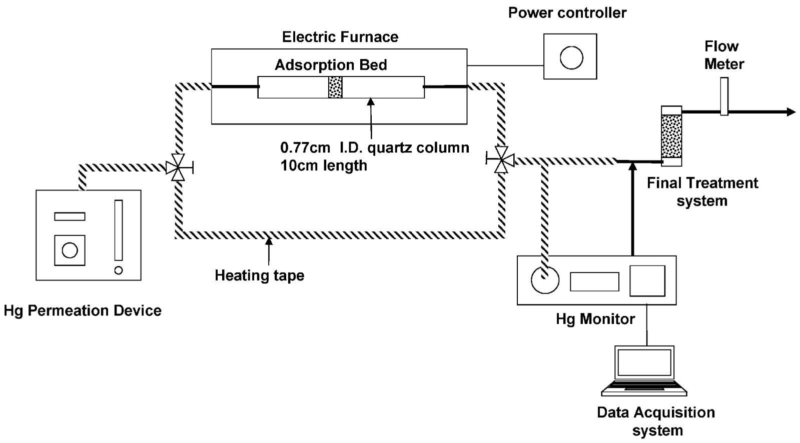

Fig. 1. Schematic diagrams of fixed-bed-type adsorption experiment.

3. Results and discussion

3.1. Characteristics of impregnated ACs

Table 2 shows the chemical content and BET surface area of the samples. One can see that the total surface area decreases with increasing chemical content. It can be assumed that a large amount of impregnated material blocks the macro-pore entrance or occupies the empty surface area of the ACs. Fig. 2 shows the surface morphology of I-impregnated ACs. The characteristics of AC surface have changed according to chemical loading. I crystals are shown as white fragments. On the other hand, the variation of surface morphology of Cl-impregnated AC is not clear and therefore is not presented in this paper. This may suggest that the amounts of impregnated Cl on ACs are relatively small and the difference of weight percentage between virgin and impregnated materials is so small as to not affect the surface morphology (Table 2).

Table 2
Chemical contents of impregnated ACs and BET surface area

	Chemical contents (wt%)	BET surface area ($m^2 g^{-1}$)
Virgin	—	1000
KI-impregnated ACs (wt% KI)		
1	1.7	488.3
5	8.6	338.0
10	17.2	314.5
20	31.0	244.7
HCl-impregnated ACs (N HCl)		
0.5	0.88	433.7
1	1.21	431.1
5	1.67	418.0
10	1.73	397.9

To determine the thermal stability of impregnated ACs, TGA (LECO 601, USA) analysis was also carried out. KI-impregnated ACs slightly lost weight in high chemical-loading ACs (e.g. 10, 20 wt%) at temperatures over 500°C (Fig. 5). This is caused by thermal decomposition of impregnated material; however, HCl-impregnated ACs did not show significant weight loss. Both impregnated ACs were thermally stable at flue gas conditions, about 120–160°C, at the inlet of (electrostatic precipitator (ESP)) or bag house.

3.2. Hg^0 removal efficiency of I-impregnated ACs

The removal efficiency of Hg^0 by each impregnated AC was evaluated. After a 4 h exposure to the gas-phase Hg^0 in the fixed bed, the total amount of removed Hg^0 per gram of ACs and breakthrough ratio ($C C_0^{-1}$) were calculated to evaluate the removal efficiency of Hg^0 adsorption. Table 3 indicates the breakthrough ratio for I-impregnated ACs with different iodine content and the total amount of removed Hg^0 during the 4 h adsorption experiment at 80°C. Above 5 wt% loading, there are no significant effects on Hg^0 adsorption ability, likely due

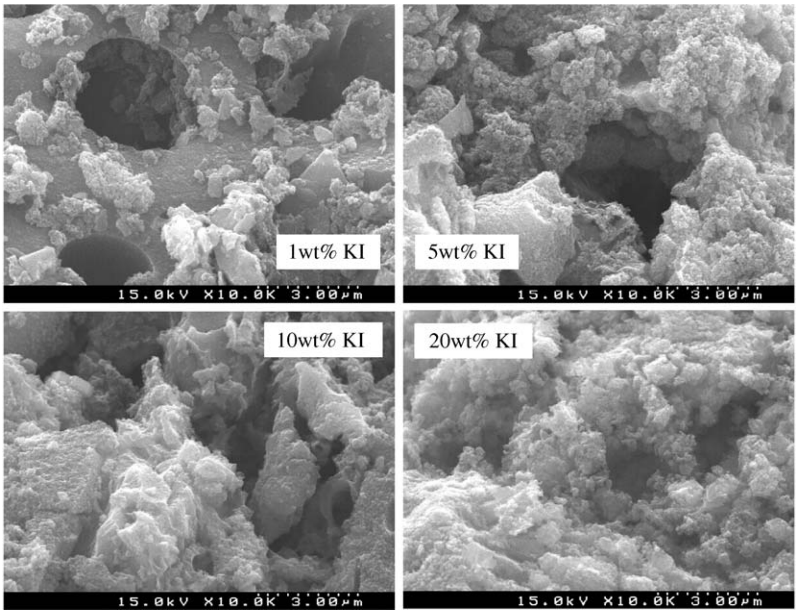

Fig. 2. The transition of surface morphology of I-impregnated ACs.

to a decrease in surface area with increased loading. Therefore, 5 wt% is deemed the maximum desirable loading.

3.3. Temperature effect of I-impregnated ACs and detection of mercury compound

To identify the temperature effects on the Hg^0 adsorption efficiencies, the adsorption bed temperature was varied from 80°C to 140°C with 5 wt% I-impregnated AC. The total amount of removed Hg^0 is summarized in Table 3.

Hg^0 removal efficiency increased with adsorption temperature and the breakthrough ratio(CC_0^{-1}) decreased. It can be assumed that Hg^0 vapor reacted with impregnated I on the carbon surface; that is, chemisorption occurred on the surface of I-impregnated AC that, being a chemical process, requires activation energy and proceeds at a limited rate which increases with rise in temperature (Gregg and Sing, 1967, Huggins et al., 2003). The reactions can be expressed as follows (US DOE, 1998).

$$Hg + I_2 + 2KI \rightarrow K_2HgI_4, \quad (1)$$

$$Hg + I_2 + KI \rightarrow KHgI_3, \quad (2)$$

$$Hg + 1/2I_2 \rightarrow HgI, \quad (3)$$

$$2KI + HgI + 1/2I_2 \rightarrow K_2HgI_4, \quad (4)$$

$$KI + HgI + 1/2I_2 \rightarrow KHgI_3. \quad (5)$$

Table 3
Experimental results of Hg^0 adsorption experiments with I-impregnated ACs (4 h)

	Cumulative adsorption Hg^0 ($\mu g\, g^{-1}$)	Breakthrough ratio (CC_0^{-1})[a]
Chemical loading effect[b] *(wt% KI)*		
1	595.6	0.28
5	680.2	0.10
10	668.3	0.12
20	669.2	0.12
Temperature effect[c] (°C)		
80°C	680.2	0.10
120°C	703.3	0.05
140°C	847.5	0.03

[a] C is effluent concentration of Hg^0; C_0 is initial Hg^0 concentration ($300\,\mu g\, m^{-3}$).

[b] Experiment at 80°C.

[c] Experiment with 5 wt% KI-impregnated AC.

The presence of the mercury compound, mercuric iodine, was confirmed indirectly through the SEM–EDS analysis that shows the mercury and I peaks in Fig. 3. The XPS result is illustrated in Fig. 4; the peaks indicate the existence of mercury compounds.

3.4. Hg^0 removal efficiency of Cl-impregnated ACs

Hg^0 removal efficiency of Cl-impregnated ACs was evaluated in the same manner as for the I-impregnated ACs. Table 4 shows the total amount of removed Hg^0 and breakthrough ratio during 4 h experiments. Among the four different concentrations of aqueous solution, 5 N HCl-impregnated carbon shows the highest Hg^0 removal efficiency and the lowest breakthrough ratio. Although the effects of HCl concentration on the removal capacity for gas-phase Hg^0 are not clear in this experiment, Cl impregnations can be considered as a promising chemical treatment for the Hg^0 adsorption. However, Vidic and Siler (2001), using copper chloride dissolved in 6 N nitric acid, have indicated that oxidized mercury, reacted with the Cl-impregnated carbon surface, could release into the effluent stream because of a weak carbon-chloride bond or weak chloride-mercury bond or both. They found that oxidized mercury was

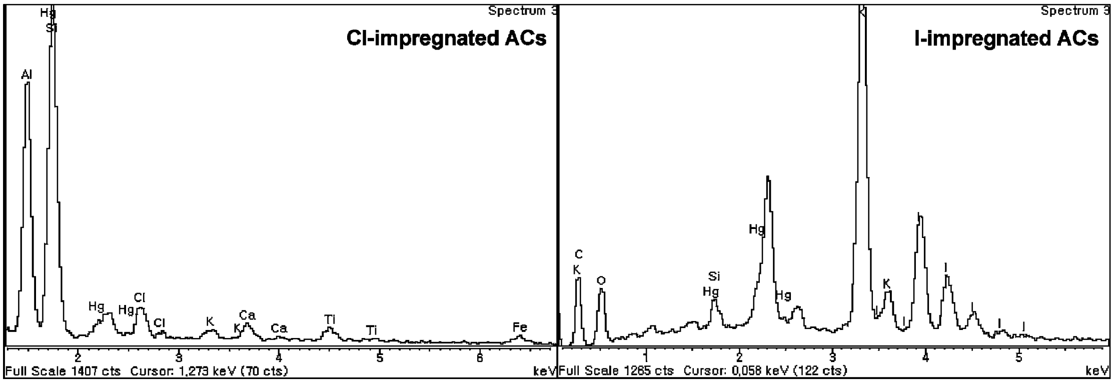

Fig. 3. The SEM-EDS analysis of I- and Cl-impregnated ACs after Hg^0 adsorption experiment.

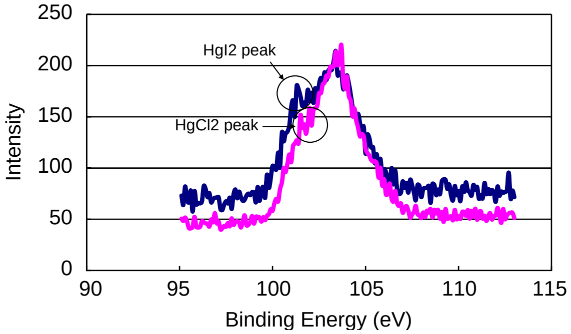

Fig. 4. XPS analysis of mercuric iodine and mercuric chloride compounds after Hg^0 adsorption experiment.

Table 4
Experimental results of Hg^0 adsorption experiments with Cl-impregnated ACs (4 h)

	Cumulative adsorbed Hg^0 ($\mu g\,g^{-1}$)	Breakthrough ratio $(C\,C_0^{-1})^a$
Chemical loading effect[b] *(N HCl)*		
0.5	590.4	0.27
1	576.5	0.31
5	649.5	0.17
10	549.0	0.28
Temperature effect[c] (°C)		
80°C	645.9	0.17
120°C	577.7	0.30
160°C	537.4	0.38

[a] C is effluent concentration of Hg^0; C_0 is initial Hg^0 concentration ($300\,\mu g\,m^{-3}$).

[b] Experiment at 80°C.

[c] Experiment with 5 N Cl-impregnated AC.

formed in the effluent of their fixed-bed-type adsorption experiments. However, the release of oxidized Hg at the effluent of the adsorption bed is negligible in this experiment, which is caused by the use of HCL; after treatment with HCl, some chlorine chemisorbed on the carbon surface (Moreno-Castilla et al., 1998).

3.5. Temperature effect of Cl-impregnated ACs and detection of mercury compound

Experiments for the temperature effect on Hg^0 adsorption were carried out with the 5 N HCl-impregnated AC at 80°C, 120°C, and 160°C. Table 4 shows the results of adsorption test. With increasing bed temperatures, the amount of cumulative Hg^0 adsorption decreased and the breakthrough ratio increased. From previous studies (Vidic and Siler, 2001; US DOE, 1998), it is known that mercury reaction with chloride or elemental sulfur shows an exothermic behavior, for this reason, the highest Hg^0 adsorption capacity is obtained at the lower temperature conditions. The formation of mercuric chloride on carbon surface or gas phase can be expressed by the following equations (Sliger et al., 2000):

$$Hg + Cl \rightarrow HgCl, \quad (6)$$

$$HgCl + Cl \rightarrow HgCl_2, \quad (7)$$

$$Hg + Cl_2 \rightarrow HgCl_2. \quad (8)$$

The final products of mercuric chloride compounds were determined by SEM–EDS analysis and XPS. The mercury and Cl peaks suggest the formation of mercuric chloride on the carbon surface in Fig. 3. Also, that the peaks in the XPS result indicate the existence of mercury compounds in Fig. 4 and 5.

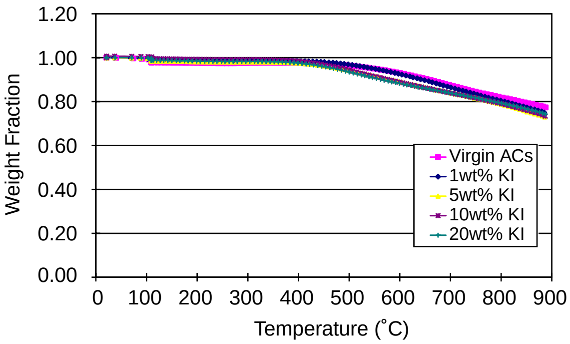

Fig. 5. TGA analysis of I-impregnated ACs at different weight concentrations.

4. Conclusion

Vapor-phase Hg^0 adsorption experiments were carried out with iodine- and chlorine-impregnated ACs using a laboratory-scale fixed-bed reactor. To optimize the chemical loading and to investigate the temperature effects of adsorption efficiency, various adsorption tests were implemented with different chemical loadings at different temperature conditions. The following are the conclusions from the results.

The I-impregnated ACs were quite effective for capture of gas-phase Hg^0, however, the removal efficiency of Hg^0 was not proportional to iodine concentration. It can be assumed that suitable impregnated concentration is more effective than the removal of Hg^0.

Also, temperature effects were not significant in case of I-impregnated ACs. It can be supposed that the chemisorption may occur on the surface of I-impregnated ACs between impregnated iodine and Hg^0, which is enhanced by increasing the temperature. Conversely, in the case of Cl-impregnated ACs, the removal efficiency of Hg^0 decreased with increasing bed temperature. In addition, mercury compounds could be identified in impregnated ACs by the surface analysis of the spent impregnated ACs.

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