



Review

Adsorbents for capturing mercury in coal-fired boiler flue gas

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Abstract

This paper reviews recent advances in the research and development of sorbents used to capture mercury from coal-fired utility boiler flue gas. Mercury emissions are the source of serious health concerns. Worldwide mercury emissions from human activities are estimated to be 1000 to 6000 t/annum. Mercury emissions from coal-fired power plants are believed to be the largest source of anthropogenic mercury emissions.

Mercury emissions from coal-fired utility boilers vary in total amount and speciation, depending on coal types, boiler operating conditions, and configurations of air pollution control devices (APCDs). The APCDs, such as fabric filter (FF) bag house, electrostatic precipitator (ESP), and wet flue gas desulfurization (FGD), can remove some particulate-bound and oxidized forms of mercury. Elemental mercury often escapes from these devices. Activated carbon injection upstream of a particulate control device has been shown to have the best potential to remove both elemental and oxidized mercury from the flue gas. For this paper, NORIT FGD activated carbon was extensively studied for its mercury adsorption behavior. Results from bench-, pilot- and field-scale studies, mercury adsorption by coal chars, and a case of lignite-burned mercury control were reviewed.

Studies of brominated carbon, sulfur-impregnated carbon and chloride-impregnated carbon were also reviewed. Carbon substitutes, such as calcium sorbents, petroleum coke, zeolites and fly ash were analyzed for their mercury-adsorption performance. At this time, brominated activated carbon appears to be the best-performing mercury sorbent.

A non-injection regenerable sorbent technology is briefly introduced herein, and the issue of mercury leachability is briefly covered. Future research directions are suggested.

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Keywords: Mercury; Sorbent; Adsorption; Activated carbon; Flue gas

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1. Background

The amount of mercury in Earth's biosphere is increasing gradually due to both natural and anthropogenic emissions. Worldwide mercury emissions from human activities are currently estimated to be 1000–6000 t/annum, which accounts for 30–55% of global atmospheric mercury emissions [1–3]. In the United States alone, mercury emissions from anthropogenic sources were estimated to be 158 t/annum [4]. In Canada, total mercury emissions from anthropogenic sources were estimated to be 7.84 t/annum in 2004 [5]. The emission of mercury into the atmosphere and its transport away from emission sources impose serious health concerns. Mercury buried deep in the ground or beneath lake and ocean floors does not appear to present a threat to either the environment or human health. However, mercury deposited in bodies of water can be transformed into more toxic organic forms and can bio-accumulate in aquatic life. Bio-accumulation provides a sink for mercury emitted from various sources. Human exposure can occur through consumption of polluted water and fish.

Compared to emissions from municipal waste incinerators, emissions from coal-fired power plants are often much lower in concentration; however, the large quantity and scale of boilers make coal burning the largest anthropogenic source of mercury emissions. After many years of coal burning and other industrial processes, the level of organic mercury in many water bodies rises to an extent that consumption of fish is unsafe. Many mercury research and engineering efforts are being explored to control mercury emissions from coal-fired boilers.

U.S. coal-fired power plants emitted 44.2 t of mercury into the air in 2004, which accounts for 40% of the total U.S. anthropogenic emissions [5]. Canadian power plants emitted 1.96 t of mercury in 2004, which accounts for 25% of total Canadian anthropogenic emissions [5]. The U.S. Environmental Protection Agency (EPA) and the Canadian Council of Ministers of the Environment (CCME) have determined that the mercury emitted from utility power plants should be controlled. EPA proposed regulations by December 2003 and promulgated them in December 2004, expecting full compliance by December 2007. Canada has established a consultative process to develop "Canada-wide standards" for mercury emissions from coal-fired electricity generation facilities.

2. Mercury emissions from coal-fired power plants

Coal contains mercury at a concentration of around 0.1–0.15 mg/kg [2]. Mercury is probably associated with the sulfide minerals in solid solution in pyrite (FeS_2) and cinnabar (HgS), and some mercury may be organically bound to coal macerals [6]. It is emitted into the air during the coal combustion process. The concentration of mercury in flue gas is around 1–20 $\mu\text{g}/\text{m}^3$ [7]. All forms of mercury decompose into elemental form during coal combustion. Some of the elemental mercury is converted to oxidized forms and some is affiliated with particulate matter leaving a high temperature furnace environment. Mercury is present in the flue gas in varying percentages of three basic chemical forms: particulate-bound, oxidized (primarily mercuric chloride), and elemental mercury. The term speciation is used to describe the relative proportions of these three forms of mercury in flue gas.

There are thermodynamics models to predict the speciation of mercury in post-combustion conditions [7]. Equilibrium calculations predict that Hg^0 should be completely converted to oxidized forms of volatile mercury(II) and particulate mercury upon cooling to 400 °C. Measurements of flue gas from different types of coals show 35–95% oxidation indicating the conversion is kinetically limited. Recent studies of mercury speciation indicate a strong correlation between high levels of mercury oxidation and high levels of chlorine in flue gas.

Components other than chlorine in coal may have subtle effects [8]. Coals containing high sulfur tend to yield less oxidized mercury in flue gas. Iron is considered to catalyze mercury oxidation and promote mercury capture by particulate matter. Calcium likely reacts with chlorine during the combustion process and appears to reduce its ability to promote mercury oxidation. The high percentage of elemental mercury is typically found in flue gas from burning subbituminous and lignite coals for their high calcium and low chlorine contents. High percentages of oxidized mercury are typically observed for flue gas from burning bituminous coals.

The National Energy Technology Laboratory (NETL) reported the mercury speciation for flue gas derived from different types of coal [9]. For bituminous coals, about 20% of total mercury is in elemental form, 35% in oxidized form, and 45% in particulate-bound form. For subbituminous coals, about 65% of total mercury is in elemental form, 20% in oxidized form, and 15% in particulate-bound form. For lignite coals, about 85% of

Table 1
Average mercury capture by coal rank and APCD configuration

APCD configurations	Average percentage of mercury capture (%)		
	Bituminous	Subbituminous	Lignite
CS-ESP	36	3	−4
HS-ESP	9	6	NA
FF	90	72	NA
PS	NA	9	NA
SDA + ESP	NA	35	NA
SDA + FF	98	24	0
SDA + FF + SCR	98	NA	NA
PS + Wet FGD	12	−8	33
CS-ESP + Wet FGD	74	29	44
HS-ESP + Wet FGD	50	29	NA
FF + Wet FGD	98	NA	NA

CS-ESP: cold-side ESP; HS-ESP: hot-side ESP; PS: particulate scrubber; SDA: spray dryer adsorber.

total mercury is in elemental form, 10% in oxidized form, and 5% in particulate-bound form.

Different countries have different mercury emission limits. In the U.S., emission limits for existing power plants are 2.0, 5.8, and 9.2 lb/TBtu (0.96, 2.8, and 4.4 $\mu\text{g}/\text{MJ}$) for bituminous, subbituminous, and lignite coals, respectively [10].

3. The role of existing APCDs

Numerous studies have shown that some degree of mercury removal can be achieved by existing conventional APCDs, which are normally used to control NO_x , SO_2 , and particulate matter from coal-fired flue gas. Mercury removal rates among existing APCDs, ranging from 0 to 90%, vary significantly depending on coal type, fly ash properties, and specific APCD configuration. Table 1 lists co-benefit mercury removal efficiencies for different coals [11]. The table shows that plants burning bituminous coals in general demonstrate significantly higher mercury removal than similarly equipped boilers burning subbituminous and lignite coals. It is reported that the observed lower performance for low-rank coals has been correlated to higher levels of elemental mercury and is also associated with the coals' low chlorine content [11]. Systems burning high-rank coals equipped with wet FGD devices show better mercury control. In the United States, only about 25% of coal-fired utility boilers are equipped with wet FGD.

4. Flue gas sorbent injection technologies

Although conventional APCDs can capture some mercury, new mercury control technologies are still needed to meet mercury emission regulations. To date, activated carbon injection has shown the most promise as a mercury control technology. Injection of activated carbon upstream of the ESP or FF could potentially be employed at the majority of coal-fired boilers not equipped with FGD.

In a typical situation, powdered activated carbon (PAC) is injected downstream of the air heater and upstream of the particulate control device (ESP, FF, etc.). The injected carbon adsorbs

mercury from flue gas and is subsequently captured along with fly ash in the ESP or FF.

Although field tests have been relatively successful, research and development efforts are still needed before carbon injection is considered a commercial technology for wide use. The sorbent costs need to be reduced. Carbon injection's long-term effects should be studied to determine its effect on plant operation, perhaps including such issues as increased particulate loading leading to possible premature filter bag failure. The amount of carbon injected needs to be kept to a certain level to avoid increased fly ash disposal costs. Mercury adsorption stability by sorbents needs to be proved.

4.1. Virgin carbon sorbents

Field- and pilot-scale tests of activated carbon injection for mercury control have achieved 25–95% removal over the injection rate range of C/Hg ratio 2000–15,000. The removal mechanisms can be explained either by mass transfer control, in which sorbent injection rates have positive effects on mercury removal efficiency, or by catalytic oxidation and capture control, in which flue gas temperature, flue gas composition, and sorbent chemical properties strongly affect mercury removal.

4.1.1. NORIT FGD activated carbon

FGD activated carbon is a commercial product developed for controlling heavy metal emissions from incinerators. It has been studied more extensively than any other mercury sorbent for capturing mercury from coal-fired flue gas. FGD activated carbon has a bulk density of 0.51 g/cm^3 and a surface area of 600 m^2/g . Particle sizes range from 9 to 15 μm . Information from detailed physical and chemical analysis is available from literature [12].

Bench-scale studies using FGD carbons were performed by Radian Corporation and the University of North Dakota Energy & Environmental Research Center (EERC) [12–17]. The typical gas environment contained 6% O_2 , 12% CO_2 , 8% H_2O , 1600 ppm SO_2 , 50 ppm HCl and 20–80 $\mu\text{g}/\text{m}^3$ Hg^0 or HgCl_2 . The findings from these studies can be summarized as follows.

Firstly, the equilibrium adsorption capacity is found to increase as temperature and inlet concentration of either Hg^0 or HgCl_2 decrease. This relationship indicates a physical adsorption mechanism, although chemical adsorption is believed to be the mechanism that ultimately binds mercury to carbon [18]. The capacity measured at a typical mercury concentration of 10 $\mu\text{g}/\text{m}^3$ is about 200 $\mu\text{g}/\text{g}$ carbon. This capacity may not be sufficient in real flue gas situations where residence time of only seconds to minutes are available for sorbent–flue gas interaction for boilers equipped with ESP or FF. The observed capture capacities of oxidized mercury are higher than those of elemental mercury, indicating FGD activated carbon will be more effective in capturing oxidized mercury.

Secondly, effects of individual gas components are also studied. In the absence of acid gases, upon exposure to a baseline gas mixture of O_2 , CO_2 , N_2 , and H_2O , the FGD carbon provides only about 10–20% of Hg^0 capture at 107 °C. Under these condi-

tions, FGD carbon is ineffective in capturing elemental mercury. The effect of HCl is to increase the equilibrium Hg^0 adsorption capacity from 0 at 0 ppm HCl to 3000 $\mu\text{g}/\text{g}$ C at 50–100 ppm HCl. The capacity of HgCl_2 adsorption increases from 500 $\mu\text{g}/\text{g}$ C at 0 ppm HCl to 1000 $\mu\text{g}/\text{g}$ C at 20 ppm HCl to 1500 $\mu\text{g}/\text{g}$ C at 100 ppm HCl. The effect of SO_2 in the absence of NO_x is to reduce the equilibrium adsorption capacity for Hg^0 from 15,000 to 2000 $\mu\text{g}/\text{g}$ C and for HgCl_2 from 4000 to 500 $\mu\text{g}/\text{g}$ C in the range of 0–3000 ppm SO_2 . The similar trend holds in the presence of HCl at 4–50 ppm. Significant reduction in adsorption capacity is observed when both SO_2 and NO_2 are present. A highly significant interaction between SO_2 and NO_2 causes a rapid breakthrough of mercury as well as conversion of the mercury to a volatile oxidized form. This effect occurs at both 107 and 163 °C and with or without the presence of HCl and NO . For the effect of NO_x , no adsorption of Hg^0 is observed in the absence of both NO_x and HCl. Increasing NO_x alone from 0 to 100 to 400 ppm causes the Hg^0 adsorption capacity to increase from 0 to 640 $\mu\text{g}/\text{g}$ C and then decrease to 250 $\mu\text{g}/\text{g}$ C. Increasing NO_x from 0 to 400 ppm in the presence of 50 ppm HCl causes the Hg^0 capacity to drop from 2600 to 1000 $\mu\text{g}/\text{g}$ C.

Thirdly, the equilibrium tests indicate no mercury adsorption when there is no mercury oxidation. HCl or NO_x alone positively affect mercury adsorption capacity while SO_2 appears to inhibit mercury oxidation, thus reducing mercury adsorption capacity. The adsorption capacity of Hg^0 is 3000 $\mu\text{g}/\text{g}$ C in the presence of 50–100 ppm HCl alone and 640 $\mu\text{g}/\text{g}$ C in the presence of 100 ppm NO_x alone. When both 50 ppm HCl and 0–400 ppm NO_x are present, the Hg^0 adsorption capacity drops from 2600 to 1000 $\mu\text{g}/\text{g}$ C. This seems to contradict the previous report [19] where the presence of both HCl and NO_x appears to have a synergistic effect on promoting mercury oxidation in simulated and real flue gas.

Lastly, in the presence of all four acidic gases, SO_2 , HCl, NO , and NO_2 , rapid breakthrough and oxidation of mercury occur at both 107 °C and 163 °C. This suggests that the NO_2 – SO_2 interaction and subsequent poor sorbent performance is a major factor that affects typical coal-fired boiler mercury control where all these gas components exist. For coal-fired systems, the acid gases produced will dominate the sorption chemistry on the sorbent surface [20] and the type of fuel and burning conditions will determine the flue gas composition with respect to acidic gases and thereby determine the effectiveness of the carbon sorbents used for mercury control.

Pilot-scale tests of injecting FGD activated carbon have also been performed. Different performances were observed over tests with different coals using FGD activated carbon. For instance, Belle Ayr subbituminous coal [14,21] and Evergreen and Blacksville bituminous coals [14,22] with similar mercury levels but different concentrations of chlorine, sulfur, iron, and calcium, have been tested. Testing results are summarized below.

For Belle Ayr coal without carbon injection, 20–80% of mercury removal is observed. When with carbon injection and the C/Hg ratio is changed from 2000 to 15,000, the removal rate increases very slightly. There is a 20% increase in removal due to the system temperature change from 177 to 110 °C. Mercury removal rates from Belle Ayr coal by ESP are 20–30% lower

than those for a FF. Different trends are observed when testing Evergreen and Blacksville coal. For Evergreen coal, increasing carbon injection rates to achieve a C/Hg ratio of 2500–10,000 results in an increase in mercury removal from 30 to 85%. For Blacksville coal, changing the C/Hg ratio from 3500 to 13,000 results in only a little increase in removal rate. Cooling flue gas from 175 to 100 °C increases removal rates from 10 to 95% at a constant C/Hg ratio of 3800. The effect of temperature is less evident for Belle Ayr coal and Evergreen coal.

These different trends observed in pilot-scale studies suggest different mechanisms of mercury removal. The results of testing with Evergreen coal can be explained by mass transfer control, by which injection rates significantly affect removal. For Belle Ayr coal and Blacksville coal, the effect of carbon injection rates is small, suggesting that mass transfer is not the limiting factor. The evident temperature effect observed for Blacksville coal indicates the heterogeneous mercury oxidation in flue gas is the rate-controlling step.

NETL performed full-scale FGD carbon injection tests on various U.S. coal-fired boilers, namely at the E.C. Gaston, Pleasant Prairie, Brayton Point, and Salem Harbor Plants [11]. Results are summarized as follows.

The E.C. Gaston Plant, which burns low-sulfur bituminous coal, was equipped with hot-side ESP and downstream FF. Baseline measurements indicated that less than 10% of mercury was captured across the FF. Average FF inlet mercury concentration was about 11 $\mu\text{g}/\text{m}^3$ of which 40% was elemental mercury. During a 9-day test, NORIT FDG was injected upstream of FF achieving a 78% mercury-removal rate with an injection rate of 1.5 lb/MMacf (million actual cubic feet flue gas). Mercury capture did not improve when a water spray cooling system was used to lower flue gas temperature. During a 5-month test, average mercury removal was 85% at 0.55 lb/MMacf using the original filter bag. After high-permeation filter bags were installed, a new 1-month test showed average mercury removal of greater than 90% with a carbon injection rate of 1.3–1.6 lb/MMacf.

The Pleasant Prairie Plant, which burns subbituminous coal, was equipped with ESP. Baseline measurements indicated less than 10% mercury capture across the ESP. Average ESP inlet mercury concentration was about 17 $\mu\text{g}/\text{m}^3$ of which 70–85% is elemental mercury. NORIT FDG activated carbon was injected during three 5-day tests, and the removal rates ranged from 46 to 66% at an injection rate of 1.6–11.3 lb/MMacf. Mercury capture did not improve when a spray cooling system was used to cool flue gas.

The Brayton Point Plant, which burns low sulfur bituminous coal, was equipped with two ESPs in series. Baseline measurements indicated mercury removal ranging from 30 to 90% across both ESPs and 0–10% across the second ESP. Average mercury concentration in the inlet to the first ESP was about 6 $\mu\text{g}/\text{m}^3$, of which 85% was particulate-bound and 5% was in elemental form. NORIT FGD was injected between two cold-side ESPs at rates of 3–20 lb/MMacf with mercury removal ranging from 25 to 90% across the second ESP.

The Salem Harbor Plant, which burns a low-sulfur, atypical bituminous coal, was equipped with cold-side ESP. Baseline measurements showed mercury removal across the ESP at about

90%. Baseline mercury removal decreased from 90 to 20% when flue gas temperature was increased from 130 to 180 °C. Average mercury concentration in the inlet to the ESP was about 10 $\mu\text{g}/\text{m}^3$, of which 95% was particulate-bound mercury. The high removal across ESP is attributed to high levels of unburned carbon (25–30% lost-on-ignition [LOI]) and low flue gas temperature (130 °C).

Results from the NETL full-scale testing indicate that FGD activated carbon injection into flue gas is an effective method to remove mercury for plants burning bituminous coals. For subbituminous coal, it is less effective. Increases in flue gas temperature cause decreased mercury removal performance. High LOI of fly ash causes increased mercury removal by fly ash.

Studies performed by ADA Environmental Solutions indicate that injecting activated carbon upstream of a COHPAC fabric filter is one of the most efficient, cost-effective approaches for reducing mercury emissions from coal-fired boilers [23]. COHPAC is an EPRI-patented concept that places a high air-to-cloth ratio baghouse downstream of an existing ESP to improve overall particulate collection efficiency. Full-scale tests achieve mercury removals for both bituminous and subbituminous coals as high as 90% at a carbon injection rate of 3–4 lb/MMacf. Another study performed by the same company shows mercury removal of about 70% at a carbon injection rate of 11 lb/MMacf [24]. This study reports that mercury removal across ESP or FF depends strongly on flue gas temperature and unburned carbon levels. Plants with high carbon levels in fly ash and low flue gas temperatures have higher mercury removals. These agree with the results from NETL's full-scale FGD carbon injection testing summarized above.

4.1.2. Adsorption of vapor-phase mercury by coal chars

Three coal chars were studied in a simulated flue gas atmosphere [6]. These three chars were derived from Pittsburgh and Illinois 6 bituminous coals and Wyodak subbituminous coal. Major results are summarized as follows.

The simulated flue gas consisted of O_2 , H_2O , CO_2 , and N_2 , but did not contain trace acidic gases such as HCl , SO_2 , NO , and NO_2 . The bituminous coals contained significant amounts of pyritic and organic sulfur while the subbituminous coal contained primarily organic sulfur. The carbon content of chars is 10–20 times higher than that of bulk fly ash from coal-fired utility boilers. The bituminous chars have lower surface areas and much higher sulfur contents than subbituminous char.

The rank of the coal appears to significantly affect the adsorption of Hg^0 : two bituminous chars adsorbed similar amounts of Hg^0 while the subbituminous char adsorbed much less. The amounts of Hg^0 adsorbed did not appear to correlate with the char sulfur contents nor the char surface areas. The dependence of mercury adsorption on coal ranks suggests that other characteristics, such as pore structure or surface functional sites, may be important to Hg^0 adsorption. A 10-fold increase in the concentration of flue gas Hg^0 results in only a twofold increase in adsorption. Increased temperature from 70 to 160 °C results in decreased Hg^0 adsorption. The three chars have a much larger adsorption capacity for HgCl_2 . Compared to the adsorption of

Hg^0 , the adsorption of HgCl_2 by bituminous chars is higher by a factor of two and the adsorption of HgCl_2 by subbituminous char is 50 times higher. The dependence of HgCl_2 adsorption on coal rank is not evident, while there is a better agreement with char surface areas.

Results of this study indicate different mechanisms for Hg^0 and HgCl_2 adsorption, although the mercury concentrations are much higher than that of real flue gas (3.6 ppmv Hg^0 and 67 ppmv HgCl_2 in this study).

4.1.3. Carbon-based sorbents for mercury control for lignite-burned utilities

A 3-year, two-phase U.S.–Canada consortium project was carried out to develop and demonstrate mercury-control technologies for lignite-burned utilities [9]. In this study, carbon sorbents were prepared from Luscar, Center, and Beulah-Zap coals and Luscar coal char. Sorbents were steam-activated at baseline temperature and increased temperature. The prepared sorbents and commercial NORIT FGD activated carbon were evaluated for mercury removal efficiency in a bench-scale, fixed-bed study using simulated flue gas of typical lignite coal-burned flue gas concentrations.

Unactivated Luscar chars are ineffective in removing Hg^0 from simulated flue gas. Carbon sorbents activated at baseline temperature are ineffective in capturing mercury for the initial period of 30–40 min of a test and then effective for 3 h. The carbon sorbents activated at increased temperature and FGD are more effective in oxidizing and capturing mercury than the carbons activated at the baseline temperature.

Tests with unactivated chars show immediate Hg^0 breakthrough, which indicates that activation is a necessary step in preparing carbon sorbents. Most carbon-based sorbents exhibit an initial breakthrough that diminishes quickly. This phenomenon is observed for all sorbents exposed to flue gas containing 1 ppm chlorine simulating lignite flue gas. A conditioning period of about half an hour is proposed to explain this early breakthrough and later efficiency of mercury removal.

The preliminary pilot-scale tests show that injection of activated carbon upstream of the particulate control device is the most effective in capturing mercury compared to other technologies.

4.2. Chemically treated sorbents and coal additives

Previous pilot- and full-scale tests have demonstrated that the low chlorine concentration of most low-rank coals is a major limiting factor in the mercury control performance of conventional activated carbons [11]. Various chemically treated carbons were developed to compensate for the lack of chlorine levels (or other halogens) in the combustion flue gas.

4.2.1. Brominated carbon sorbents

Sun et al. studied brominated activated carbon Hg^0 adsorption capacity and dynamics [25]. The bromination causes enhanced and faster Hg^0 adsorption. The adsorption capacity increases 80 times to 0.2 mg/g C when bromination is 0.33%. The capacity

Table 2
B-PAC test results across all coals and plant configurations

Coal type	Particulate control	Hg removal (%)	Injection rate (lb/MMacf)	Scale
Bituminous low S	FF	94	0.5	Slipstream
Bituminous high S	CS-ESP	70	4.0	Full-scale
Bituminous low S	HS-ESP	>80	6.4	Full-scale
Subbituminous blend	CS-ESP	90	3.0	Full-scale
Subbituminous	CS	>90	3.0	Full-scale
Subbituminous	CS	89	4.9	Slipstream
Subbituminous	FF	87	0.5	Slipstream
Subbituminous	SD/FF	82	<1.8	Slipstream
Lignite	SD/FF	95	1.5	Full-scale
Lignite	CS-ESP	70	1.5	Full-scale

increases with the degree of bromination and decreases slightly with increasing temperature. The presence of SO₂ in flue gas has some inhibitive effect.

Brominated mercury sorbent B-PACTM marketed by Sorbent Technologies Corporation has been tested by Apogee [10]. The injection of brominated powdered activated carbon into power-plant flue gases for mercury control was tested at seven different power plants. This sorbent consistently demonstrated highly efficient mercury removal. Mercury removal at these sites varies from 70 to 90% at sorbent consumption cost of US\$ 2000–20,000/lb of mercury removal, significantly less than previous technologies. The plants burn bituminous, subbituminous, and lignite coals and coal blends and are equipped with different configurations of pollution control devices, hot-side ESPs, cold-side ESPs, spray dryers, and fabric filters. Table 2 presents detailed results, which indicate that the injection of brominated carbon to remove mercury from flue gas is effective for different types of coal and different APCD configurations.

NETL also performed some full-scale tests with injecting bromine-treated activated carbon [11]. Tests were performed at three sites, namely the St. Clair Plant, Holcomb Station, and AmerenUE. The findings of NETL testing can be summarized as follows.

The St. Clair Plant, burning a blend of 85% Powder River Basin (PRB) and 15% bituminous coal, was equipped with an ESP. Baseline mercury removal across the ESP varies from 0 to 40%. Mercury concentration at the ESP inlet varies from 4 to 10 µg/m³ of which 80–90% is elemental mercury. Average mercury removal during a 1-month test is 94% using a brominated activated carbon at injection rate of 3 lb/MMacf.

Sunflower Electric's Holcomb Station burns PRB subbituminous coal and is equipped with a spray dryer absorber and fabric baghouse (SDA/FF). SDA inlet mercury concentration is 11.7 µg/m³ of which 100% is in elemental form. Baseline mercury capture is 13% across SDA/FF when burning 100% PRB coal. Blending 15% western bituminous coal with PRB coal increases mercury capture to 80%. The mercury contents of these two coals are similar but the chlorine contents are different, 106 µg/g versus 8 µg/g. Three sorbents are tested at this site, namely NORIT FGD, Calgon 208CP (an activated carbon), and NORIT FGD E-3 (a brominated activated carbon). Mercury removal is about 50% with injection of FGD and 208 CP at rate of 1.0 lb/MMacf. FGD E-3 achieves 77% mercury

removal with injection rate of 0.7 lb/MMacf and greater than 90% at 4.3 lb/MMacf. When injected with KNX, a chemical coal additive by ALSTOM Power, FGD removes 50–86% of mercury at 1.0 lb/MMacf. FGD E-3 mercury removal is 77% at 0.7 lb/MMacf and 93% at 1.2 lb/MMacf in a 30-day, long-term test.

AmerenUE's 140-MW Unit 2 station burns PRB coal and is equipped with an ESP. Mercury inlet concentration is 8.5 µg/m³. Baseline mercury removal across the ESP is 15–18%. FGD injection results in 74% removal at 5 lb/MMacf. FGD E-3 injection results in 97% removal at 3.3 lb/MMacf. When injected with KNX, FGD results in 87% removal at 5 lb/MMacf.

ADA Environmental Solutions also performed a study of KNX as a chemical coal additive [26]. Results show enhanced performance of a standard activated carbon. Mercury removal of 86% is measured at a carbon injection rate of 1.0 lb/MMacf. Their study of FGD-E3 also indicates the viability of the approach of injecting FGD-E3, which removes greater than 90% mercury [26].

For plants burning lignite coals, injecting untreated activated carbons has shown lower mercury removal performance than for plants burning other coals, such as bituminous coals. The low chlorine and high calcium contents of lignite coals result in low reactivity between sorbent and mercury, thereby resulting in poorer performance. The low reactivity between mercury and sorbent can be improved by using chemically treated carbons or coal additives to increase the mercury oxidation and subsequent mercury capture. EERC tested enhancements to activated carbon injection to increase mercury capture for plants burning lignite coals [27–29]. Two sorbent enhancement additives were developed: SEA-1 (calcium chloride) and SEA-2 (a halogen-based chemical). Injecting conventional activated carbon with SEA was tested at Basin Electric's Leland Olds Station Unit 1, which is equipped with an ESP. ESP inlet mercury concentration was 7.3 µg/m³ of which 56% was elemental. Baseline mercury removal was 15% across the ESP. Injecting activated carbon alone achieved 45% mercury removal at 3 lb/MMacf. Injecting carbon at 3 lb/MMacf and SEA-1 at 7 lb/MMacf achieved 65% mercury removal.

URS Corporation performed tests on a lignite coal-fired site using conventional activated carbon and bromine-treated carbon [30]. The total vapor-phase mercury concentration ranged from 7.5 to 13 µg/m³ of which less than 10% was oxidized mer-

cury. Native mercury removal across spray dryer and baghouse was less than 10%. The benchmark sorbent FGD achieved 75% mercury removal at 6.0 lb/MMacf. Chemically treated carbons provided improved performance over untreated carbons. FGD-E3 and ST BAC (a brominated carbon) achieve greater than 85% mercury removal at 1.0 lb/MMacf and greater than 90% at 1.5 lb/MMacf.

Results from these studies suggest that brominated activated carbon is effective at removing mercury from coal-fired flue gas.

4.2.2. Sulfur-impregnated carbon sorbents

Karatzas and Lancia performed a bench-scale study in which HGR activated carbon (commercial product by Calgon Carbon Corp.) and sulfur-impregnated activated carbon were exposed to elemental mercury carried by nitrogen gas [31]. Results indicated that mercury is adsorbed on the carbon surface on particular sites where high sulfur concentration exists.

Hsi et al. studied the mercury adsorption by sulfur-impregnated activated carbon fiber [32,33]. Raw activated carbon fiber (ACF) has 0% sulfur, a 1886 m²/g micropore surface area, and a 350 μg/g equilibrium adsorption capacity. ACF was impregnated with sulfur between 250 and 650 °C. The total sulfur content of the sulfur-impregnated ACF samples decreased with increasing impregnation temperatures from 250 to 500 °C, then remained constant to 650 °C. Analyses showed that sulfur impregnated on ACF was in both elemental and organic forms. As sulfur impregnation temperature increased, the relative amount of elemental sulfur decreased while the amount of organic sulfur increased. In general, sulfur impregnation decreased surface area and increased equilibrium Hg⁰ adsorption capacity compared to raw ACF. Sulfur impregnation of ACF at 250 °C resulted in the largest total sulfur content (64 wt%), undetectable micropore surface area, and the smallest equilibrium Hg⁰ adsorption capacity of 755 μg/g in a simulated flue gas stream containing 50 μg/m³ Hg⁰ at 140 °C. Sulfur impregnation at 400 °C with 44 wt% total sulfur content and 81 m²/g micropore surface area resulted in the largest equilibrium Hg⁰ adsorption capacity of 11,343 μg/g. Sulfur impregnation at 650 °C resulted in 13 wt% sulfur content, 12% reduction in micropore surface area, and equilibrium Hg⁰ adsorption capacity of 1907 μg/g, comparable to those of activated carbons derived from high organic sulfur content coals [32,34]. Results also indicated that the total sulfur content or total surface area do not necessarily determine the sample's mercury adsorption capacities independently. Elemental sulfur provides one of the most active sites for Hg⁰ adsorption. Micropores are also necessary to achieve large Hg⁰ adsorption capacities. Detailed adsorption mechanisms are still unknown.

Yan et al. studied several commercially available activated carbons [1]. Results from a bench-scale study using N₂ + Hg⁰ indicated that the sulfur-impregnated carbons perform better than non-impregnated carbons. For sulfur-impregnated carbons, both physical adsorption and chemical adsorption played a role in Hg vapor removal. Physical adsorption decreased with increasing temperature while chemical adsorption could be

increased, limited by the melting point of sulfur. A large external surface area is necessary for a sulfur-impregnated carbon to achieve high performance.

Liu et al. studied the preparation methods of impregnating activated carbon with sulfur [35]. Adsorption of Hg⁰ tests in nitrogen showed that carbons impregnated with sulfur at high temperature exhibit the highest efficiency of mercury removal. As the impregnation temperature decreased, the performance of the carbons decreased. When the sulfur to carbon ratio was changed from 4:1 to 1:2, the sulfur content decreases slightly. The impregnation temperature was the most important factor influencing the efficiency of these sorbents. The actual form of sulfur on the sorbents was a critical factor governing the chemical sorption process. Large surface area and large fraction of mesopores in the sorbents also contributed to the enhanced performance.

Liu et al. also studied the effects of flue gas conditions on mercury uptake by sulfur-impregnated activated carbons (SIACs) using a fixed-bed, bench-scale system [36]. Results show that CO₂ (up to 15%) had no impact on mercury uptake by SIACs. The presence of O₂ (up to 9%) increased the adsorption capacity up to 30%. Moisture presence (up to 10%) can decrease the mercury uptake of SIACs by as much as 25% due to competitive adsorption and additional internal mass-transfer resistance. SO₂ (1600 ppm) and NO (500 ppm) showed no impact on mercury uptake in the presence of 10% moisture. Adsorption capacity decreased significantly when system temperature increased from 140 to 400 °C due to the exothermic nature of HgS formation. Increasing gas-sorbent contact time can partially improve the capacity.

Bench-scale studies with sulfur-impregnated carbons indicate large mercury adsorption capacities. More full-scale studies need to be performed to evaluate their performance in a real flue gas environment. The cost estimates of mass production of these sorbents are unavailable.

4.2.3. Chloride-impregnated carbons

Ghorishi et al. studied the chlorine-impregnated carbon using a bench-scale system [37]. NORIT FGD is impregnated by dilute solutions of hydrogen chloride. Treated carbon achieves 80–90% Hg⁰ removal with inlet concentration of 86 ppb and contact time of about 3–4 s. This performance is observed for a wide range, i.e., 1000–5000, of C/Hg ratio. These results indicate significant enhancement of activated carbon performance compared to virgin carbon and suggest potential use in the industry.

Zeng et al. studied ZnCl₂-impregnated activated carbon [38]. Adsorption of Hg⁰ vapor from coal-burning derived flue gas by treated carbon showed that chloride impregnation, particularly with 5 wt% ZnCl₂ solution, significantly enhanced carbon performance. Analyses showed decreased surface area of the impregnated carbon when compared to the virgin carbon due to blockage of micropores by the impregnated chemicals. Tests over a wide range of temperature confirm both physisorption and chemisorption exist.

As was the case with sulfur-impregnated sorbents, full-scale performance and cost estimates are unavailable.

4.3. Calcium-based mercury sorbents

Ghorishi and Sedman studied three types of calcium-based sorbents [39]. The goal of this study was to improve the existing SO₂ control sorbents for a potentially co-benefit mercury removal. The capture of elemental mercury and mercuric chloride by hydrated lime, Advacate, and modified Advacate were studied. (Advacate sorbent is produced by slurring ground fly ash of 4.3- μ m median particle size with Ca(OH)₂ at a weight ratio of 3:1 at 90 °C for 3 h to yield solids with 30 wt% of initial free moisture. Modified Advacate means an additional chemical such as alkaline earth material is added during the preparation process.) Ca-based sorbent performances were compared with that of an activated carbon. Hg⁰ capture of about 40% (about half that of an activated carbon) was achieved by two of the Ca-based sorbents. The presence of sulfur dioxide in the simulated flue gas enhanced Hg⁰ capture from 10 to 40%, indicating the reaction of SO₂ and sorbents creates active sites for the adsorption of Hg⁰, possibly through the formation of Hg–S bonds. Increasing the temperature in the range of 65–100 °C also caused an increase in the Hg⁰ capture by the two Ca-based sorbents. Mercuric chloride capture exhibited a totally different pattern. The presence of SO₂ inhibited the HgCl₂ capture by Ca-based sorbents from about 25% to less than 10%. Increasing the temperature caused a decrease in HgCl₂ capture.

The Southern Research Institute performed studies of calcium-based sorbents using their combustion research facilities [40]. Major findings of their research are summarized here. Ordinary hydrated lime was found to be effective at capturing oxidized mercury on the baghouse; ordinary hydrated lime was also able to capture approximately 33% of the total mercury above 136 °C if the sorbent is dispersed in the flue gas before the baghouse; above 288 °C, no capture of mercury by hydrated lime occurred; simultaneous capture of SO₂ (~50%) from the high temperature flue gas and 80–90% of the mercury on the baghouse (132 °C) was obtained by injecting ordinary hydrated lime right after the overfire air (1150 °C); high temperature (1150 °C) injection of ordinary hydrated lime, known to react with chlorine above 1000 °C to form calcium chloride, did not alter the mercury speciation downstream of sorbent injection. No elemental mercury was captured.

The overall performance of calcium-based sorbents is less effective than activated carbon.

4.4. Petroleum coke

Lee et al. studied the mercury adsorption by pyrolyzed petroleum coke [2]. The pyrolyzed petroleum coke contained 7% sulfur. It is believed that if petroleum is not pyrolyzed, it cannot capture mercury. After pyrolysis, mercury capture can occur with a capacity of 65% that of an activated carbon. Pyrolysis is simple compared to the manufacturing of activated carbon. TPO (temperature programmed oxidation) analysis showed that part of the sulfur in petroleum coke was shifted to the surface from inside during pyrolysis. It is this sulfur that is believed to capture mercury. Mercury removal increased with inlet mercury concentration and remains constant above a certain C/Hg

ratio. Mercury removal increased with decreased particle size and remained constant below 400 mesh.

4.5. Zeolites

Two types of zeolites were treated and their performances were comparable to that of an activated carbon [41]. Mercury capture performance of each sorbent is a function of sorbent/Hg ratio. One of the sorbents displays 100% mercury removal at a sorbent/Hg ratio of 25,000. More studies are needed to understand the general performance of commonly used zeolites.

4.6. Fly ash

Carey et al. performed field tests of mercury removal by sorbents [13]. Subbituminous fly ash with 82% LOI was injected into both lignite and bituminous combustion flue gas at a concentration of about 5–10 g/m³. Fly ash equilibrium mercury adsorption capacities are 10 μ g Hg/g fly ash for bituminous field conditions and 30 μ g/g for lignite field conditions. Senior et al. analyzed the fly ash LOI and mercury content at two sites [42]. At the Gaston site, which burns bituminous coal and was equipped with a COHPAC baghouse, the ash had 10–15% LOI and a mercury concentration of 0.2–2 μ g/g. At the Pleasant Prairie site, which burns subbituminous coal and is equipped with an ESP, the ash had an LOI of 0.5% and <0.5 μ g/g of mercury. Serre and Silcox had to determine whether the unburned carbon that remains in coal fly ash could be used as an inexpensive and effective replacement for activated carbon [43]. The results indicated that a negligible amount of Hg⁰ can be adsorbed by a dilute suspension of fly ash. The best option for controlling mercury emission using fly ash appears to be injection in pulses upstream of a baghouse. Dunham et al. performed bench-scale Hg⁰/HgCl₂ adsorption tests [44]. Hg⁰/HgCl₂ vapor was generated and mixed with flue gas simulating various coal-burned flue gas. For Hg⁰ adsorption tests, the mercury content of the spent ash is 0.2–2.51 μ g/g. For HgCl₂ adsorption tests, the mercury content is 0.37–2.9 μ g/g. Fly ash can catalyze the oxidation of elemental mercury and can adsorb elemental mercury. The oxidation of elemental mercury increases with increasing amount of magnetite in the ash. Surface area and surface nature appear to be important for oxidation and adsorption of elemental mercury.

Bench- and pilot-scale studies have indicated fly ash can also adsorb mercury. In general, fly ash adsorbs substantially less mercury than activated carbon at similar conditions. Even with relatively low capacities, the ash may potentially be able to remove substantial amounts of mercury considering the high concentration of ash in flue gas environments. Studies indicate that flue gas composition, unburned carbon content (LOI), unburned carbon surface area and chemical treatment all affect fly ash's adsorption of mercury.

4.7. Other chemically treated carbons or carbon substitutes

Vidic and Siler studied the mercury sorbents of activated carbon impregnated with chloride and chelating agents [45] using a fixed-bed, bench-scale system that employed

a dry nitrogen carrier gas. Commercially available granular activated carbon (BPL) impregnated with copper chloride (BPL-C), β -aminoanthraquinone (BPL-A), 2-(aminomethyl)pyridine (BPL-P), and 2-aminoethanethiol (BPL-T) were analyzed. The dynamic adsorption capacity of BPL-C increased as empty bed contact time and chloride content increased and decreased with an increase in operating temperature. BPL carbon impregnated with 5 wt% chloride exhibits a higher dynamic adsorption capacity than sulfur-impregnated carbon [35,46]. Observations indicated that the bond between mercury and BPL-C is either unstable or BPL-C lacks the thermal stability required for full-scale use. BPL-A and BPL-T exhibited high dynamic adsorption capacities at 25 °C but had much lower capacities at 140 °C. BPL-P performed very poorly at both temperatures. These chelating-agent-impregnated carbons would not be cost-effective considering the high costs associated with producing them.

Granite et al. studied metal oxides and sulfides as a possible alternative to activated carbon sorbents using a packed-bed reactor system [47]. MnO_2 , Cr_2O_3 and MoS_2 all exhibit moderate capacities for mercury removal. Chemical promotion of these increases elemental mercury removal.

Abu-Daibes and Pinto studied a novel nano-structured sorbent [48]. A chelating adsorbent was developed to remove gaseous mercuric chloride directly from flue gas. The adsorbent was composed of a structured active nano-layer on a mesoporous silica substrate. Chelation was achieved by using a molten salt coating on an immobilized chelating group. Elemental analyses indicated that the theoretical adsorption capacity for mercury is very high—up to 33 mg/g. The adsorbent can be used in the low-temperature flue-gas treatment with a maximum operational temperature of 135 °C. Evaluation of the dynamic adsorption capacity of mercuric chloride showed very efficient uptake and a minimum operating capacity of 12 mg Hg^{2+} /g. The formation of a chelating complex between captured HgCl_2 and cysteine ligands is confirmed.

Lee et al. studied the mercury removal performance of three (Ti-, Si-, and Ca-based) sorbent materials [3]. Titania particles in conjunction with UV irradiation were the most effective for elemental mercury removal (>98%), followed by CaO particles (33%). SiO_2 showed no effectiveness in elemental mercury removal. Presence of SO_2 in the simulated flue gas resulted in a decrease in Hg^0 capture for both TiO_2 and CaO particles due to the competition for active sites by SO_2 gas molecules.

Lee et al. reported a bench-scale study of non-carbon sorbents for removing Hg^0 [49]. Non-carbonaceous materials or mineral oxides were modified with various functional groups and active additives to examine their potential as sorbents for removing Hg^0 from simulated flue gas. The functionalized silica samples with amine, urea, thiol, and amide functionalities are tested under argon flow at 70 °C. Results indicated that the Hg^0 adsorption mechanism is completely different from the adsorption of mercuric ions in the liquid phase where the sorbents are used to remediate aqueous phase. Montmorillonite was evaluated at 70 and 140 °C, and insignificant adsorption was observed. Elemental sulfur-containing sorbents (montmorillonite, molecular sieve, and alumina) showed no significant

Hg^0 uptake capacities at 70 and 140 °C. Sodium-sulfide-doped montmorillonite demonstrated an average adsorption capacity of 283 $\mu\text{g Hg}^0/\text{g}$ at 70 °C while the capacity at 140 °C was negligible. Sodium-polysulfide-doped montmorillonite showed 157 $\mu\text{g Hg}^0/\text{g}$ adsorption capacity while the capacity at 140 °C was much smaller. Montmorillonite and coal fly ash are similar in chemical composition. These two materials are cost-effective at US\$ 0.05/lb for 5 wt% sodium polysulfide synthesis at mass production, and the synthesis is simple. They may provide an additional alternative to mercury control for coal-fired flue gas.

5. Non-injection mercury sorption technologies

The Mercur-RE process developed by ADA uses a regenerable sorbent that allows for recovery and recycling of mercury from the flue gas [50]. The Mercur-RE process is based on the ability of noble metals to repeatedly adsorb large quantities of mercury at flue gas conditions and to desorb the mercury when heated to several hundred degrees above flue gas temperatures. The Mercur-RE process has the following advantages: highly efficient mercury removal with efficiency exceeding 95% regardless of the chemical form of the mercury; substantial reduction in the cost of mercury control compared with alternative approaches; minimal mercury-contaminated solid or liquid wastes; potential removal of mercury from the bio-system; and favorable economics.

The Mercur-RE process involves the following steps: capturing 10 $\mu\text{g}/\text{m}^3$ of Hg for 24 h from 100,000 actual cubic feet per minute (ACFM) of flue gas at 300–400 °F; taking one sorbent module off-line; regenerating the off-line sorbent module for 8 h at 600–700 °F by passing a hot purge gas through the module, thereby creating a highly concentrated mercury stream; capturing the mercury contained in the purge gas; putting the sorbent module back on-line; and shipping the recovered mercury for recycle or disposal.

Regenerable sorbent clearly is the next-generation technology for flue gas mercury control.

6. Stability of mercury adsorption by sorbents

A study performed by Apogee Scientific, Inc., compared low-cost novel sorbents for mercury removal by assessing the effect of sorbent injection on vapor-phase mercury control at three sites: Midwest Generation's Powerton Station (Powerton), We Energies' Valley Power Plant (VAPP), and We Energies' Pleasant Prairie Power Plant (P4) [10]. Most interesting are their results of the by-product (spent sorbent) analysis demonstrating that no mercury was released during the air stability or leaching evaluations. Results of room temperature and 140 °F landfill simulation tests indicated no measurable amounts of mercury loss for any of the by-product samples from Powerton or VAPP. Results from leaching tests indicate that none of the Powerton or VAPP samples were at the threshold of being considered hazardous by the U.S. Federal Maximum Contaminant Level criteria, which for mercury is 0.2 ppm. Most samples were below analytical detection limits for mercury. Desorption testing results indicated sorbent-containing by-product mixtures

would be less susceptible to mercury losses at high ambient temperatures up to 200 °F.

More leachability studies are necessary to have a clear picture of the long-term fate of captured mercury.

7. Conclusions

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 (e.g., flue gas temperature, particulate control equipment); sorbent characteristics; and the presence of other active additives (e.g., pre-combustion coal treatment chemicals, mercury oxidation enhancement additives).

In a post-combustion flue gas environment, vapor-phase mercury is present in oxidized and elemental forms. Oxidized mercury is generally believed to be mercuric chloride (HgCl₂), although other forms of oxidized mercury may be present. There is a positive correlation between the amount of oxidized mercury and the amount of mercury adsorbed by sorbents.

Research has demonstrated that mercury adsorption decreases as the reaction temperature increases or as the bulk mercury concentration in the flue gas decreases. These results indicate that the mercury adsorption mechanism partly involves physical adsorption.

Flue gas chemical composition significantly affects mercury adsorption by sorbents. Higher concentrations of SO₂ or NO_x typically hinder mercury adsorption by activated carbons. Increased HCl concentration enhances mercury adsorption. The presence of NO_x in flue gas decreases the individual effects of SO₂, HCl, and temperature. Results indicate that the mercury adsorption mechanism involves chemical adsorption for carbon-based sorbents. Non-carbon-based sorbents may be affected differently, indicating different mercury adsorption mechanisms.

Although the above factors affect mercury adsorption and removal by sorbents, the most important factors are the sorbent type and associated sorbent properties. Sorbent properties, such as size, shape, surface area, micropore volume, and pore size distribution may affect sorbent adsorption performance. The surface functional groups, such as bromine, chlorine, and sulfur species, can strongly affect mercury adsorption through the chemical adsorption mechanism.

Injecting activated carbon has been proven an effective mercury-control method for power plants not equipped with wet FGD. However, the costs associated with this are high, which suggests alternative low-cost sorbents or lower sorbent processing cost is necessary. The diverse power plant trials indicate that brominated carbon injection upstream of a particulate control device can be a relatively low-cost and effective mercury-emission-reduction strategy.

8. Future work

Studies with sorbents and flue gas interactions are useful in providing a general understanding of mercury reactions. However, the ability of a given sorbent to remove mercury in full-scale

systems cannot be predicted based on laboratory results alone. A more fundamental mechanistic approach is needed to understand why some sorbents are effective while some are not and how to control the effectiveness. This knowledge will have great value in developing control strategies. A comprehensive mathematics model incorporating factors such as flue gas chemistry, mass transfer, physical adsorption, chemical adsorption, and particulate control equipment configurations will be very helpful for predicting the performance of a sorbent for a specific coal-fired site.

Considering its low cost and abundance, fly ash might be an alternative for activated carbon. A better understanding of mercury removal by fly ash is needed, as well as a study promoting fly ash by chemical treatment or separation of unburned carbon from fly ash. This will help reduce the costs associated with mercury control either by better design of boiler operating conditions or injecting fly ash as a sorbent to remove mercury from flue gas.

Research and development of novel sorbents, such as nano-structured sorbents with large mercury adsorption capacity and/or regenerability, are needed to reduce mercury-control cost and recover mercury from coal-burning processes. Processes like Mercur-RE are promising technologies.

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