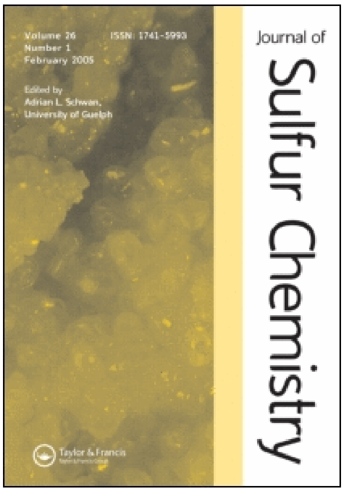

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REVIEW ARTICLE

Understanding the effects of sulfur on mercury capture from coal-fired utility flue gases

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Coal combustion continues to be a major source of energy throughout the world and is the leading contributor to anthropogenic mercury emissions. Effective control of these emissions requires a good understanding of how other flue gas constituents such as sulfur dioxide (SO_2) and sulfur trioxide (SO_3) may interfere in the removal process. Most of the current literature suggests that SO_2 hinders elemental mercury (Hg^0) oxidation by scavenging oxidizing species such as chlorine (Cl_2) and reduces the overall efficiency of mercury capture, while there is evidence to suggest that SO_2 with oxygen (O_2) enhances Hg^0 oxidation by promoting Cl_2 formation below 100 °C. However, studies in which SO_2 was shown to have a positive correlation with Hg^0 oxidation in full-scale utilities indicate that these interactions may be heavily dependent on operating conditions, particularly chlorine content of the coal and temperature. While bench-scale studies explicitly targeting SO_3 are scarce, the general consensus among full-scale coal-fired utilities is that its presence in flue gas has a strong negative correlation with mercury capture efficiency. The exact reason behind this observed correlation is not completely clear, however. While SO_3 is an inevitable product of SO_2 oxidation by O_2, a reaction that hinders Hg^0 oxidation, it readily reacts with water vapor, forms sulfuric acid (H_2SO_4) at the surface of carbon, and physically blocks active sites of carbon. On the other hand, H_2SO_4 on carbon surfaces may increase mercury capacity either through the creation of oxidation sites on the carbon surface or through a direct reaction of mercury with the acid. However, neither of these beneficial impacts is expected to be of practical significance for an activated carbon injection system in a real coal-fired utility flue gas.

Keywords: sulfur dioxide; sulfur trioxide; mercury capture; coal-fired power plant; activated carbon

1. Introduction

1.1. *Motivation*

It is widely known that mercury in the environment can have severe consequences for both wildlife and human health. Metallic mercury, after being converted to methyl mercury by aquatic micro-organisms, is bioconcentrated and accumulates as it moves up the food chain. In the 1950s, this resulted in tragic consequences in Minimata, Japan, where several hundred people died and debilitating birth defects occurred (*1*, *2*). The presence of methyl mercury in aquatic ecosystems

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is also thought to carry potential risks to wildlife, in particular to those species at higher tropic levels such as large fish and piscivorous birds and mammals (*3*).

Estimates of the percentage of atmospheric mercury emissions that originate from anthropogenic sources range from 59% (*4*) to 70% (*5*). The primary source, which has consistently contributed over 60% of anthropogenic mercury emissions worldwide, is stationary fossil fuel combustion, particularly that of coal (*6*, *7*). Numerous studies have demonstrated the ability of anthropogenic mercury to be transported via meteorological patterns over long distances on sub-continental (*8–11*) and inter-continental (*12*, *13*) scales. Findings such as these, coupled with the potential for biomagnification, have led most jurisdictions to place strict regulations and reduction targets on mercury emissions.

In 2005, the US Environmental Protection Agency introduced the Clean Air Mercury Rule (CAMR), a cap-and-trade system which set a limit on mercury emissions from coal-fired power plants across the USA of 38 tons by 2010 and 23 tons by 2018 (*14*). Mercury from US coal combustion was estimated to be 51.3 tons in 2005, so this represents an overall reduction of 55% in 13 years (*15*). Numerous states chose not to participate in CAMR, opting instead to implement more stringent policies that will require up to 95% reductions in the short term (*16*). Similarly, Canada-Wide Standards were introduced in 2006 in which a 60% overall reduction was required by 2010 and 80% by 2018 (*17*). Individual provinces proposed their own mercury emissions caps for coal-fired power generation based on regional factors such as plant configurations, power supply issues, provincial policy commitments, and the range of coals used across the country. Alberta, which is Canada's largest emitter of atmospheric mercury from coal combustion, is expected to achieve at least 50% reduction by the end of 2010 and will require proposals from individual utilities in 2013 to reduce emissions by 80% (*18*). Similar strategies have been implemented in Europe, most notably European Directive 96/61/CE (*19*), although there are still no legal limits on atmospheric emissions of mercury from power plants in certain jurisdictions such as Poland (*20*).

1.2. *Importance of SO_2 and SO_3 for mercury capture in coal-fired utilities*

During the combustion of coal, SO_2 and SO_3 will be formed as products of sulfur oxidation reactions. Depending on the sulfur content of the coal, SO_2 concentrations in the flue gas may exceed 1000 ppm, while SO_3 may be present in amounts ranging from a few to more than 40 ppm. A small percent of SO_2 will be oxidized to SO_3 in the boiler, and more may be oxidized downstream due to the presence of reactive sites on fly ash (*21*). There is also considerable evidence to suggest that sulfur in SO_2 is oxidized to S(VI) on carbon surfaces (*22–24*), which may result in additional gaseous SO_3 when activated carbon is injected for mercury control. In addition, many coal-fired power plants intentionally add SO_3 to condition the flue gas for more effective removal of fly ash using electrostatic precipitators (*25*, *26*).

Among coal-fired utilities, the consensus in recent years has been that SO_3 in flue gas is a serious detriment to the efficacy of mercury removal via activated carbon injection (*25*, *27*). Potential mechanisms for the inhibition of mercury adsorption by both SO_2 and SO_3, including competitive adsorption, scavenging of surface oxygen or halogens, and the formation of H_2SO_4 with concomitant blocking of pores, have been suggested by Granite and coworker (*28, 29*). Yet, an industrial process (Outokumpu Process) was developed in the 1970s for capturing mercury species in non-ferrous smelter flue gases using 80–90% H_2SO_4 at 150–200 °C (*30*). While converting Hg species into $HgSO_4$, this process also captures other metal species present in the flue gas. Although concentrated H_2SO_4 is a known oxidizer at elevated temperatures, these metal species may make the mechanism of mercury capture more complicated. More recently, a patented technique for removing Hg from liquid hydrocarbons was developed based on activated carbon impregnated with H_2SO_4, HCl, or H_3PO_4 (*31*). Previous authors took note of these industrial applications (*28*, *29*), but reasons for the difference between these cases and that of coal-combustion flue gas are still unknown. Furthermore, there have been recent studies indicating that H_2SO_4 has a positive impact on mercury capacity (*32*, *33*). We attempt to resolve this question on the apparent discrepancy for H_2SO_4 promotion or poisoning of activated carbon surfaces later in this paper.

When activated carbon injection is not used, SO_2 and SO_3 may still have significant effects on mercury capture. Many utilities rely on catalytic oxidation of Hg^0 to Hg^{2+}, followed by capture of the oxidized mercury using wet scrubbers. At temperatures exceeding 350 °C, SO_2 is known to hinder Hg^0 oxidation. This may occur through the inhibition of other oxidizing species or through competition for the same catalytic surface sites as Hg^0, whereupon SO_2 is oxidized to SO_3 (*34*).

This report seeks to summarize and clarify the impacts of sulfur species on the capture of mercury from coal combustion flue gases by reviewing the relevant literature. The focus will be on their effects on the two most widely researched methods of mercury removal: (1) Hg^0 oxidation, either in the gas phase or on solid surfaces, followed by Hg^{2+} absorption by wet scrubbers, and (2) Hg^0 removal via adsorption onto activated carbon materials. Other techniques such as adsorption to fly ash and zeolites have been the focus of much research; however, these are not as commonly used in industry.

2. Impacts of SO_2 and SO_3 on mercury oxidation state

2.1. *Homogeneous oxidation of mercury*

From the perspective of simplifying mercury removal, gas-phase interactions which affect the oxidation state of mercury in flue gas are quite important. Being more water-soluble, oxidized mercury compounds can efficiently be removed using existing flue gas desulfurization (FGD) equipment, typically wet scrubbers. For this reason, many researchers have looked at homogeneous reaction mechanisms of mercury in flue gas with the goal of maximizing the proportion of oxidized to elemental mercury. The findings discussed here are summarized in Table 1.

The effect of SO_2 on homogeneous oxidation of Hg^0 has been observed to be negligible at temperatures ranging from 20 to 900 °C (*35*). For this reason, studies tend to focus on the effect of SO_2 on other oxidizing species that may be present in typical coal combustion exhausts. Of these, Cl_2 is generally believed to have the greatest potential for oxidizing Hg^0 to Hg^{2+}. The main source of Cl_2 in flue gas is thought to be through gas-phase reaction of HCl, as per the Deacon reaction:

$$4HCl + O_2 \longrightarrow 2H_2O + 2Cl_2. \tag{1}$$

Xie *et al.* (*36*) tested the impact of SO_2 on the Deacon reaction by flowing 250 ppm HCl and 0–1230 ppm SO_2 through a tube furnace at 800 °C in a background gas of N_2 containing 15% CO_2, 0.2% CO, 5% O_2, and 5% H_2O. The product gases were trapped in a solution of phenol in methylene chloride, which formed chlorinated phenol when contacted with Cl_2. It was observed that the amount of chlorinated phenol decreased as SO_2 concentration increased, suggesting that molecular chlorine is rapidly consumed by the following reaction:

$$SO_2 + Cl_2 + H_2O \longrightarrow SO_3 + 2HCl. \tag{2}$$

The feasibility of this reaction is supported by prior pilot-scale studies that looked into reducing emissions of polychlorinated dioxins and furans from municipal waste incinerators by mixing in sulfur-containing coals (*37*, *38*). Co-combustion of coal produced SO_2, which was found to dramatically reduce dioxin and furan generation.

Sterling *et al.* (*39*) added Cl_2, HCl, and SO_2 to a methane combustion gas to simulate the radical pool of a coal flame exhaust. Adding SO_2 at 100 and 400 ppm in the presence of 100 ppm HCl had negligible effect on oxidation of Hg^0. In contrast, addition of 100 and 400 ppm SO_2 to

Table 1. Summary: effects of SO_2 on homogeneous mercury oxidation in combustion gases.

Reference	°C	Hg (μg/m^3)	Baseline gases[a]	Variable gases	Key findings
Hall *et al.* (*35*)	20–900	100	Propane combustion gas	115 ppm SO_2	No effect on homogeneous oxidation of Hg^0 by SO_2
Xie *et al*. (*36*)	800	–	15% CO_2, 5% O_2, 5% H_2O, 0.2% CO, 250 ppm HCl	0–1250 ppm SO_2	Cl_2 produced by Deacon reaction consumed by SO_2 and H_2O forming HCl and SO_3
Sterling *et al.* (*39*)	350	Unspecified	Methane combustion gas ($\varphi^d = 0.9$, 1,0)	0–300 ppm HCl, 0–500 ppm Cl_2, 0–400 ppm SO_2	Insignificant effect of SO_2 on Hg oxidation with 100 ppm HCl Strong inhibition of oxidation due to SO_2 with 500 ppm Cl_2
Zhao *et al.* (*41*)	750–480	12[b]	Pure N_2, 13 ppm Cl_2	0–2000 ppm SO_2, 0–8% H_2O	Insignificant decrease in Hg oxidation with Cl_2, slight increase in $HgCl_2$ reduction due to SO_2 H_2O with SO_2 reduced Hg oxidation with Cl_2 by 35%, increased $HgCl_2$ reduction by 35% SO_2 and H_2O consume Cl and Cl_2
Agarwal *et al*. (*42*)	538–177	10	13.5% CO_2, 3.5% O_2, 2 ppm Cl_2	0–370 ppm SO_2, 0–13% H_2O	Addition of SO_2 reduced Hg oxidation by 18% Slight increase in inhibition due to addition of H_2O with SO_2
Zhou *et al.* (*40*)	400–800	10.5	13% CO_2, 800 ppm NO	4–7% O_2, 0–1200 ppm SO_2, 0–60 ppm HCl	Without HCl, SO_2 enhanced Hg oxidation With HCl, Hg oxidation was inhibited SO_2 may consume Cl reaction intermediates
Krishnakumar and Helble (*43*)	350	–	Methane combustion gas ($\varphi^d = 0.9$), 150 ppm HCl, 130 ppm NO	0–100 ppm SO_2	SO_2 inhibits Hg oxidation by Cl through scavenging of OH radicals[c]
Ko *et al*. (*45*)	90	45	10% O_2, 3% H_2O, 105 ppm NO, 80 ppm HCl	0–200 ppm SO_2	SO_2 inhibits Cl species by scavenging of OH radicals formed by pulsed corona discharge

Notes: [a]Balanced with N_2, unless otherwise noted. [b]Hg^0 and $HgCl_2$. [c]Simulation results. [d]φ, equivalence ratio.

500 ppm Cl_2 inhibited oxidation by approximately 40% and 50%, respectively. Zhou *et al*. (*40*) obtained similar results in which addition of 1200 ppm SO_2 to a simulated flue gas containing 60 ppm HCl reduced Hg oxidation by roughly 10–30% between 400 °C and 800 °C. When HCl was not present, however, increasing SO_2 from 0 to 400 ppm resulted in an increase in Hg oxidation of a similar magnitude. The authors postulated that this might be the result of SO_2 scavenging Cl reaction intermediates in a manner similar to that shown in reaction (2).

Zhao *et al*. (*41*) investigated the impacts of SO_2, NO, and Cl_2 on Hg^0 oxidation and $HgCl_2$ reduction using a horizontal reactor where the temperature varied from 750 °C to 480 °C from inlet to outlet. It was observed that adding 2000 ppm SO_2 to a baseline concentration of 13 ppm Cl_2 had no significant effect. However, when 8% H_2O was added along with the 2000 ppm SO_2, Hg^0 oxidation dropped from more than 40% to ∼5% across the reactor. Similarly, the same concentrations of SO_2 and H_2O were found to increase $HgCl_2$ reduction from ∼45% to 80% while SO_2 on its own caused a slight decrease. The authors attributed this behavior to SO_2 and H_2O scavenging Cl and Cl_2 according to reactions (2) and (3).

$$Cl + SO_2 + H_2O \longrightarrow HCl + HOSO_2. \tag{3}$$

Results obtained by Agarwal *et al*. (*42*) disagree somewhat. By adding 370 ppm SO_2 to a simulated flue gas containing 3.5% O_2, 13.5% CO_2, 2 ppm Cl_2, and 10 $\mu g/m^3$ elemental mercury, a decrease in mercury oxidation from over 70% to 52% was observed. Furthermore, the addition of 13% H_2O did strengthen the inhibitory effect of SO_2, but only very slightly.

A somewhat different explanation for observed inhibition of mercury oxidation due to SO_2 was supported by Krishnakumar and Helble (*43*) based on the oxidation mechanism proposed by Qiu *et al*. (*44*). The observed results of Sterling *et al*. (*39*) were found to correlate quite well with those found using the Qiu mechanism under the same experimental conditions. A sensitivity analysis was thus performed using this mechanism, and it was suggested that SO_2 inhibits Hg^0 oxidation through scavenging of OH radicals as opposed to Cl species.

$$HCl + OH \longrightarrow Cl + H_2O \tag{4}$$

$$HOSO_2 + O_2 \longrightarrow HO_2 + SO_3 \tag{5}$$

$$HO_2 + OH \longrightarrow H_2O + O_2. \tag{6}$$

The reaction of HCl with OH, which was determined to be the main pathway for producing Cl atoms, is thus blocked by the addition of SO_2. Lower levels of Cl in the flue gas would result in lower levels of Hg^0 oxidation. Evidence in support of this conclusion has been observed by Ko *et al*. (*45*).

No literature could be found describing experiments in which the effect of SO_3 on homogeneous mercury oxidation was studied. It has been speculated, though, that SO_3 may enhance photochemical oxidation of elemental mercury that has been promoted to an excited state by the application of 253 nm ultraviolet light according to reaction (7) (*46*):

$$Hg^0 + h\upsilon \longrightarrow Hg^* + SO_3 \longrightarrow HgO + SO_2. \tag{7}$$

In this reaction, Hg^* is elemental mercury in the $6(^3P_1)$ excited state. The validity of this reaction needs to be confirmed through experiments.

The overall body of work pertaining to the effect of SO_2 on homogeneous mercury oxidation seems to suggest that it indirectly inhibits the conversion of Hg^0 to Hg^{2+}. Although SO_2 on its own appears to have little effect in the gas phase, its interactions with oxidizing species such as Cl_2 reduces their availability to react with mercury. In order to understand the situation in a real coal combustion flue gas, however, it is important to incorporate these findings with those of heterogeneous systems.

2.2. *Heterogeneous oxidation of mercury*

Heterogeneous oxidation is loosely defined as oxidation in the presence of a solid material such as fly ash. Due to the presence of fly ash in coal combustion flue gas, the effects of sulfur species on heterogeneous oxidation of mercury may be different from that in a homogeneous system. The change in mercury speciation will affect its removal in the existing equipment such as FGD, as previously mentioned. Findings extracted from the literature are summarized in Table 2.

Zacharewski *et al.* (*47*) used Fourier transform infrared spectroscopy to investigate the reaction of solid mercuric oxide (HgO) with SO_2 at room temperature. Over a period of weeks, absorption spectra indicating the existence of Hg_2SO_4 and $HgSO_4$ were observed. The following reactions were proposed to explain the findings:

$$\mathrm{HgO(s)} + \mathrm{SO_2(g)} \longrightarrow \mathrm{Hg^0(g)} + \mathrm{SO_3(g)} \tag{8}$$

$$\mathrm{2HgO(s)} + \mathrm{SO_2(g)} \longrightarrow \mathrm{Hg_2SO_4(s)} \tag{9}$$

$$\mathrm{HgO(s)} + \mathrm{SO_3(g)} \longrightarrow \mathrm{HgSO_4(s)}. \tag{10}$$

These reactions suggest a direct participation of SO_2 in the reduction of Hg^{2+} to Hg^0. Although the reaction rate was exceedingly slow, it is conceivable that these reactions may proceed at a more significant rate on the surfaces of solid particles such as fly ash or activated carbon at the elevated temperatures associated with coal-fired utility stack gases. Apparently, the authors did not consider the possibility of Hg^+ forming through reaction between Hg^{2+} and Hg^0; therefore, reaction (9) may be questionable.

Using the Ontario Hydro Method, Laudal *et al.* (*48*) investigated the impact of 1500 ppm SO_2, 50 ppm HCl, and 10 ppm Cl_2 on the oxidation of Hg^0 at 20 μg/m^3. Tests were performed in N_2 containing 15% CO_2, 4% O_2, and 10% H_2O with and without the gas mixture flowing through a bed of coal fly ash. Results indicated that, without fly ash, SO_2 greatly reduced the ability of Cl_2 to oxidize Hg^0, reducing the proportion of oxidized mercury in the outlet from 84.8% to 1.9%. The addition of fly ash, however, increased the oxidized mercury to 28.5%, confirming its involvement in Hg^0 oxidation. Fly ash is rich in silica (SiO_2), lime (CaO), and unburnt carbon, all of which may participate in catalyzing the oxidation of mercury. The alkaline minerals that are present may also help to neutralize acid gases such as SO_2, which reduces oxidized mercury, and SO_3, which may combine with H_2O to form H_2SO_4 on the ash surface and physically hinder further oxidation (*25*, *26*). HCl (without Cl_2) was not observed to have any significant impact on Hg^0 oxidation, with and without fly ash. Although HCl is not an oxidizer for Hg^0, it is believed to be the source of Cl_2 according to the Deacon reaction. Apparently, under the conditions studied, this reaction did not proceed in any substantial way. In a follow-up study under similar conditions but without Cl_2 in the input stream, the effect of NO_x on mercury oxidation was investigated (*49*). While SO_2 on its own with fly ash was not observed to produce any oxidized mercury, its combination with 20 ppm NO_2 was found to increase Hg^{2+} to 24%. A very similar enhancement was observed when both HCl and NO_2 were added, suggesting that the overall impact of NO_2 in mercury oxidation in the presence of fly ash is greater than that of Cl resulting from HCl via the Deacon reaction. NO at 300 ppm was found to reduce oxidation under all gas combinations studied.

After studying the data collected from a 100 MW coal-fired boiler, Kellie *et al.* (*50*) reported a statistically significant positive relationship between SO_2 concentration in the flue gas and the level of oxidized mercury. The observed enhancing effect of SO_2 was justified with the mechanism described by Frandsen *et al.* (*51*):

$$\mathrm{HgCl_2} + \mathrm{SO_2} + \mathrm{O_2} \longleftrightarrow \mathrm{HgSO_4} + \mathrm{Cl_2}. \tag{11}$$

With this reaction, Frandsen *et al.* indicated that $HgSO_4$ is more stable than $HgCl_2$ in an equilibrium system containing the elements C, H, N, O, S, and Cl in addition to Hg, but only at

Table 2. Summary: effects of SO_2 and SO_3 on heterogeneous mercury oxidation in coal combustion gases.

Reference	Surface	°C	Hg, $\mu g/m^3$	Baseline gases[a]	Variable gases	Key findings
Zacharewski *et al.* (*47*)	HgO(s)	25	–	SO_2	–	Hg_2SO_4 and $HgSO_4$ observed after weeks of reaction
Laudal *et al.* (*48*)	Fly ash	175	20	15% CO_2, 4% O_2, 10% H_2O	0–1500 ppm SO_2, 0–50 ppm HCl, 0–10 ppm Cl_2	SO_2 reduced Hg^0 oxidation by Cl_2 from 85% to 2% or 29% with fly ash HCl has a negligible effect on Hg oxidation
Norton *et al.* (*49*)	Fly ash	180	12	12% CO_2, 6% O_2, 10% H_2O, 100 ppm CO	0–1600 ppm SO_2, 0–50 ppm HCl, 0–300 ppm NO, 0–20 ppm NO_2	NO_2 added to SO_2 increased Hg oxidation from 0% to 24% Adding HCl to NO_2+O_2 increased Hg oxidation to 29% NO always detrimental
Kellie *et al.* (*50*)	Fly ash	Unspecified	Unspecified	11.9–16.3% CO_2, 3.7–7.1% O_2, 481–1328 ppm SO_2, 66–359 ppm HCl, 221–384 ppm NO[b]		Both S in coal and SO_2 concentration have positive correlation with Hg oxidation
Cao *et al.* (*52*)	Fly ash	365–155	9–24	11.1–13.7% CO_2, 6.2–7.3% O_2, 569–1165 ppm SO_2, 66–298 ppm HCl, 204–328 ppm NO[b]		Hg oxidation increased by Cl in coal, mitigated by SO_2
Zhuang *et al.* (*57*)	SCR	343	13	12% CO_2, 6% O_2, 8% H_2O, 600 ppm NO, 18.5 ppm NO_2, 550 ppm NH_3	0–2000 ppm SO_2, 0–50 ppm SO_3, 0–50 ppm HCl	SO_2 and SO_3 reduced Hg oxidation by HCl from 71% to 64% and 45%, respectively Effect of SO_3 masked by that of SO_2 when both added with HCl
Yang *et al.* (*53*)	Fly ash	Unspecified	0–1.6	Unspecified[b]	Unspecified[b]	Negative correlation between S in coal and Hg oxidation
Wang *et al.* (*54*)	Fly ash	Unspecified	1–32	Unspecified[b]	Unspecified[b]	Positive correlation between SO_2 concentration and Hg oxidation

Notes: [a]Balanced with N_2, unless otherwise stated. [b]Variable gas composition due to different coals tested at different locations in boiler or different plants.

temperatures below ∼100 °C. This is considerably lower than temperatures normally encountered in coal combustion flue gases. Nonetheless, this reaction suggests that, under certain conditions, SO_2 along with O_2 may liberate Cl_2, which is a known oxidant for Hg^0. In contrast to Kellie *et al.*, Cao *et al.* (*52*) suggested an opposite trend while studying the same 100 MW boiler (Figure 3(b) in (*52*)). However, a closer inspection of the data revealed that the trend was based on a rather weak correlation that was greatly influenced by a single point at the highest SO_2 concentration (∼ 1250 ppm). It should be pointed out that with O_2 the role of SO_2 in Hg^0 oxidation is very different from that without O_2. It is anticipated that the conversion of $HgCl_2$ to $HgSO_4$ according to reaction (11) also depends on the level of O_2.

Yang *et al.* (*53*) analyzed the coal combustion gases from a 220 MW power plant in China using the Ontario Hydro Method and observed a negative correlation between sulfur content of coal (which is typically indicative of SO_2 and SO_3 levels in the stack gas) and Hg oxidation. In contrast, Wang *et al.* (*54*) used the same technique to sample flue gases from five Chinese coal-fired power stations and observed a positive correlation between SO_2 concentration and Hg oxidation. The conflicting evidence seems to underscore the complicated nature of the effect of sulfur on Hg^0 oxidation and the involvement of other active species such as Cl_2 and NO_2. It should also be noted that mercury speciation in coal-fired power plants is not a simple task that is carried out readily or routinely.

Many coal-fired utilities utilize vanadium-based selective catalytic reduction (SCR) devices in order to reduce NO_x emissions. These catalysts have been shown to promote oxidation of Hg^0 to Hg^{2+}, and thus provide an attractive means of reducing mercury emissions when combined with FGD (*34*, *55*, *56*). However, the NH_3 injected as a reducing agent may reduce a portion of the oxidized mercury, and vanadium catalysts also promote oxidation of SO_2 to SO_3 with possible undesired effects (25). Zhuang *et al.* (*57*) studied the impacts of adding HCl at 50 ppm, SO_2 at 2000 ppm, and SO_3 at 50 ppm on the oxidation of 13 $\mu g/m^3$ Hg^0 across an SCR catalyst at 343 °C under 6% O_2, 12% CO_2, 8% H_2O, 600 ppm NO, 18.5 ppm NO_2, and 550 ppm NH_3. Adding SO_2 in addition to HCl was found to reduce oxidation from 71% to 64%. When both SO_2 and SO_3 were added, oxidation dropped only to 63%, suggesting competition between the sulfur species over catalytic sites. Since SO_3 cannot reduce oxidized mercury, its negative impact on Hg^0 oxidation is likely an indirect effect on the catalyst.

Several other catalyst materials have been tested at the bench-scale for their ability to oxidize Hg^0 in flue gas conditions, including gold, palladium, platinum, iridium, and carbon-based catalysts (*58–60*). Although these materials displayed great promise for future industrial application, it was suggested that SO_2 could scavenge oxygen or chlorine from the catalyst surface and that this could have an impact on the rate of mercury oxidation. A similar concern has been raised for titania-based catalysts that may be used in conjuction with photocatalytic oxidation of Hg^0 (*61*).

2.3. *Mercury capture using wet FGD scrubbers*

It is well understood that once oxidized to a readily soluble form such as $HgCl_2$, mercury from coal combustion gases can be efficiently captured using wet FGD scrubbers. However, the presence of SO_2 may yet impact the overall effectiveness of these devices. In order to explain observed increases in Hg^0 across wet FGDs, Chang and Ghorishi (*62*) proposed a model by which absorbed mercury in the form of $HgCl_2$ interacts with sulfite or bisulfite in the scrubbing solution to form Hg–S(IV) complexes. A fraction of these complexes then undergo a series of chain reactions to ultimately produce insoluble Hg^0:

$$HgCl_2 + S(IV) \longrightarrow Hg\text{-}S(IV)complexes \longrightarrow Hg^0. \qquad (12)$$

Evidence to support this model was observed by Díaz-Somoano *et al.* (*19*) using a CaO slurry at 50–60 °C with a background gas consisting of 6% O_2, 7% H_2O, and 50 μg/m^3 Hg (the Hg^0:Hg^{2+} ratio was undetermined). As SO_2 concentration increased from 250 to 2000 ppm, a near-linear decrease in mercury removal from ~60% to 30% was found. This observation is consistent with the well-documented reducing nature of SO_2 or S(IV) in general.

3. Effect of SO_2 and SO_3 on uptake of mercury using activated carbons

3.1. *Chemical interactions of SO_2 and Hg with carbon surfaces*

3.1.1. *Chemisorption of SO_2 and formation of H_2SO_4*

From the perspective of mercury uptake to activated carbons, the interaction of SO_2 with the carbon surface and its potential for forming H_2SO_4 is highly relevant. As mentioned above, H_2SO_4 has found practical use with regards to capture of mercury (*30, 31*). However, H_2SO_4 is widely regarded as a poison to both Hg^0 oxidation and retention via activated carbons.

In studying the enthalpy of adsorption of SO_2 on the surface of a graphitized carbon black, Beebe and Dell (*63*) found that removal of surface oxygen complexes resulted in a sharp decrease in the amount of sulfur dioxide adsorbed at 0 °C. Davini (*64*) came to a similar conclusion, finding that oxygen-containing surface basic groups enhanced SO_2 chemisorption at 25 °C. Other authors have found contradictory results, however, when the carrier gas used contained O_2 and H_2O. Using activated carbon fibers, Daley *et al.* (*65*) found that the presence of oxygen functional groups decreased SO_2 adsorption capacity from a gas mixture containing 5% O_2, 7% H_2O, and 2500 ppm SO_2. Under the same gas conditions, Lizzio and DeBarr (*66*) obtained similar results using Illinois coal char. These results were explained in terms of a decrease in both pore volume and available surface sites for SO_2 adsorption due to the presence of oxygen surface complexes. The authors thus proposed the following adsorption mechanism:

$$\text{SO}_2\text{ adsorption: } SO_2 + C \longrightarrow C\text{-}SO_2 \tag{13}$$

$$\text{SO}_2\text{ oxidation: } C\text{-}SO_2 + O_2 + C \longrightarrow C\text{-}SO_3 + C\text{-}O \tag{14}$$

$$\text{H}_2\text{O adsorption: } C + H_2O \longrightarrow C\text{-}H_2O \tag{15}$$

$$\text{H}_2\text{SO}_4\text{formation: } C\text{-}SO_3 + C\text{-}H_2O \longrightarrow C\text{-}H_2SO_4 + C. \tag{16}$$

This mechanism suggests that adsorbed SO_2 is primarily oxidized by vapor-phase oxygen, as opposed to chemisorbed oxygen as is normally assumed. Corroborating evidence has been found with 5% O_2 and 10% H_2O using activated carbon fibers at 100 °C and 1000 ppm SO_2 (*22*), at 100 °C and 3000 ppm SO_2 (*23*), and at 25 °C with 1000 ppm SO_2 (*24*). These findings indicate that free O_2 plays a more important role than adsorbed oxygen in oxidizing SO_2 to SO_3 on the carbon surface. However, oxygen surface complexes likely play a minor role as suggested by the results of Beebe and Dell (*63*) and Davini (*64*).

Using molecular modeling software, Yang and Yang (*67*) determined that the only viable route in which H_2SO_4 can be formed from SO_2 on an oxygen-free graphite surface is through a H_2SO_3 precursor. This implies that the order of the oxidation and hydration steps in the mechanism shown above is reversed, with H_2SO_3 being the intermediate as opposed to SO_3. In addition, the authors found that surface oxygen sites can enhance SO_2 adsorption, but only when the oxides are not present on neighboring sites (*i.e.* when the surface is only sparsely covered with oxygen functional groups). This supports the previous mentioned results in which a decrease in SO_2 capacity with increased surface oxygen was observed in the presence of O_2 and H_2O (*22–24, 65, 66*).

3.1.2. *Oxidation of Hg on carbon surfaces*

Activated carbons are widely used for the removal of both Hg^0 and Hg^{2+} species from flue gas. The complexity of the carbon surface is thought to enable this relatively indiscriminate adsorptive behavior. Huggins *et al.* (*68*) performed X-ray absorption fine structure analyses on a variety of carbonaceous sorbents that had been exposed to simulated flue gases containing Hg^0 and/or $HgCl_2$ at temperatures below 200 °C. The resulting spectra in each case gave no indication of elemental Hg existing on the surface, suggesting that the adsorption process is dominated by chemisorption. Elemental mercury adsorption, it was reasoned, must involve a step where Hg^0 is oxidized to Hg^{2+} at the surface by anions of Cl, I, S, or O (other possibilities such as Br were not included in the standard spectra).

A model to explain this behavior has been proposed in which the carbon surface has multiple sites which are necessary for effective mercury binding. First, carbenium ion oxidation sites are formed by reaction of HCl with zigzag edge structures. Hg^0 is then oxidized by NO_2 or other oxidizing gases at these oxidation sites (*69*). The oxidized mercury is then bound to similar zigzag structure carbenium ions which act as Lewis basic sites (*70*). XPS evidence was found suggesting that NO_2 actively oxidizes sulfur in SO_2 to SO_3, which, when combined with H_2O to form H_2SO_4, then deactivates the basic binding sites which are necessary for retention of Hg^{2+} (*71*, *72*).

3.2. *Uptake of mercury to virgin activated carbon*

All relevant studies on mercury uptake to virgin activated carbon thus far have focused on SO_2, as shown in Table 3. It was shown by Ghorishi and Gullett (*73*) that SO_2 on its own enhanced an activated carbon's capacity for elemental mercury. Two different commercial activated carbons were tested at 100 °C and 140 °C using 262 $\mu g/m^3$ Hg^0 with and without 1000 ppm SO_2. For one of them, a significant increase in Hg uptake capacity was reported while the other was apparently unaffected by the presence of SO_2. This finding seems to suggest that the effect of SO_2 was not via a homogeneous reaction. The observed difference in SO_2 effect between the two carbons was attributed to different levels of calcium (0.13 wt% versus 1.82 wt%), which the authors proposed may act as a catalyst in the formation of active sulfur sites for mercury capture. This explanation has not been verified by other research, however.

In order to more accurately reflect typical industrial stack conditions, most recent studies have incorporated SO_2, O_2, and H_2O (among other components) in Hg sorption experiments. Using a simulated flue gas composed of 6% O_2, 12% CO_2, 7% H_2O, 50 ppm HCl, and 60–70 $\mu g/m^3$ Hg^0 at 135 °C, Carey *et al.* (*74*) observed a decrease in Hg capacity from 15 to 4 mg Hg/g sorbent with the addition of 100 ppm SO_2. Increasing the SO_2 concentration up to 3000 ppm resulted in a slight decrease to 2 mg Hg/g sorbent. Using the same sorbent material, Eswaran *et al.* (*75*) tested the effect of 369 ppm SO_2 and 163 ppm NO on Hg sorption under 3.6% O_2, 13.5% CO_2, and 10–16 $\mu g/m^3$ Hg^0 at approximately 50 °C and 92 °C. At the lower temperature, SO_2 and NO were found to dramatically decrease mercury capacity from $\sim$200 to 10 mg Hg/g sorbent, in agreement with Carey *et al.* However, this decrease in capacity was not observed at 92 °C. In fact, a 20% increase in initial adsorption rate was found with SO_2 and NO at this temperature, which was thought to be due to increased reactive sites on the carbon surface under these conditions. A similar pronounced increase in Hg adsorption efficiency from 0 to 1000 ppm SO_2 was observed by Yan *et al.* (*76*) using IndoGerman® activated carbon in a simulated flue gas at 90 °C. The authors attributed this improvement to the formation of H_2SO_4 at the surface according to a mechanism similar to that shown in reactions (13)–(16). Granite and Presto (*77*) tested two commercial activated carbons derived from coal under pure N_2 and under N_2 containing 16% CO_2, 5% O_2, 2000 ppm SO_2, 500 ppm

Table 3. Summary: effect of SO_2 on uptake of mercury on virgin activated carbons.

Reference	Sorbent	°C	Hg (μg/m^3)	Baseline gases[a]	Variable gases	Key findings
Ghorishi and Gullett (*73*)	Norit FGD®, PC-100®	100–140	262–237[b]	Pure N_2	0–1000 ppm SO_2	SO_2 enhanced Hg uptake with FGD, but had no effect with PC-100 Ca in FGD may form active S sites with SO_2
Carey *et al*. (*74*)	Norit FGD®	135	60–70, 30–45[c]	12% CO_2, 6% O_2, 7% H_2O, 50 ppm HCl	0–3000 ppm SO_2	Large decrease in Hg^0 and $HgCl_2$ uptake with 100 ppm SO_2 Slight further decrease from 100 to 3000 ppm
Miller *et al*. (*78*)	Norit FGD®	107–163	15	12% CO_2, 6% O_2, 8% H_2O	0–1600 ppm SO_2, 0–50 ppm HCl, 0–300 ppm NO, 0–20 ppm NO_2	Slight enhancement with SO_2 Adding HCl and NO with SO_2 greatly improved Hg uptake NO_2 found to cause rapid oxidation and breakthrough of Hg in all cases
Yan *et al*. (*76*)	IndoGerman®	90	10	12% CO_2, 6% O_2, 40% RH	1000 ppm SO_2	14% improvement in adsorption efficiency with SO_2
Granite and Presto (*77*)	FP-AC, Norit FGD®, Norit Insul®	138, 204	1600[b]	Pure N_2	16% CO_2, 5% O_2, 2000 ppm SO_2, 500 ppm NO	Simulated flue gas increased Hg capacity by factor of 7 for FP-AC and FGD at 138 °C and factor of 3 for Insul at 204 °C
Eswaran *et al*. (*75*)	Norit FGD®	50–92	10–16	13.5% CO_2, 3.6% O_2	0–369 ppm SO_2, 0–163 ppm NO	SO_2 and NO reduce Hg capacity at 50 °C At 92 °C, SO_2 and NO accelerate adsorption
Mibeck *et al*. (*79*)	Lignite-based AC	135	10–15[c]	12% CO_2, 6% O_2	0–8% H_2O, 0–1600 ppm SO_2, 0–50 ppm HCl, 0–400 ppm NO, 0–20 ppm NO_2	SO_2 + NO_2 caused rapid breakthrough, abated by omitting H_2O H_2SO_4 poisons carbon sorbent SO_2 tended to reduce $HgCl_2$ to Hg^0

Notes: [a]Balanced with N_2, unless otherwise noted. [b]Provided in ppb, converted to μg/m^3 assuming ideal gas law at operating temperature. [c]Hg^0, $HgCl_2$.

NO, and 1600 μg/m^3 Hg^0 at 138 °C. In agreement with the findings of Eswaran *et al.* and Yan *et al.*, both sorbents exhibited approximately an 85% reduction in Hg^0 capacity under pure N_2. A similar, yet less dramatic result was noted for a third commercial activated carbon at 204 °C.

Miller *et al.* (*78*) undertook a comprehensive, full-factorial experiment under similar conditions using continuous emission monitoring (CEM) to analyze the individual and combined effects of SO_2, HCl, NO, and NO_2. The CEM used in this study detected only Hg^0. By passing the outlet gases through a reduction cell containing tin(II) chloride prior to quantification, oxidized mercury species were reduced to Hg^0. This allowed for the measurement of total Hg, and, by comparison with Hg^0, oxidized Hg. It was found that the addition of 1600 ppm SO_2 provided a slight enhancement but, nonetheless, resulted in inadequate mercury sorption performance. Addition of 50 ppm HCl and/or 300 ppm NO along with SO_2 provided considerable improvement in mercury uptake kinetics as evidenced by enhanced capture efficiency. On the other hand, adding 20 ppm NO_2 in the presence of SO_2, even with HCl and/or NO, resulted in a rapid breakthrough accompanied by a complete oxidation of the mercury. An explanation for this finding came in a later study in which uptake of $HgCl_2$ and Hg^0 onto a fixed bed of lignite activated carbon was monitored under similar baseline and acid gas conditions at 135 °C (*79*). Combining SO_2 with NO_2 once again resulted in rapid breakthrough and saturation of the activated carbon. However, this was not observed when H_2O was omitted, indicating the formation of H_2SO_4 via NO_2-oxidized SO_2, in good agreement with Laumb *et al.* (*71*) and Olson *et al.* (*72*). Thus, while NO_2 is important for Hg^0 oxidation and retention as per the mechanism described by Olson *et al.* (*69, 70*), the combination of NO_2, SO_2, and H_2O leads to poisoning of the surface by H_2SO_4. Furthermore, adding SO_2 alone and in combination with NO resulted in reduction of the $HgCl_2$ to Hg^0, which could also hinder uptake performance. This effect was counteracted by addition of NO_2 and HCl.

At temperatures typical of coal combustion flue gases, oxidation in the gas phase and on the carbon surface is a critical step in the removal of mercury using activated carbon. However, the formation of H_2SO_4 on a sorbent under oxidizing conditions can hinder mercury uptake by blocking access to pores and by competing for basic sites with oxidized mercury. It is therefore important to address uptake capacity and oxidation kinetics separately when evaluating the performance of a mercury capture system.

3.3. *Uptake of mercury to chemically impregnated activated carbon*

To improve the efficiency of mercury capture, many activated carbons are treated with chemicals such as S, Cl, Br, or I in order to augment the carbon surface with additional reactive sites. It is to be expected that the effect of SO_2 and SO_3 on mercury uptake will be different when the activated carbon is chemically impregnated. Table 4 summarizes the results discussed here. Liu *et al.* (*80*) tested the effects of adding SO_2 with and without the presence of H_2O using Calgon BPL® impregnated with elemental sulfur at 140 °C and 55 μg/m^3 Hg^0. While 1600 ppm SO_2 showed no effect at all, increasing H_2O from 0% to 10% was found to hinder Hg uptake, possibly due to increased mass transfer resistance. The combination of SO_2 with H_2O led to results similar to those of H_2O alone. This was explained by the low SO_2 concentration: if any H_2SO_3 formed on the surface, it would be at a concentration too low to have an effect. Similarly, Yan *et al.* (*76*) found there to be no significant effect of varying SO_2 from 0 to 2000 ppm in a simulated flue gas using Waterlink® S-impregnated carbon at 90 °C. Granite *et al.* (*81*) tested two commercial activated carbons, one impregnated with elemental iodine and potassium iodide and the other impregnated with elemental sulfur. Although these tests were done in pure argon, they can be compared with a later study in which the same sorbents were analyzed under N_2 with 16% CO_2, 5% O_2, 2000 ppm SO_2, and 500 ppm NO (*77*). Under pure Ar at 138 °C, the S-impregnated carbon had an adsorption

Table 4. Summary: effect of SO_2 and SO_3 on uptake of mercury using chemically impregnated activated carbons.

Reference	Sorbent	°C	Hg (μg/m^3)	Baseline gases[a]	Variable gases	Key findings
Liu *et al*. (*80*)	Calgon BPL® w. S	140	55	Pure N_2	0–10% H_2O, 0–1600 ppm SO_2	No significant effect of SO_2
Granite *et al*. (*81*)	I-AC, S-AC	138–178	3480[b]	Pure Ar	–	S-promoted carbon: 3.5 mg/g I-promoted carbon: 4.8 mg/g
Olson *et al*. (*82*)	Calgon F-400®, Centaur®	150	80–86	Pure N_2	0–21% O_2 (air)	Dramatic improvement observed upon H_2SO_4 treatment for both carbons Improvement more pronounced in air
Granite and Presto (*77*)	I-AC, S-AC	138	1600[b]	16% CO_2, 5% O_2, 2000 ppm SO_2, 500 ppm NO	–	Capacity of S-promoted and I-promoted carbon reduced to 1.6 and 0.2 mg/g, respectively, in simulated flue gas
Werner *et al*. (*32*)	Lignite HOK® w. S, H_2SO_4	90–120	1000	Pure N_2	O_2, H_2O, SO_2 (unspecified concentrations)	Hg uptake improved over time due to H_2SO_4 formation from O_2, H_2O, SO_2 Direct H_2SO_4 impregnation gave greatest enhancement
Presto *et al*. (*28*, *29*)	Norit FGD®, Hg-LH®, FGD + H_2SO_4	149	9.3	12.5% CO_2, 5.3% O_2, 50 ppm HCl, 500 ppm NO	0–1.5% H_2O, 0–1870 ppm SO_2, 0–100 ppm SO_3	$SO_2 + H_2O$, SO_3 greatly reduce Hg capture, exacerbated by Br-impregnation Direct H_2SO_4 impregnation effectively eliminates all Hg capacity
Uddin *et al*. (*33*)	Coconut shell AC w. SO_2, H_2SO_4	60–100	32	10% CO_2, 5% O_2, 14.7% H_2O	0–500 ppm SO_2	O_2, H_2O necessary for Hg removal when SO_2 present SO_2- and H_2SO_4-treated samples showed improved uptake, mitigated by SO_2(g)
Sjostrom *et al*. (*26*)	Norit Hg-LH®, Hg-E26®	Unspecified	Unspecified	Coal combustion gas	5.4–39 ppm SO_3	Negative correlation between SO_3 concentration and Hg removal Alkaline-promoted sorbent mitigated negative effect of SO_3

Notes: [a]Balanced with N_2, unless otherwise noted. [b]Provided in ppb, converted to μg/m^3 assuming ideal gas law at operating temperature.

capacity of 3.5 mg/g. This value was seen to decrease to 1.6 mg/g in the presence of other gases. The case of the I-promoted carbon was more extreme in that the capacity decreased from 4.8 to 0.2 mg/g by using the simulated flue gas as opposed to Ar. It should be noted, however, that the pure Ar test for the I-impregnated sample was performed at a temperature 50 °C higher than that of the simulated flue gas.

As mentioned previously, one of the key concerns with SO_2 and SO_3 in flue gas is the possibility of formation of H_2SO_4 on the carbon surface, which is widely held to be a poison for effective mercury removal. However, a number of studies have produced mixed results concerning the effect of H_2SO_4. Olson *et al.* (*82*) added 5% H_2SO_4 to Calgon F-400® and Centaur®, a catalytic carbon containing nitrogenous edge structures, and subsequently dried them at 110 °C. For the catalytic carbon, this treatment was found to increase the 50% breakthrough time from 8 min to 209 and 575 min in pure N_2 and air, respectively. For Calgon F-400® in air, the 50% breakthrough time increased from 1 to 171 min due to the acid treatment. The improvement in the air stream implied a chemisorption mechanism; however, a series of experiments were performed in which Hg adsorption improved slightly with decreased temperature. This might suggest that the overall process is controlled by an interfacial step, rather than mass transfer which often has positive temperature dependence.

Werner *et al.* (*32*) investigated the effect of different gas mixtures containing SO_2, O_2, and H_2O on uptake of Hg^0 vapor (1000 μg/m^3) at 120 °C using a lignite-based activated carbon impregnated with elemental sulfur to 5% by weight. The best performance was seen when all three gases (SO_2, O_2, and H_2O) were present, resulting in what the authors interpreted as the formation of H_2SO_4 over time along with a relative increase in uptake. This contrasts with the lack of any effect observed under similar conditions by Yan *et al.* (*76*) using a Waterlink® S-impregnated carbon; however, different treatment methods and sulfur contents may be the reason for this discrepancy. The same uptake enhancement trend was recorded by Werner *et al.* (*32*) when H_2O was not present, which was attributed to residual H_2O on the carbon surface. With SO_2 alone, however, the performance was the worst among the conditions studied. The effect of H_2SO_4 on Hg^0 adsorption was explicitly shown by soaking the virgin activated carbon in 8% H_2SO_4 for 30 s, filtering, and drying at 105 °C for 4 h. This treated sample showed no sign of breakthrough after ∼16 h of uptake at 90 °C, at which point the elemental sulfur impregnated sample had reached ∼ 8% breakthrough. A similar result was found by Uddin *et al.* (*33*) using a coconut shell derived activated carbon with 5% O_2, 10% CO_2, 14.7% H_2O, 0–500 ppm SO_2, and 32 μg/m^3 Hg^0. It was observed that O_2 and H_2O were necessary for Hg^0 removal in the presence of SO_2. Samples pre-treated with SO_2 or 0.2% H_2SO_4 showed excellent Hg^0 removal capacity; however, this enhancement was reduced in the presence of SO_2. The authors suggest that this may be due to reduction of oxidized mercury species (such as HgO) via reaction with SO_2. More direct evidence of mercury binding to sulfate species was provided by Hutson *et al.* (83) for conventional, Br-impregnated, and Cl-impregnated activated carbon using X-ray absorption spectroscopy. In this study, the sulfate was presumed to originate from the 650 ppm SO_2 in the simulated flue gas used while contacting the samples with Hg^0.

Several studies, on the other hand, have indicated that H_2SO_4 originating from either SO_2 or SO_3 have negative impacts on Hg capture. Using a simulated flue gas containing 5.25% O_2, 12.5% CO_2, 0–1.5% H_2O, 500 ppm NO, 50 ppm HCl, 0–1870 ppm SO_2, 0–100 ppm SO_3, and 9.3 μg/m^3 Hg at 149 °C, Presto and Granite (*28*) tested two commercial activated carbons, one of which was bromine-impregnated. In all cases, SO_3 was found to greatly reduce Hg^0 uptake (nearly 80% at 20 ppm), while the addition of moisture was also found to decrease uptake when SO_2 was present rather than SO_3. The authors attribute these findings to competitive adsorption between Hg^0 and S(VI) species (*i.e.* SO_3, sulfate, or H_2SO_4), which was supported by XPS data indicating a dominance of sulfate over other sulfur functional groups. This inhibition of Hg^0 capture was more pronounced with the brominated carbon, due to the increase in surface reactivity toward both mercury and sulfur oxides. The raw activated carbon was also impregnated directly with 95% H_2SO_4 and dried at 110 °C, after which it exhibited effectively zero capacity for Hg^0. In a companion study using CEM, exposure to SO_3 and H_2SO_4 impregnation were shown to greatly reduce initial mercury removal efficiency in addition to reducing its overall uptake capacity (*29*). Sjostrom *et al.* (*26*) carried out a full-scale study of the impact of SO_3 on Hg adsorption from a 630 MW coal-fired power plant using several varieties of activated carbon. Using Norit Darco Hg-LH®, a commercial brominated carbon, a negative correlation was found between increasing SO_3 concentration and Hg removal, in agreement with Presto and Granite. The negative effect of SO_3 was reduced when using a similar sorbent which had also been treated with alkaline materials to neutralize acid gases.

3.4. *Understanding the effect of H_2SO_4 on mercury uptake*

Several of the studies described above were performed under conditions in which H_2SO_4 could potentially form, and for some, this was hypothesized to be the reason behind observations of mercury uptake inhibition (*28*, *29*, *79*). On the other hand, it has been suggested by several researchers that the formation of H_2SO_4 at the carbon surface was the cause of observed improvements in mercury uptake capacity (*32*, *76*). To make matters more complicated, different studies in which H_2SO_4 was directly impregnated on activated carbon surfaces have given polar opposite results (*28*, *29*, *32*, *33*, *82*).

This apparent contradiction may be explained by understanding the different mercury uptake conditions used in each case. Considering the experiments in which H_2SO_4 was directly impregnated, Presto *et al.* (*28*, *29*) observed the most negative effects. In this study, 200 mg of sorbent were placed in a cylindrical reactor of 22 mm ID. Assuming a bulk density of 0.5 g/cm^3 (typical of activated carbons), this yields a bed height and volume of approximately 1 mm and 0.4 cm^3, respectively. Since the gas flow rate used in that study was 8 l/min, the empty bed residence time (EBRT) is estimated to be only 0.003 s. With such a short residence time, mercury capture is most likely limited by the rate of uptake. Using another H_2SO_4-impregnated activated carbon, Werner *et al.* (*32*) carried out Hg^0 uptake experiments using a sorbent bed made up of three to six layers of activated carbon (each approximately 0.5 g) separated by 2 mm layers of quartz wool. With a reactor ID of 30 mm, flow rate of 540 cm^3/min, and assuming a bulk density of 0.5 g/cm^3, as before, the bed height, bed volume, and EBRT are estimated to be 1.0–2.1 cm, 7.2–14.5 cm^3, and 0.8–1.6 s, respectively. As previously described, excellent mercury capacity was observed under these conditions. It is possible that the much longer gas–solid contact time resulted in a system that was not limited by the rate of uptake, consequently allowing the determination of mercury uptake capacity and its dependence on H_2SO_4 impregnation.

Table 5 lists the bench-scale studies done under conditions where H_2SO_4 could conceivably form (H_2O with SO_2 and an oxidant, O_2 and/or NO_2), as well as those in which H_2SO_4 was added directly. The calculated EBRT for each case is shown, along with an indication of the general observed effect of H_2SO_4 on mercury uptake (regardless of whether or not the acid was in fact formed). The study done by Miller *et al.* (*78*) provided inadequate information regarding bed dimensions, so it was not included. Likewise, Carey *et al.* (*74*) mixed activated carbon with sand in their study, thereby complicating the comparison. For the remaining studies, it can be seen from Table 5 that positive effects of H_2SO_4 or H_2SO_4-forming conditions correlate well with higher values of EBRT while negative effects correlate with the lowest EBRTs. Although the EBRT for the study done by Olson *et al.* (*82*) was relatively low (0.006 s), it must considered that this is a very rough comparison which does not take into account factors such as temperature, particle size, sorbent characteristics, etc. In a full-scale coal-fired power plant where activated carbon injection is used, the gas–solid contact is likely less efficient than that of bench-scale tests using fixed bed

Table 5. EBRT and impregnation concentration as indicators of relative impact of H_2SO_4.[a]

Reference	Gas flow rate (cm^3/min)	Fixed bed volume (cm^3)	EBRT (s)	[H_2SO_4] (vol%)	Overall effect of H_2SO_4
Olson *et al.* (*82*)	3780	200[b]	0.006	5.0	Positive
Yan *et al.* (*76*)[a]	300	2.1	0.42	N/A	Positive
Werner *et al.* (*32*)	540	1.5–3[b]	0.8–1.6	8.0	Positive
Presto *et al.* (*28*, *29*)	8000	0.4[b]	0.003	95.0	Negative
Uddin *et al.* (*33*)	500	0.5	0.06	0.2	Positive
Mibeck *et al.* (*79*)[a]	14100	0.63	0.003	N/A	Negative

Notes: [a]Direct H_2SO_4 impregnation not used. [b]Based on assumed bulk density of 0.5 g/cm^3.

adsorbers. Thus, studies in which the EBRT is very short tend to be more realistic from a practical perspective.

Another factor that may affect the role of H_2SO_4 is its amount on the carbon surface. For the cases where H_2SO_4 was directly impregnated, Table 5 also indicates the concentration of the aqueous H_2SO_4 solution used. It is readily seen that positive effects were observed in the experiments where the concentration of H_2SO_4 was low (0.2–8.0%), while that which used a high concentration (95.0%) found detrimental effects. Large amounts of H_2SO_4 on an activated carbon surface may block access to pores, thus eliminating the vast majority of the surface area on which oxidation and binding of mercury may occur. On the other hand, small amounts of H_2SO_4 which do not affect mass transfer of mercury into the inner pores may actually improve the adsorption capacity by creating oxidation sites (*69, 70*). However, a coal combustion flue gas is at an elevated temperature and contains substantial amounts of moisture, oxidants, SO_2, and SO_3. Thus, it is probable that the amount of H_2SO_4 on the carbon surface would rapidly exceed the small amount at which enhanced adsorption could occur. The accumulating H_2SO_4 would first overwhelm the basic binding sites necessary for retention of oxidized mercury, and eventually obstruct the carbon pores.

Overall, the role of H_2SO_4 in mercury adsorption on activated carbon is not yet fully understood. Carefully designed experiments are needed to quantify to kinetics and capacity of mercury adsorption and to clearly elucidate the capture mechanisms.

4. Summary

Most of the current literature suggests that SO_2 hinders Hg^0 oxidation, with and without other condensed phases such as fly ash, by scavenging oxidizing species such as Cl_2. However, there is evidence to suggest that SO_2 with O_2 enhances Hg^0 oxidation by promoting Cl_2 formation below 100 °C. Any process that inhibits Hg^0 oxidation will likely reduce the efficiency of its capture, since oxidized mercury is much more readily retained on carbon surfaces and in FGD scrubbing solutions. However, studies in which SO_2 was shown to have a positive correlation with Hg^0 oxidation in full-scale utilities indicate that these interactions may be heavily dependent on operating conditions, particularly chlorine content of the coal and temperature.

The general consensus among full-scale coal-fired utilities is that the presence of SO_3 in flue gas has a strong negative correlation with mercury capture efficiency, while bench-scale studies explicitly targeting SO_3 are scarce. What remains unclear is the exact reason behind this observed correlation. SO_3 is the inevitable product of the oxidation of SO_2 by O_2; since SO_2 oxidation is known to inhibit Hg^0 oxidation, the observed correlations may simply be a consequence of this process rather than direct interaction of mercury with SO_3. For the case of activated carbons, this negative effect has been attributed to the formation of H_2SO_4 at the surface which physically hinders mercury uptake. On the other hand, H_2SO_4 on carbon surfaces may increase mercury capacity either through creation of oxidation sites or through a direct reaction of mercury with the acid, or both. Oxidation sites are of great importance due to the fact that they convert Hg^0 to Hg^{2+}, which is then captured at basic surface sites. An examination of operating conditions used reveals that the reaction of mercury with the acid, if it indeed occurs, may be too slow to be of practical significance in capturing mercury by activated carbon injection.

Gaseous sulfur oxides in coal-fired utility flue gases interfere with homogeneous and heterogeneous mercury oxidation reactions, alter physical and chemical characteristics of adsorbents, and affect, directly and indirectly, mercury adsorption in a complex manner. To avoid the conflicting and confusing results that are often seen in the literature, mercury uptake capacity and kinetics need to be analyzed separately when evaluating the performance of a mercury capture system. Other components in flue gases, including Cl_2, NO_2, O_2, and fly ash, may also actively participate and/or influence mercury oxidation and its ultimate capture. Their participation can further complicate the roles of sulfur in mercury removal. There seems a need to map out the pathways involving Hg, S, Cl, O, H, and N with/without activated carbon at various temperatures. Given the ongoing importance of coal combustion in meeting the world's energy demands and increasingly stringent mercury emission regulations, there exists much opportunity for research in this field.

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