

Preparation of Novel Sorbents for Gas-phase Mercury Removal

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Abstract

In the present research, we prepared the activated carbon (AC) sorbents to remove gas-phase mercury. The mercury adsorption of virgin AC, chemically treated AC and fly ash was performed. Sulfur impregnated and sulfuric acid impregnated ACs were used as the chemically treated ACs. A simulated flue gas was made of SO_x, NO_x and mercury vapor in nitrogen balance. A reduced mercury adsorption capacity was obtained with the simulated gas as compared with that containing only mercury vapor in nitrogen. With the simulated gas, the sulfuric acid treated AC showed the highest performance, but it might have the problem of corrosion due to the emission of sulfuric acid. It was also found that the high sulfur impregnated AC also released a portion of sulfur at 140°C. Thus, it was concluded that the low sulfur impregnated AC was suitable for the treatment of flue gas in terms of stability and efficiency.

Keywords : Chemically treated activated carbons, Gas-phase mercury removal, Impregnated activated carbons, Mercury adsorption

1. Introduction

In the U.S., where the coal consumption is relatively high, it is known that about 45 tons of mercury is emitted in the gas-phase a year and mercury emission in power plants has attracted attention [1]. Accordingly, the country is requiring that all power plants should be equipped with mercury control facilities by 2007. Recently, the members of EU decided to investigate mercury emission and develop mercury control technologies in collaboration. They are establishing a plan to control mercury emission not only from incinerators but also from power plants, and developing control technologies [2]. Such a global trend will affect the Asian region soon. Therefore, Korea is also at the point when plans should be prepared in response to mercury emission from incinerators as well as power plants. Gas-phase mercury emission is not yet regulated in Korea. The current limit of regulation 5 mg/m³ seems not to be applied in reality. However, the limit of 80~100 µg/m³ is going to be applied to incinerators first at the beginning of 2005

Technologies studied recently as methods of removing gas-phase mercury are process modification using WFGD (Wet Flue Gas Desulfurization) facility [2], and activated carbon (AC) or sorbent injection [3-6]. The process modification using WFGD has the advantage of that it does not require additional facilities but the disadvantage of that it is inefficient in removing elemental mercury. On the other hand, the AC injection system is highly efficient but sorbent cost is expensive. To overcome the shortcoming, there have

been attempts to develop low cost sorbent with a reasonable efficiency.

The present research was carried out to develop novel AC for treating gas-phase mercury. The mercury adsorption performances of virgin AC, chemically treated AC, and fly ash were compared, focusing on the adsorption rate rather than the adsorption capacity.

2. Experimental

2.1. Materials

SH of Shinkwang Chemical Industry in Korea was selected and compared as virgin AC. The AC made by treating SH with sulfuric acid (SH-H₂SO₄), MAG (Japan) impregnated with N,S-chelate, HGR (Calgon in U.S.) impregnated by 10 wt% sulfur, and the AC made by impregnating SH with 1 and 15 wt% sulfur (SH-S1, SH-S15) were used for the mercury adsorption experiments. The physical properties of AC used are shown in Table 1. The mercury adsorption with the fly ash was also studied for comparison [7].

In general, there are three types of impregnation materials for removing mercury as shown in Table 2. Among the three ACs, the impregnated AC with sulfur shows the most stable performance.

2.2. Mercury Adsorption

The mercury adsorption experiment utilized a packed bed apparatus as shown in Fig. 1. Mercury vapor was generated

Table 1. Properties of selected activated carbons

Activated carbons	Proposed mercury adsorption capacity (%w/w)	Carbon precursor	Packing density (g/L)	Specific surface area (m ² /g)	Average pore diameter (Å)	Particle size (mesh)
SH	–	Bituminous coal	0.45	1017	23.7	4 × 8
MAG	10-12	Bituminous coal	0.45	980	24.0	4 × 10
HGR ^a	12-16	Bituminous coal	0.45	573	24.8	4 × 8

^a: proposed sulfur contents; 10 wt%.

Table 2. Comparison of impregnation material for vapor phase mercury removal

Impregnation Reagent	Purification Efficiency	Adsorption Capacity	Corrosion Problem
None	Poor	Poor	None
KI	Good	Good	None
H ₂ SO ₄	Good	Very Good	Possible
S	Very Good	Very Good	None

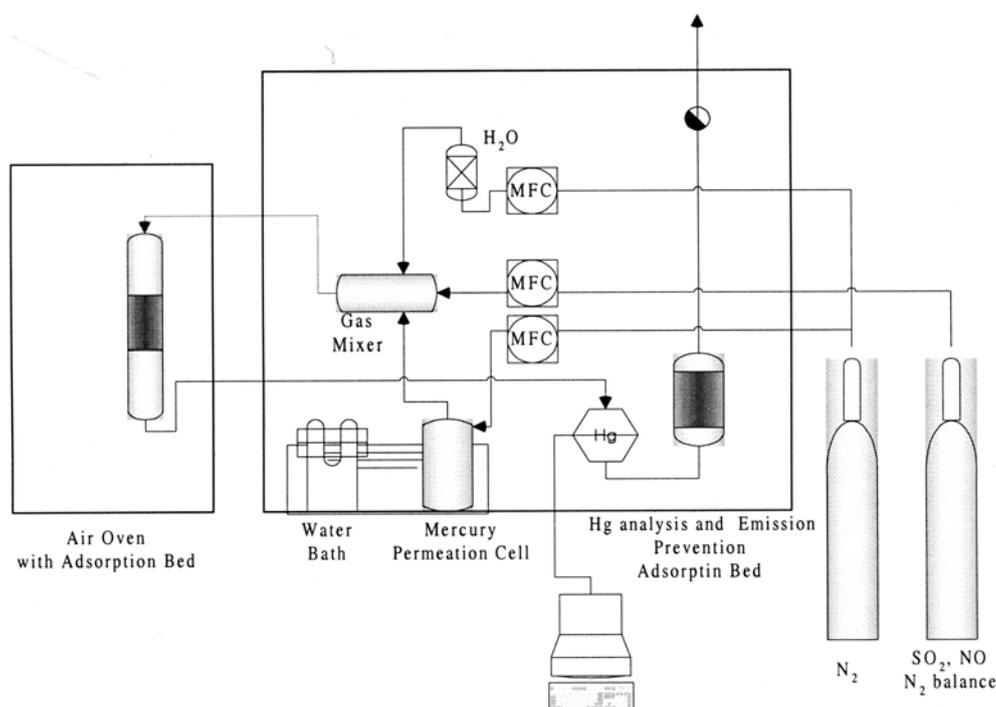
by placing a certain amount of mercury in a mercury permeation cell and flowing nitrogen into the cell. The mercury concentration was controlled by diluting the mercury-nitrogen mixture with the other nitrogen flow. The mercury concentration was adjusted to 50~100 µg/m³. The simulated flue gas was made from the mixed gas of SO₂ and NO, which concentration was 1000 ppm each in nitrogen. The concentration of SO₂ and NO was also adjusted to 50 ppm each.

2 g of AC was filled in a column of 20 mm in diameter, through which mercury containing gas was passed and the mercury vapor was adsorbed. The temperature was set to 140°C, which was the simulated temperature of emitted gas,

and adsorption was made for 30 minutes. The experiment focused on observing the adsorption characteristics during the initial stage of adsorption. A cold vapor mercury analyzer (Jerome, U.S.) was used for the mercury analysis.

3. Results and Discussion

Fig. 2 and Fig. 3 show the mercury adsorption results of the respective adsorbents. In these cases, SH-S1 contained 1.21 wt% of sulfur and SH-S15 did 13.9 wt%. SH-H₂SO₄ was treated with the solution of 2 wt% sulfuric acid for 1

**Fig. 1.** Schematic flow diagram of experimental apparatus.

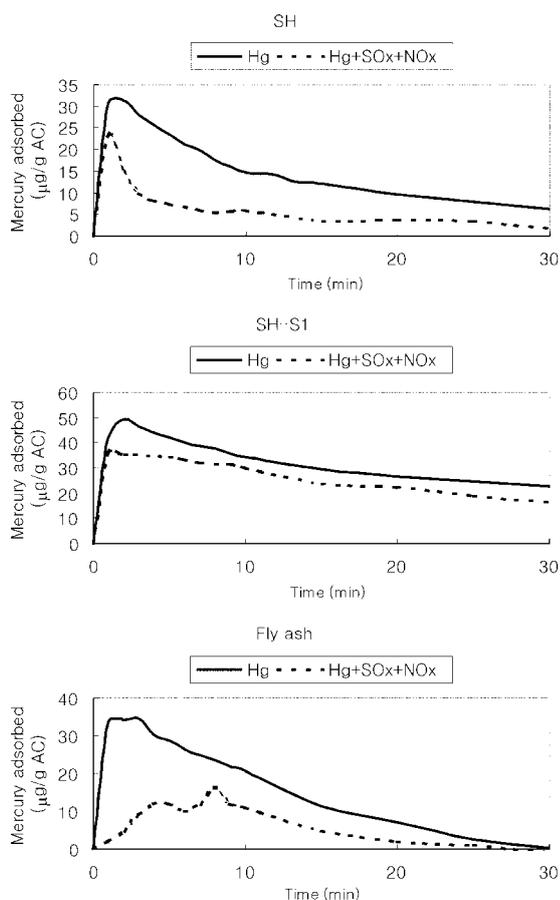


Fig. 2. Adsorption performance of SH, SH-S1 and fly ash for Hg at 140°C (C_0 ; 50–100 $\mu\text{g}/\text{m}^3$, flow rate; 2 L/min, AC; 2 g).

hour and dried at 110°C for 24 hours. As shown in the figures, SH, SH-S1 and fly ash (Fig. 2) had similar adsorption characteristics. The three kinds of adsorbents, which adsorption capacity were relatively low, showed the trend that mercury was rapidly adsorbed during the initial stage of adsorption but the adsorption rate decreased gradually. SH-S15, SH-H₂SO₄, HGR and MAG (Fig. 3), which had a large adsorption capacity, appeared to maintain their initial adsorption performance during the experiment. The result showed the differences of the adsorbents in adsorption capacity.

Adsorption amounts during the first 30 minutes of the experiments were integrated and compared in Fig. 4. Each AC shows different adsorption characteristics between when only mercury vapor was contained in nitrogen and when the simulated gas was contained in nitrogen. However, it was a general trend that when SO_x and NO_x existed, the adsorption amounts decreased, and that the ACs with high adsorption capacity were less affected by the introduction of SO_x and NO_x (51% of reduction for AC in Fig. 2 and 27.7% reduction for AC in Fig. 3).

SH-H₂SO₄ showed the most excellent adsorption perfor-

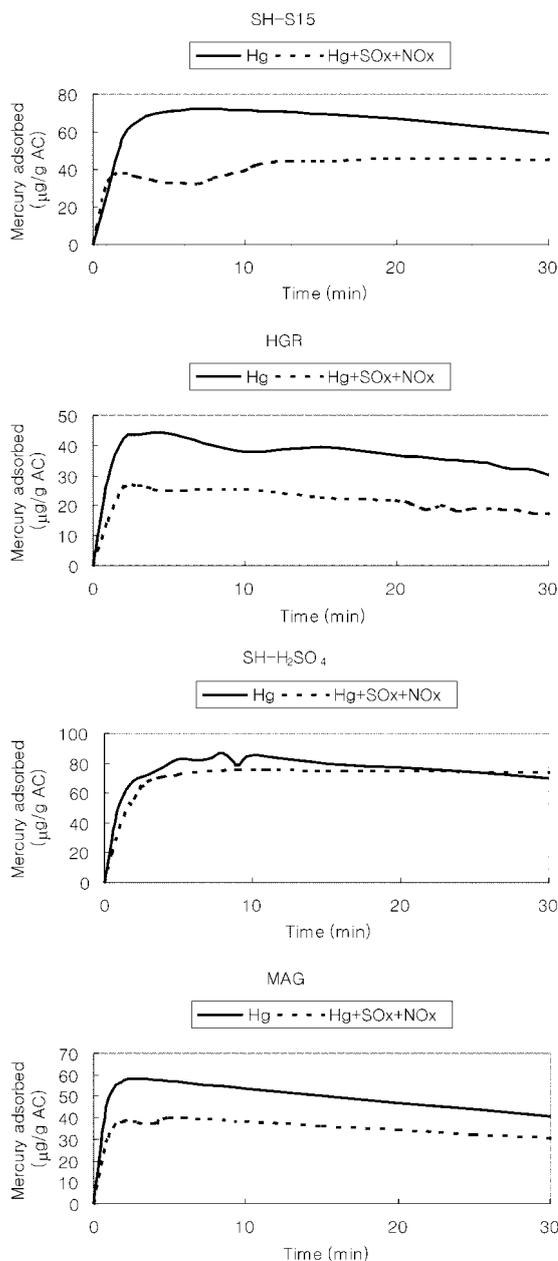


Fig. 3. Adsorption performance of SH-S15, SH-H₂SO₄, HGR and MAG for Hg at 140°C (C_0 ; 50–100 $\mu\text{g}/\text{m}^3$, flow rate; 2 L/min, AC; 2 g).

mance. It could be found that the sulfur impregnated AC could not perform properly at 140°C. It was because the activity of sulfur lowered at over its melting temperature of 120°C. It was considered that, for this reason, SH-S15 and HGR, which were impregnated with sulfur, showed low adsorption performance

The adsorption performance of SH-S1 was twice as high as that when SH was used, and between SH-S15 and HGR that had a similar content of sulfur, SH-S15 was superior to HGR in performance. Such results depended on the proper-

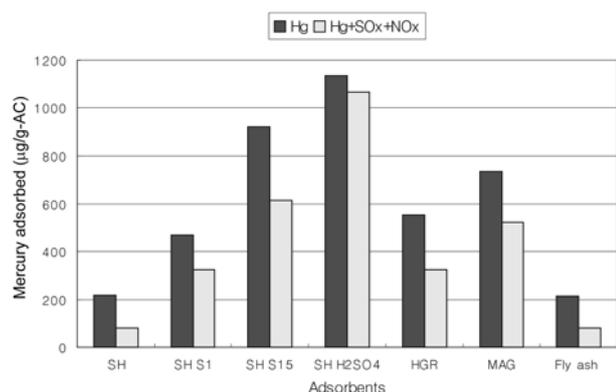


Fig. 4. Comparison of Hg adsorption capacity with various activated carbon at 140°C in 30 minutes (C_0 ; 50~100 $\mu\text{g}/\text{m}^3$, flow rate; 2 L/min, AC; 2 g).

ties of the impregnated sulfur. Sulfur has various types of allotropes. Among them, S_2 and S_4 , which are synthesized at a high temperature, are known as reactive sulfur [4]. SH-S15 was impregnated with sulfur at higher temperature than HGR, resulted in having the higher fraction of reactive sulfur than HGR.

AC to be used in treating flue gas from incinerators and power plants must not be expensive, nor cause additional pollution problems. SH- H_2SO_4 smelled of sulfuric acid during the experiment and sulfur was detected in the flue gas treated with SH-S15. These results suggest that SH-S1 is a sorbent fit for stable use, because of its lower amounts of sulfur used and higher efficiency of sulfur utilization to remove mercury vapor.

For applying AC injection, it is needed to select AC that has a high adsorption rate and available cost rather than excellent adsorption capacity. Virgin AC is low-cost, but if it is needed to raise the C/Hg ratio significantly due to its low performance, it will be uneconomical. Sulfur impregnation puts up the cost, but it may put down the C/Hg ratio. How-

Table 3. Comparison of mercury removal rate at the steady state conditions with low and high sulfur AC (C_0 ; 50~100 $\mu\text{g}/\text{m}^3$, flow rate; 1 L/min, AC; 0.05 g)

		Mercury removal rate at steady state condition		
		$\mu\text{g Hg}/\text{g AC}/\text{min}$	% Removal	$\mu\text{g Hg}/\text{g S}/\text{min}$
Raw AC	SH	0.116	6.5	—
Low sulfur (0.9~1.1%) AC	SH-S1	0.372	24.0	32.01
		0.28	18.0	21.2
High sulfur (13~15%) AC	SH-S15	0.632	37.7	9.6
		0.32	18.8	4.57
		0.6	31.0	8.57

ever, if the utilization efficiency of the impregnated sulfur is low, the AC is uneconomical, too.

From the above results, it is needed to create high efficiency AC at low cost in a way to impregnate a little amount of reactive sulfur. With the three ACs in which the sulfur content were about 1 wt%, a mercury adsorption experiment was performed. The high sulfur ACs prepared at the selected conditions were also tested. The test results were compared in Table 3. For the high sulfur AC, it could be found that the adsorbed amounts at any instant time increased markedly due to increased sulfur amount. However, sulfur utilization efficiency was not superior to low sulfur AC. The sulfur utilization efficiency of low sulfur AC were about 3 times larger than that of high sulfur AC. Low sulfur AC could be prepared at low temperature and low flow rate of carrier gas, so that the sulfur loss minimized and the duration of impregnation was also short.

4. Conclusions

By comparing the mercury adsorption performances of the virgin AC, the AC treated with sulfuric acid, the AC impregnated with sulfur, and the fly ash in a simulated environment of flue gas, the following conclusions were drawn. When the mercury vapor existed in the simulated gas with SOx and NOx, the adsorption capacity of mercury reduced by about 40% as compared with the case when only mercury vapor was contained in nitrogen. The AC treated with sulfuric acid showed the highest adsorption performance, but it was considered possibly to cause the problem of corrosion due to the emission of sulfuric acid. The AC impregnated with high sulfur content also emitted a portion of sulfur at 140°C. Thus, it was concluded that the AC impregnated with low sulfur content was fit for treating flue gas for the mercury removal.

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