Mercury adsorption and oxidation in coal combustion and gasification processes

Jennifer Wilcox [a,*], Erik Rupp [a], Samantha C. Ying [b], Dong-Hee Lim [a], Ana Suarez Negreira [c], Abby Kirchofer [d], Feng Feng [a], Kyoungjin Lee [a]

[a] Department of Energy Resources Engineering, School of Earth Sciences, Stanford University, Green Earth Sciences, 367 Panama Street, Stanford, CA 94305, United States
[b] Department of Environmental Earth System Science, School of Earth Sciences, Stanford University, Green Earth Sciences, 367 Panama Street, Stanford, CA 94305, United States
[c] Department of Chemical Engineering, School of Engineering, Stanford University, 381 North–south Mall, Stanford, CA 94305, United States
[d] Department of Earth, Energy, and Environmental Sciences, School of Earth Sciences, Stanford University, Green Earth Sciences, 367 Panama Street, Stanford, CA 94305, United States

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ABSTRACT

Preventing the release of mercury from coal-fired power plants continues to be a challenge. The design of effective and affordable control strategies depends upon the speciation of mercury from the high temperature region of the boiler to the lower temperature environment of the stack. Both homogeneous and heterogeneous oxidation pathways play a role in determining mercury's speciation over the temperature range of coal-fired flue gas.

This review explores the current state of knowledge associated with the kinetically-limited homogeneous reaction pathways in addition to the complexities associated with heterogeneous oxidation processes. In particular, oxidation pathways associated with selective catalytic reduction and precious metal catalysts are considered. In addition, adsorption mechanisms on various materials are discussed, including fly ash and activated carbon for flue gas applications and precious metals for fuel gas applications.

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Contents

1. Introduction

The major mechanism by which anthropogenic mercury finds its way into the environment is the release from coal-fired power plants. Throughout the coal combustion process, mercury speciates to the

following three forms: elemental mercury (Hg^0), oxidized mercury (Hg^{2+}), and particulate-bound mercury (Hg_p). The speciation of mercury emitted from coal-fired power plants dictates its subsequent lifetime in the atmosphere. For instance, Hg^{2+} is water-soluble and can easily enter a water source, in which anaerobic bacteria convert it into methyl mercury, which is highly toxic and bioaccumulates in organisms through protein binding. Elemental mercury, however, can be transported long distances in the atmosphere where its toxic effects can have global-scale impacts; for example, mercury has been shown to enter the food chain and interfere with ozone depletion in the arctic (Ariya et al., 2004; Pacyna and Keeler, 1995), with inhabitants of this region exhibiting elevated levels of mercury that correlate with birth defects and other ailments, despite minimal local anthropogenic mercury emissions (Hansen, 2000; Mergler et al., 2007; Van Oostdam et al., 2005). The toxicity of mercury is associated with its bioaccumulation in fish, which then enters the food chain, thereby influencing human health. In addition to accumulation in the Arctic, mercury also accumulates in the sediment of large bodies of water, including rivers and lakes, presenting a worldwide issue.

Due to its toxicity, the United States (U.S.) Congress placed mercury and its compounds in the 1990 Clean Air Act Amendments as a hazardous air pollutant. The Clean Air Mercury Rule (CAMR) would have placed additional limits on the mercury emissions associated with coal-fired power plants; however, the U.S. Court of Appeals District of Columbia Circuit vacated CAMR in 2008. In December 2011, final standards have been issued for limiting mercury, acid gases, and other toxic species from coal-fired power plants under the US Environmental Protection Agency's (EPA's) Mercury and Air Toxics Standards (MATS) ruling (United States Environmental Protection Agency, 2011).

Understanding the speciation of mercury throughout the coal-combustion process is crucial to the design of effective mercury removal technologies. Mercury oxidation takes place through combined homogeneous (i.e., strictly in the gas phase) and heterogeneous (i.e., gas–surface interactions) pathways. Both bench-scale combustion experiments (Cauch et al., 2008) and quantum chemistry-based theoretical model efforts (Padak, 2011; Wilcox, 2004) indicate that homogeneous mercury oxidation is responsible for, at most, 10% of the overall oxidation in a typical coal-fired flue gas with chlorine levels at 500 ppmv (e.g., HCl equivalent). This review will focus on the work carried out to date regarding both homogeneous and heterogeneous mercury oxidation pathways throughout a coal-fired flue gas system.

Fig. 1 shows a schematic of a coal-fired power plant. We summarize the current state of knowledge about the speciation of mercury at the various coal combustion stages:

- the *boiler* contains elemental mercury (i.e., Hg^0) and halogen and oxygen radical species that may oxidize Hg^0 to some extent at the boiler exit temperatures,
- within the *economizer*, Hg^0 tends to oxidize to Hg^{2+} (Wilcox, 2009, 2011; Wilcox et al., 2003, 2004),
- the *particulate control device* removes particulate matter such as fly ash and unburned carbon on which Hg_p is bound,
- the *wet flue gas desulfurization chamber* (WFGD) removes Hg^{2+}, and
- the *stack* contains particulate-bound Hg in addition to Hg^0 and Hg^{2+}. These are the forms that most commonly escape into the atmosphere.

The extent to which Hg_p, Hg^{2+}, and Hg^0 are emitted from the stack is dependent upon the existing pollution controls in a given power plant. Throughout the remainder of the review elemental mercury (Hg^0) will be referred to simply as Hg. The effective removal of Hg through existing flue gas control technologies acts as a co-benefit. For instance, electrostatic precipitators (ESP), in particular cold-side ESPs and hot-side ESPs, capture, on average, 27% and 4% of Hg, respectively, while fabric filters (FF) are more effective with approximately 58% Hg removal (Wang et al., 2010). In general, Hg_p or Hg^{2+} are easier to capture using one of these control technologies. Activated carbon injection (ACI) is a direct method used for Hg capture, in which powdered activated carbon (PAC) is injected into the plant's flue gas stream where it adsorbs gaseous Hg and is collected in downstream particulate control devices, such as FFs or ESPs.

Heterogeneous investigations include both adsorption and oxidation mechanisms associated with natural surfaces present in the flue gas such as fly ash, but also include surfaces associated with existing control technologies, such as SCR catalysts. Additionally, we will review and highlight major findings associated with adsorption and oxidation across precious metal catalysts and activated carbon. Precious metal catalysts have been considered for both coal combustion and gasification processes, and as such, findings associated with both applications will be reviewed and discussed.

2. Homogeneous mercury oxidation

Elemental Hg is thermodynamically favored in the high temperature combustion zone of a coal-fired power plant boiler (e.g., 1400 °C), ranging in concentration from 1 to 20 μg/m³ (Senior et al., 2000). Gas-phase
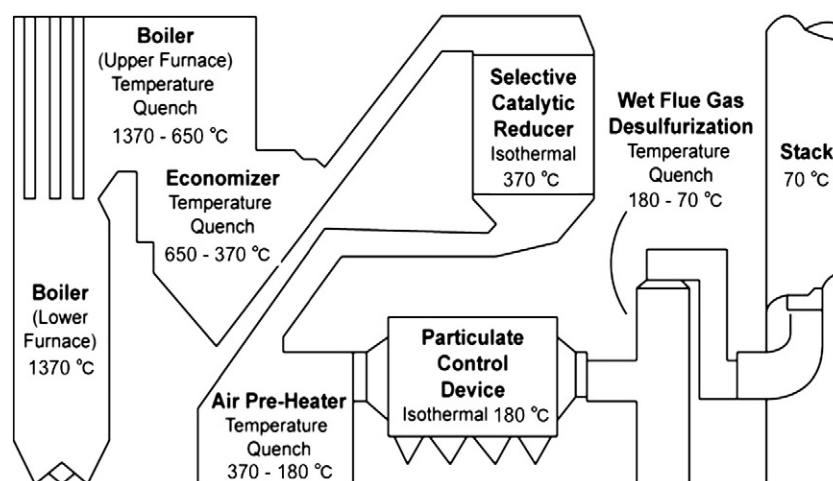

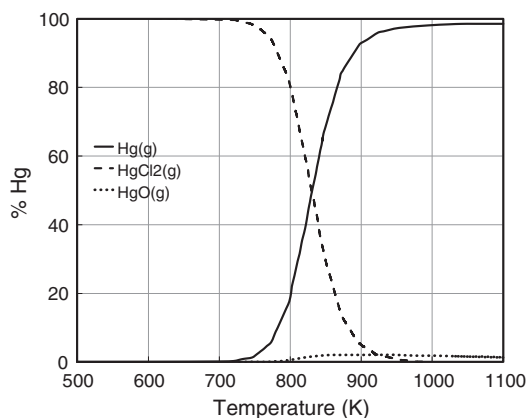**Fig. 1.** Schematic of a coal-fired power plant.

Fig. 2. Equilibrium mercury speciation in flue gas as a function of temperature (Pittsburgh bituminous coal) (Senior et al., 2000).

oxidation occurs primarily via chlorine species originally present in the coal as the gases cool down through the air preheater and air pollution control devices. However, the extent of homogeneous Hg oxidation is highly dependent upon the coal rank, concentration of Cl present in the coal, and the conditions of the utility boiler (e.g., air-to-fuel ratio and temperature). A study consisting of Hg speciation measurements from fourteen different coal combustion systems reported anywhere from 30% Hg^{2+} to 95% Hg^{2+} upstream of the air pollution control devices (Prestbo and Bloom, 1995). A literature survey reveals that Hg oxidation falls primarily in the range of 45–80% (Carpi, 1997; Galbreath and Zygarlicke, 1996; Senior et al., 2000). Although current techniques used in these studies cannot speciate among the oxidized forms of Hg, it is hypothesized to be $HgCl_2$ (Carpi, 1997; Fahlke and Bursik, 1995; Galbreath and Zygarlicke, 1996; Meij, 1994; Senior et al., 2000).

Thermodynamic calculations predict that Hg oxidation occurs at temperatures below approximately 700 °C and that Hg will be completely oxidized at or below 450 °C (Senior et al., 2000). A plot of the equilibrium Hg speciation in a flue gas generated from burning Pittsburgh coal (bituminous rank) as a function of temperature is shown in Fig. 2 (Senior et al., 2000). The formation of $HgCl_2$ between the temperatures of 450 °C and 700 °C is determined by the chlorine content of the coal. For example, Sliger et al. (1998) reported that the 50% equilibrium conversion to $HgCl_2$ takes place at approximately 675 °C in the presence of 500 ppm HCl and at approximately 550 °C in the presence of 50 ppm HCl. Other studies also yield Hg equilibrium conversion to its oxidized form in the range of 527–627 °C (Frandsen et al., 1994).

Regardless of the thermodynamic equilibrium model predictions, experimental evidence has found that not all of the Hg is oxidized in the flue gas, regardless of the chlorine content of the coal. These experimental findings have led the Hg control community to determine that Hg oxidation is kinetically, rather than thermodynamically limited (Senior et al., 2000).

Numerous studies have been carried out to measure the extent of homogeneous Hg oxidation in simulated coal-fired flue gas environments, some of which will be highlighted next. Some of the first studies to include quantum chemistry into the examination of the oxidation kinetics of Hg for flue gas applications are those of Sliger et al. (1998, 2000), in which a homogeneous kinetic model for Hg oxidation via chlorine was determined and coupled with bench-scale combustion experiments. Based on these experiments, it was found that oxidation increases with increasing HCl concentration, which is consistent with the other experiments (Hall et al., 1991; Widmer et al., 1998). Additionally, it was suggested that the direct elementary oxidation pathway of Hg by HCl will not occur due to the high energy barrier of the $Hg + HCl \rightarrow HgCl + H$ reaction, but instead occurs via an intermediate derived from HCl. Since the

oxidation is temperature-dependent, the concentration of the intermediate should be promoted by high temperatures, which is not the case for Cl_2, but could be the case for Cl radicals; therefore, the first oxidation step could take place by the reaction of radical species Hg and Cl yielding the intermediate radical species HgCl, and the subsequent oxidation this intermediate to $HgCl_2$ may occur via several paths including reaction with Cl radical, HCl or Cl_2 species. These results are consistent with those of Wilcox et al. (2003, 2009), in which high-level quantum chemistry calculations predict an activation barrier for the Hg + HCl direct pathway of 82 kcal/mol using the Becke, three-parameter, Lee–Yang–Parr (B3LYP) exchange-correlation functional with the relativistic-inclusive pseudopotential RECP60VDZ level of theory. Additional investigations of Wilcox et al. (2004, 2011) reveal that the second-stage oxidation, i.e., the intermediate HgCl radical oxidation to $HgCl_2$ is likely via a Cl radical, which is barrierless, or via a direct HCl pathway with an activation barrier of approximately 30 kcal/mol using Quadratic Configuration Interaction including single and double excitations with the relativistic-inclusive RECP60VDZ pseudopotential. The radical combination reactions involving HgCl and Cl intermediate species are barrierless, and are likely to be the dominant pathways, provided the conditions are met that support the existence of the chlorine radical chemistry.

Fry et al. (2007) carried out experiments to evaluate the effects of quench rate and quartz surface area on Hg oxidation and performed a detailed kinetic modeling analysis of homogeneous Hg oxidation reactions. In their system, Hg and Cl_2 are injected into a natural gas-fired pre-mixed burner to produce a radical pool representative of real combustion systems and passed through a quenching section following the hot temperature region in the furnace as the quench rate of the flue gas can influence the extent of Hg oxidation. Two different temperature profiles were employed, producing quench rates of −210 K/s and −440 K/s. The Hg concentration in the reactor was 25 μg/m³, while Cl_2 concentrations ranged from 100 to 600 ppmv (equivalent HCl concentration). At Cl_2 concentrations of 200 ppmv, the larger quench rate resulted in a 52% increase in Hg oxidation compared to the lower quench rate. Based on kinetic modeling of the post-flame chlorine species, it was assumed that the Cl_2 molecules are converted to Cl radical species as they pass through the flame and then are subsequently converted predominantly to HCl. When investigating the effect of surface area of the quartz reactor, a threefold increase in surface area resulted in a 19% decrease in Hg oxidation, which is explained by the chlorine radical termination at the surface. It was concluded that quartz surfaces do not catalyze Hg oxidation reactions, but inhibit them, and that these surface interactions are negligible.

Recent experimental results of Cauch et al. (2008) have shown that all previous experimental studies associated with Hg oxidation should be questioned due to the sampling measurement techniques employed. Linak et al. (2001) have shown that Cl_2, in a simulated flue gas in the absence of SO_2, creates a bias in the Ontario Hydro method and over-predicts the concentrations of oxidized Hg. It has been shown that as little as 1 ppmv Cl_2 is enough to create a bias of 10% to 20% in the amount of oxidized Hg captured in the KCl solution. Within this study, the bias was eliminated by adding SO_2 to the flue gas or adding sodium thiosulfate ($Na_2S_2O_3$) to the KCl impinger. Similarly, Ryan and Keeney (2004), in an actual flue gas environment, have demonstrated that 10 ppmv Cl_2 added to the flue gas without SO_2 resulted in 91.5% oxidized Hg, while this value decreased to 39% when the KCl impingers were spiked with sodium thiosulfate. Adding 500 ppmv of SO_2 to the flue gas created the same results as adding sodium thiosulfate. Linak et al. (2001) hypothesized that Cl_2 gas may dissolve in the KCl impinger solution and form hypochlorite ion (OCl^-), which oxidizes Hg to Hg^{2+} in solution. Dissolved SO_2 or thiosulfate ion in solution reduces the hypochlorite ion, thereby eliminating the measurement bias. To further study this effect, Cauch et al.

(2008) injected Cl_2 directly into the KCl impinger at a concentration of less than 10 ppm along with the reactor flue gas. The addition of Cl_2 yielded significant oxidation; however, adding 0.5 wt.% $Na_2S_2O_3$ to the KCl impinger completely removed the oxidation. This gives rise to the conclusion that the decrease in oxidation observed in the previous experiments performed by Fry et al. (2007) in the presence of SO_2 was in fact an inhibition of Hg oxidation in the KCl solution, as SO_2 reacted with the Cl_2 before the hypochlorite ion could be formed; therefore, the high extents of oxidation reported by Fry et al. (2007) are biased by oxidation in the impinger, suggesting further homogeneous oxidation experiments need to be performed with the addition of $Na_2S_2O_3$ to the KCl impinger to quantify actual levels of oxidation in the gas phase.

3. Mercury adsorption

3.1. Mercury adsorption on fly ash

Concentrations of trace metals and their association with fly ash through adsorption are dependent upon coal composition and boiler conditions. A great number of studies have examined the mechanisms involved in Hg adsorption onto unburned carbon in fly ash under varying conditions in an effort to optimize fly ash use for Hg capture to decrease emissions during coal combustion processes (Granite et al., 1998, 2000; Senior and Johnson, 2005; Sjostrom et al., 2006). Conversely, although fly ash is composed mainly of inorganic materials (i.e., up to >98%), adsorption of Hg onto inorganic compounds within fly ash has not been thoroughly explored. Determining the sorption strength of Hg and other trace metals on fly ash may also provide insight into the leachability of the metal under aqueous conditions (Hassett et al., 2005; van der Hoek et al., 1994). Accordingly, the following section reviews the composition of the organic and inorganic phases of fly ash and the adsorption of Hg onto unburned carbon in addition to inorganic phases in fly ash.

3.1.1. Inorganic fly ash

Greater than 420 million tons (MT) of fly ash is produced per year from coal combustion in the world, with 75 MT produced in the U.S.; greater than 44 MT in the E.U.; and over 300 MT in China and India (American Coal Ash Association, 2002; Feuerborn, 2005; Manz, 1997; Mehta, 2004); hence, any applications utilizing fly ash can help decrease its environmental accumulation and impact as a source of inhalable particulate matter. Many studies have shown that trace metals, including Hg, are enriched on fine particles produced during coal combustion (Linak and Wendt, 1994); therefore, exposure to such particles can have multiple adverse effects due to the mixture of trace metals present in inhalable fly ash particles.

In order to reduce the quantity of fly ash stored or placed in landfills, up to one third of fly ash is now reused in cement production and other structural and stabilization applications (American Coal Ash Association, 2002). Materials containing fly ash that come into contact with aqueous phases can undergo solid phase dissolution, leading to the leaching and release of heavy metals originally associated with the fly ash (Hassett et al., 2005; Ram et al., 2006). These findings spawned the establishment of strict guidelines regarding the form and composition of fly ash allowed for market usage. Specifically, two classes of fly ash, Class F[1] and Class C[2] are allowed for use in concrete production, which comprises a large majority of fly ash market use (ASTM C618). Class F ash tends to be non-self-cementitious and contains a higher proportion (i.e., greater than 70%) of SiO_2, Al_2O_3, and Fe_2O_3, along with a lower concentration of calcium compared to Class C fly ash (ASTM C618). The major inorganic phases in fly ash produced from the combustion of subbituminous coal include

aluminosilicate glass (Al_2SiO_5), mullite ($Al_6Si_2O_{13}$), quartz (SiO_2), magnetite (Fe_3O_4), anorthite-albite ($(Ca,Na)(Al,Si)_4O_8$), anhydrite ($CaSO_4$), hematite (Fe_2O_3), and lime (CaO) (Querol et al., 1995). Trace metals can be adsorbed onto the surface of ash particles or be incorporated into the aluminosilicate matrix during combustion (Hansen et al., 1984; Henry and Knapp, 1980), where surface adsorbed metals are more easily mobilized than those incorporated into the crystalline matrix (Ramesh and Kozinski, 2001). The toxicity of fine aluminosilicate cenospheres is attributed to their high surface area and condensation–adsorption processes, which can lead to the enrichment of trace elements in the external layer of the particles by a factor of up to 35 (Querol et al., 1995).

The major mineral phases in fly ash can be separated into three groups based on their magnetic and density characteristics. The non-magnetic fractions are comprised of aluminosilicates and silicates in the 2.4–2.8 g/cm^3 density range, while calcium oxides and sulfates exist as the densest non-magnetic fraction; iron oxides (hematite and magnetite) are concentrated into the >2.8 g/cm^3 comprising the magnetic fractions (Querol et al., 1995). In coal, Hg is associated with iron sulfides as determined by statistical analysis of mineralogical and chemical composition of the density fractions of the coal. An analysis of Franklin coals, from the Puget Group coal of Washington state, found that Hg was associated with both organic complexes and Hg-bearing minerals, including cinnabar, metacinnabar, realgar and orpiment (Brownfield et al., 2005). In a review of 200 papers, Yudovich and Ketris reported that the average "Clarke value"[3] for Hg in coal is 0.10 ppm (±0.01 ppm), independent of coal rank, but on a per ash basis, bituminous coals have a higher Hg content than lower rank coals. The increase in Hg across coal ranks was largely due to an increase in Hg associated with pyrite (Yudovich and Ketris, 2005). Up to 100% of Hg in coal was found to be associated with the sulfide fraction (Querol et al., 1995). While Hg is commonly, though not exclusively, associated with pyrite fractions in coal (Diehl et al., 2004; Feng and Hong, 1999; Hower et al., 2008; Zhang et al., 2002), it is generally associated with the organic phases in fly ash after coal combustion (Hower et al., 2010), where total sorptive area of fly ash is generally determined by the carbon content considering the inorganic mineral portion tends to have lower surface area (<1 m^2/g) (Gao et al., 2002). Iron oxides comprise a significant amount of the inorganic portion of fly ash and are commonly used as an adsorbent for trace metals, including Hg, in flue gas (Wu et al., 2006, 2007, 2008). Dunham et al. (2003) exposed 16 different fly ash samples to simulated flue gas containing Hg or $HgCl_2$ and found that adsorption and oxidation of Hg increased with increasing magnetite content up to approximately 13% as demonstrated in Fig. 3. Additional studies have also found other iron oxide phases in fly ash, such as maghemite, to be correlated with Hg oxidation (Miller et al., 1998; Zygarlicke et al., 2002). Both magnetite and maghemite are categorized as spinel-type iron oxides, which is the structure of iron oxide most commonly found in fly ash, though the two Fe oxide phases are difficult to distinguish using XRD (Dunham et al., 2003).

Although a paucity of information is available regarding the sorption of Hg on inorganic components of fly ash, numerous studies have examined Hg sorption processes on metal oxides at the mineral–water interface (Kim et al., 2004a, 2004b; Lockwood and Chen, 1973; Slowey and Brown, 2007; Tiffreau et al., 1995), including interactions with the Fe- and Al-oxides commonly found in fly ash (Panday et al., 1985; Theis and Wirth, 1977; Zhuang and Biswas, 2001). Kim et al. (2004a) investigated the sorption of aqueous Hg^{2+} on Fe- and Al-(hydr)oxides, demonstrating the strong sorption of Hg^{2+} on goethite (α-FeOOH), forming a bidentate corner-sharing surface complex.

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[1] Class F fly ash produced from the combustion of anthracite or bituminous coal;
[2] Class C fly ash produced from the combustion of subbituminous or lignite coal.

[3] The "Clark value" is a widely-used term in Russian literature and refers to the worldwide chemical element average content in the earth's crust, in sedimentary rocks etc.
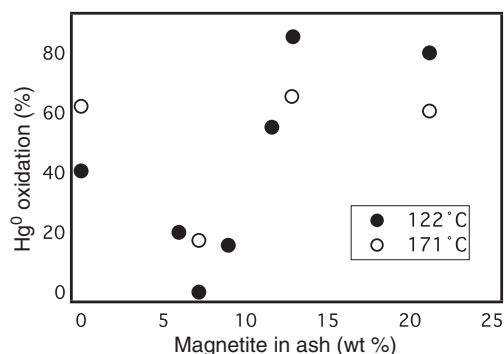
Fig. 3. Effect of magnetite content of bituminous ash samples on oxidation of elemental mercury at 121 and 177 °C (Dunham et al., 2003).

Sorption on bayerite (β-Al(OH)$_3$) forms monodentate, corner-sharing bidentate, and edge-sharing bidentate complexes. Oxidized Hg only weakly sorbed on γ-alumina (γ-Al$_2$O$_3$), demonstrating the impact of oxide structure on Hg sorption strength.

The presence of complexing ligands can increase or decrease sorption of Hg on metal oxides due to competitive ligand sorption on oxide surfaces, formation of stable non-adsorbing Hg-ligand aqueous complexes, and changes in surface charge. The presence of chloride can inhibit Hg^{2+} sorption on goethite by forming stable HgCl$_{2(aq)}$ complexes less prone to adsorbing onto oxide surfaces (Kim et al., 2004b). Conversely, increasing concentrations of sulfate are accompanied by increasing Hg^{2+} surface coverage on both Fe- and Al-(hydr)oxides by adsorbing on the oxide surfaces and decreasing positive surface charge, and thereby, decreasing repulsion of Hg^{2+} ions (Kim et al., 2004b).

3.1.2. Organic fly ash

Organic phases in fly ash, most notably the unburned carbon (UBC) portion, may strongly adsorb and sequester Hg both during coal combustion and during its application as a trace metal sorbent. Unburned carbon content in fly ash can vary dramatically ranging from less than 1% to greater than 35% (Hower et al., 2010; Lu et al., 2007). Most coal combustion units in the U.S. are capable of producing fly ash with less than 1% unburned carbon to maximize energy production; however, the introduction of the 1990 Clean Air Act Amendments required many plants to lower the combustion temperature and oxygen levels to decrease NO$_x$ emissions, where NO formation rate is strongly dependent upon the flame temperature (Bowman, 1992; Pedersen et al., 2009; Song et al., 1982).

The adjustments in plant conditions lead to an increase in unburned carbon content in fly ash, with an average of less than 10% unburned carbon content in fly ash output from well-tuned combustion plants (Hower et al., 2010; Hurt and Gibbons, 1995; Veranth et al., 2000). Although application of fly ash to concrete and asphalt production is an efficient method to decrease the environmental impact of fly ash disposal, the loss-on-ignition (LOI) property of the ash, which can be used to estimate the unburned carbon content, is required to be less than 6% for its use in cement applications. Subsequently, many researchers have developed methods to utilize the high carbon content fly ash ineligible for cement applications as a low-cost alternative to activated carbon for Hg capture. Carbon sorbents can be injected into the flue gas upstream of an ESP or baghouse filter, which then collects the sorbates and ash. Here, we discuss the physical and chemical characteristics of organic phases in fly ash with particular emphasis on unburned carbon, along with mechanisms involved in the adsorption of Hg on various types of fly ash particles.

The content, reactivity, and surface area of carbon in fly ash determine the effectiveness of the ash as a sorbent for Hg and are dependent upon the composition, coal rank, and combustion conditions

(Gao et al., 2002; Hassett and Eylands, 1999; Hower et al., 2010; López-Antón et al., 2009). Multiple forms of unburned carbon are present in fly ash, which can be categorized based on their anisotropic or isotropic texture, fused character, structure and morphology, and material origin (a thorough overview of the effects of unburned carbon morphology on Hg capture is provided by Hower et al. (2010)). The association of Hg with particles is also strongly affected by Hg speciation, which varies during different stages of the combustion process. Mercury that is originally mineral- or organic-bound dissociates during the combustion process and is transformed to gaseous form when entering pollution control devices (Frandsen et al., 1994; Linak and Wendt, 1994). Elemental Hg within the flue gas can subsequently be oxidized through a combination of both homogeneous gas-phase reactions and heterogeneous reactions (discussed in detail within following portions of this review); ultimately, a mixture of Hg species interacts with the carbon surface within air pollution control devices.

Coal rank and carbon content within fly ash have been shown to be correlated (Hower et al., 1999, 2000), with carbon from low-rank coals having the highest Hg capture efficiency: higher-rank coals (i.e., anthracite and bituminous) produce lower carbon-content fly ash with low BET surface area (less than 1 m^2/g); whereas the highest concentration of unburned carbon is usually found in fly ash produced from combustion of lignite, with surface areas up to 400 m^2/g (Gao et al., 2002). For example, it has been shown that Hg concentrations in ash collected from ESPs and baghouses at Kentucky power plants are well-correlated with the carbon content (Hower et al., 2010) (Fig. 4). Mercury capture as a function of fly ash carbon content has also been observed in fly ash obtained from lignite and subbituminous coal burned at Bulgarian power plants (Kostova et al., 2011).

Temperature can greatly affect adsorptive behavior of Hg on unburned carbon by influencing the sintering extent, or aggregation of small particles, and, thereby, affecting their surface area. High-temperature conditions decrease the fly ash carbon surface area as the particles are more likely to sinter (Hurt and Gibbons, 1995), while low-temperature combustion has been found to increase the specific surface area of the unburned carbon (Gao et al., 2002), which can then enhance Hg uptake (Mardon and Hower, 2004; Sakulpitakphon et al., 2000; Serre and Silcox, 2000).

Fly ash surface area can be an indication of the adsorptive capacity for Hg. The greater adsorption capacity of the organic portion of fly ash as compared to the mineral phases is due in part to the greater external surface area of unburned carbon (Hassett and Eylands, 1999). Serre and Silcox (2000) determined the rate and extent of Hg adsorption on multiple fly ash samples and activated carbon using fixed- and fluidized-bed reactors. Nitrogen was used as the
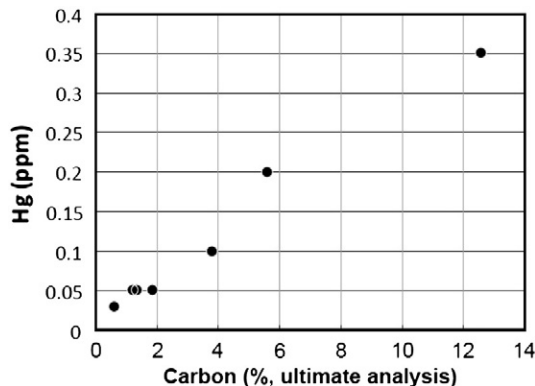

Fig. 4. Fly-ash carbon versus Hg for the first and second rows of electrostatic precipitators and baghouses at Kentucky power plants burning bituminous and subbituminous coals. Points represent sample collections in 2002 and 2007 (Hower et al., 2010).

carrier gas and also to dilute the Hg to the desired concentration, while temperatures were fixed at 121 or 177 °C. Similar to other studies discussed previously in this review, fly ash carbon content was positively correlated with adsorbed Hg concentrations. The adsorption of Hg on fly ash without separating the unburned carbon from inorganic phases, could be described using a Langmuir isotherm, with the adsorption maximum being dependent upon the unburned carbon content and porosity (Serre and Silcox, 2000). However, concentrations of Hg utilized in the experiments were approximately ten times greater than those typically found in coal combustion flue gases and the coal source was not disclosed (Hower et al., 2010). Also, the adsorptive behavior of mixed mineral and organic phases likely differs from adsorption on the individual phases (Hower et al., 2005). The unburned carbon structure is determined by the coal feed and combustion conditions (Hower et al., 2010); therefore, additional information regarding the carbon structure may be needed to confirm the extent of Hg adsorption and the underlying mechanisms responsible for adsorption.

To characterize the factors affecting Hg carbon sorption kinetics, Olson et al. (2000) studied the impact of carbon type, particle size, temperature, and reactive gases on sorption kinetics and capacities of lignite- and bituminous-derived carbon at typical flue gas temperatures and controlled gas composition. Elemental Hg was injected into a flow-through reactor containing carbon sorbent heated within a gas chromatograph oven, and effluent Hg concentrations were measured with a continuous Hg UV analyzer. From these experiments, Olson et al. (2000) were able to determine that at control-device temperatures, chemisorption of oxidized Hg, rather than physisorption as Hg, is the primary Hg sorption mechanism. Additionally, experiments showed that sorption kinetics are inversely proportional to temperature, demonstrating that the initial Hg physisorption step on the sorbent surface is rate-limiting. The use of X-ray absorption fine structure spectroscopy (XAFS) showed that oxygen functional groups serve as both Hg-binding sites and as catalytic sites for Hg oxidation (Huggins et al., 2003). Similarly, high concentrations of chlorine in coal result in greater oxidation and particulate-bound Hg, in which chlorine acts as both an oxidizing and adsorbing site. Low-rank coals can have greater concentrations of Ca, which can also promote Hg oxidation and may subsequently increase adsorption (Gale et al., 2008; Niksa and Fujiwara, 2005a).

3.2. Mercury adsorption on activated carbon

Activated carbon (AC) has been extensively tested in lab-scale and full-scale systems and has shown capacity to capture both elemental and oxidized Hg in coal combustion flue gas. A relatively large amount of activated carbon injection is required for the control of Hg from subbituminous-coal- or lignite-combustion flue gas. Depending on the system conditions, an activated carbon-to-mercury mass ratio of at least 3000–20,000 (C/Hg) can be necessary to achieve 90% Hg removal (Padak and Wilcox, 2009). Currently, the design of more effective Hg capture technology is limited by incomplete understanding of the mechanism(s) of Hg oxidation and adsorption (Hower et al., 2010; Padak and Wilcox, 2009).

The complicated nature of Hg adsorption on activated carbon arises from the multiple mechanisms that play a role in Hg uptake by activated carbon. When considering the removal of Hg from a gas stream using activated carbon, both physisorption and chemisorption must be considered. In general, physisorption has only a small impact on Hg removal, while chemisorption, which involves the heterogeneous oxidation of Hg to Hg^{2+}, is dominant. Furthermore, other species present in the gas stream (including HCl, Cl_2, SO_x, NO_x, H_2O, and O_2) often play a role in the capture, having either competing or beneficial effects on the oxidation that tend to vary with temperature and preparation of the sorbents. It is generally accepted that acidic sites on the surface are responsible for elemental Hg capture on activated

carbon (Mibeck et al., 2009; Olson et al., 2004). In its atomic state, Hg acts as a base in that it has the propensity to oxidize (i.e., donates electrons to a surface or another gas-phase molecule); therefore, Hg will readily interact with acidic sites on the carbon surface. However, once oxidized, and thus acidic in nature, Hg species are thought to compete with acidic gases for the basic sites available on the carbon surface. In general, experimental and theoretical investigations of Hg adsorption on activated carbon sorbents reveal no evidence of Hg adsorbed on the surface, but support chemisorption mechanisms (Huggins et al., 2003; Hutson et al., 2007; Padak and Wilcox, 2009). To gain further insight into the effect of halogen and acid gas presence on the adsorption of Hg on AC, each will be discussed next.

3.2.1. The effect of halogens

The presence of halogens (i.e., bromine, chlorine, and iodine) promotes the oxidation of Hg on carbon surfaces (Ghorishi and Gullett, 1998; Olson et al., 2004). Subsequently, AC demonstrates higher Hg removal performance in the flue gas of coals with greater chlorine content, since the combustion of such coal results in a higher concentration of HCl in the flue gas. Hutson et al. (2007) exposed brominated and chlorinated AC to Hg-laden simulated flue gas and characterized the sorbents using X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS). Within this work no evidence was found for homogeneous oxidation of Hg, and no Hg was on the AC surface; however, oxidized Hg was found on the surface, present as a chlorinated or brominated species. It is important to note that, due to the low coverage of Hg on the carbon, the speciation of Hg was not determined. Given the results, the authors proposed that Hg capture on chlorinated and brominated carbons occurs via surface oxidation of Hg with subsequent adsorption on the carbon surface. Bromine is thought to have a stronger promotional effect on Hg oxidation/adsorption, but the reason for the difference between bromine and chlorine is not well understood. Homogeneous oxidation studies indicate that the higher polarizability of bromine may be responsible for its enhanced ability to oxidize Hg (Wilcox and Okano, 2011). Lee et al. (2006) examined the effects of pyrolyzed pulverized carbon and noted that Hg capture by AC is not linked to surface area, but instead due to chemisorption, which is in line with Hg oxidation on the carbon surface. Recently, the oxidation of Hg was demonstrated on a wood-derived Cl-promoted AC in both N_2 and flue gas (Hu et al., 2010). The adsorption of Hg on AC was shown to be a complete chemisorption process, where all Hg was oxidized to Hg^{2+} on the surface due to chlorine promotion. While chlorine was consumed, Hg^{2+} was still noted as being present in the outlet gas, indicating that the AC was still capable of catalyzing Hg with flue gas components.

3.2.2. The effect of sulfur species

Experimental work has shown that sulfur can have either a positive or negative impact in oxidizing and capturing Hg on AC, depending on the species and presence either on the surface or in the gas phase. Lopez-Anton et al. (2002) investigated sulfur-treated AC versus untreated AC for both combustion flue gas and gasification fuel gas applications. The capture of Hg was more extensive on the sulfur-treated AC in both gas environments, but with only minor differences between the two. The sulfur-treated AC demonstrated an absence of temperature dependence, while the untreated AC proved to be ineffective at Hg capture above 120 °C. Again, it was concluded that the difference in capture capacity was due to differences in sorption mechanisms, with both physisorption and chemisorption taking place on the sulfur-treated AC and only physisorption taking place on the untreated AC. Olson et al. (2005) found that HCl and S^{4+} compete for the basic binding site, suggesting that the decrease in AC performance with increasing sulfur is due to competition between Hg^{2+} and S^{4+} for the basic carbon site. Presto and Granite (2007) indicated that

that Hg capture by activated carbon is independent of SO_2 but the presence of SO_3 can reduce or completely eliminate Hg capture. Further investigation showed that SO_3 significantly impacted Hg capture on activated carbons due to the adsorption of SO_3 and Hg at the same surface sites (Presto et al., 2007). Uddin et al. (2008) noted the complex relationship between Hg capture and SO_2 using both treated and untreated commercial ACs. Mercury capture was more effective at lower temperatures, which is indicative of physisorption. Sulfur dioxide, O_2 and H_2O were shown to be required for capture on unpromoted AC, while AC pretreated with either SO_2 or H_2SO_4 removed Hg in the absence of SO_2. However, the presence of SO_2 and sulfur-treated AC resulted in a suppression of Hg removal. In coal-derived fuel gas, the oxidation of Hg was noted on commercial AC due to the presence of HCl. The presence of H_2S decreased Hg removal even in the presence of HCl, while the Hg species captured on the AC was less stable when H_2S was present. The Hg species stability was similar to that of $HgCl_x$ species, indicating oxidation even in a reductive environment (Uddin et al., 2009). A recent study on two commercial ACs in an inert atmosphere indicated that the presence of SO_2 increases Hg adsorption while HCl and O_2 increase Hg adsorption due to heterogeneous oxidation (Diamantopoulou et al., 2010).

3.2.3. Effect of other acidic gases

Increasingly, experiments involve simulated flue gases to investigate the effects of various combinations of halogens, NO_x, SO_x, and H_2O. The oxidant for Hg oxidation may be provided from the interaction between the carbon surface and acid gas-phase components such as HCl and NO_2. For the subsequent adsorption of oxidized Hg, other acidic gas components, especially SO_2 and H_2O, may also interact with the carbon surface and affect the oxidized Hg adsorption mechanism. For instance, investigations of the effect of acid gases on Hg adsorption support a competition model: SO_2 oxidation (by NO_2) and subsequent hydrolysis (on the carbon surface) lead to the formation of H_2SO_4, which is thought to displace surface-bound Hg^{2+}, resulting in release of $HgCl_2$ (Carey et al., 1998; Laumb et al., 2004; Olson et al., 2005). Granite et al. (2000) discuss a variety of activated carbon sorbents, comparing commercially available activated carbons with sulfur-, iodine-, chlorine- and nitric acid-promoted carbons. The promoted carbons outperformed the unpromoted carbons, due to chemisorption and the oxidation of Hg on the surface, contrasted with simple physisorption on the unpromoted carbon surface. Wang et al. (2009) studied Hg transformation and removal in five coal-fired-boiler flue gases. It was observed that Hg oxidation is promoted by NO_x, SO_2, HCl and Cl_2 and the presence of unburned carbon on fly ash impacted the capture and removal of Hg from the gas stream. This work demonstrated that the laboratory-scale results were consistent with industrial scale applications. Sjostrom et al. (2010) provide an overview of activated carbon injection for Hg control. This study noted industry-wide trends in activated carbon injection for Hg removal:

1. SO_3 and NO_2 hinder removal,
2. fabric filters, in addition to ESPs with activated carbon injection (ACI), are more effective than just ESPs,
3. Hg removal can be increased in low halogen coals using halogen-treated activated carbon,
4. ACI is more effective in lignite coals than bituminous coals, and
5. an increase in sulfur can reduce the Hg control effectiveness.

Huggins et al. (2003) characterized activated carbon samples after testing in Hg-laden simulated flue gas conditions using XAFS. The XAFS results revealed that chlorine and sulfur are adsorbed on the activated carbon surface after exposure to HCl and SO_2, and Hg-anion
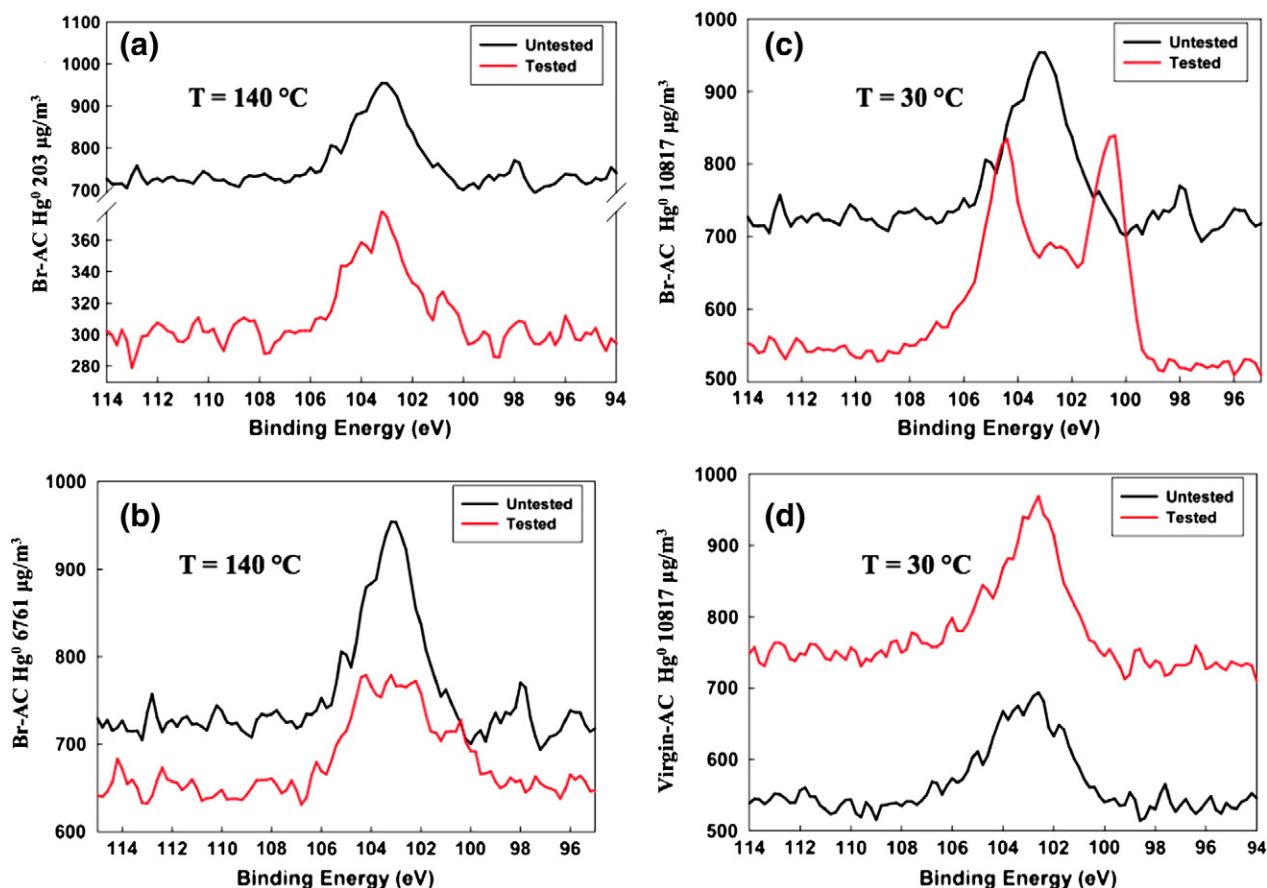

Fig. 5. Hg 4f core level XPS spectra for activated carbon sorbents at various indicated conditions; (a)–(c) brominated AC sorbents and (d) virgin AC sorbent (Wilcox et al., 2011).

chemical bonds are formed in the sorbent materials. They suggest that the acidic flue gas species (e.g., HCl, HNO_3, H_2SO_4) promote the creation of active sites for Hg chemisorption on the carbon surface, and that an oxidation process, either in the gas phase or simultaneously as the Hg atom interacts with the sorbents, is involved in the capture of Hg.

Olson et al. (2004) performed fixed-bed tests with various gas conditions for Hg and $HgCl_2$ adsorption on activated carbon and found that the presence of both HCl and NO_2 reduced the induction period of Hg oxidation, and that in general acid flue gas components significantly impact the adsorption of oxidized Hg species. The formation and presence of the oxidized form, $Hg(NO_3)_2$, were observed in the effluent gas in the presence of NO_2, but in the absence of HCl. Laumb et al. (2004) carried out surface analyses using XPS on activated carbons exposed to Hg-laden simulated flue gas (e.g., SO_2, NO_2, HCl, H_2O), but were unable to determine the oxidative state of surface-bound Hg due to interference with silicon (Si), which is present at comparable levels to Hg within the carbon matrix. Wilcox et al. (2011) investigated the binding mechanism of Hg on brominated activated carbon sorbents with a combination of XPS and theoretical modeling, which will be discussed next. It was found that Hg exists in the oxidized forms on brominated carbon surfaces as shown in Fig. 5.

Ab initio electronic structure investigations based on density functional theory (DFT) have been conducted to elucidate the interaction of Hg with activated carbon, using simplified carbon models to represent activated carbon. There have been a limited number of theoretical investigations, and, to the authors' knowledge, the effect of other acid flue gas species on Hg-activated carbon interactions has not been investigated.

Activated carbon is very difficult to model given its highly inhomogeneous structure. Several initial theoretical investigations were conducted using cluster models to represent graphene, ranging from single benzene rings to multiple fused rings with embedded halogens (Padak and Wilcox, 2009; Padak et al., 2006; Steckel, 2005). Carbon with Cl-containing functional groups exhibits enhanced Hg adsorption capacity (Padak et al., 2006). Furthermore, the most stable Hg surface species was HgCl, while Hg and $HgCl_2$ were found to be thermodynamically unstable on these simplified surfaces of AC (Padak and Wilcox, 2009). Theoretical calculations by Olson et al. (2009) supported the role of acidic sites on the activated carbon in Hg capture. They hypothesized that HCl is energetically stable at the cationic zigzag edge sites of activated carbon and proposed three possible models of Hg oxidation:

1. Hg charge transfer complex forms on the cationic center of HCl on AC and is subsequently attacked by Cl^-,
2. elemental Hg interacts simultaneously with the cationic HCl–AC site and Cl^-, or
3. oxidation by the dication site formed by HCl and NO_2 on activated carbon.

Olson et al. (2009) suggest that Hg has the propensity to be oxidized by donating its electrons to a surface or another gas-phase molecule; therefore, in its elemental state, Hg, acts as a Lewis base with the desire to interact with an acidic site, thereby forming a strong C–Hg covalent bond on the carbon surface.

More recent investigations have used plane-wave DFT to model activated carbon, which allows for the use of periodic systems such as a graphene. Graphene ribbons with exposed edge sites have been used for investigations of the reactivity of carbonaceous surfaces to various gas species (Chen and Yang, 1998; Padak and Wilcox, 2009; Radovic, 2005; Radovic and Bockrath, 2005; Yang and Yang, 2002). Several investigations support the zigzag carbene[4] structure model, where the zigzag edge site acts as a Lewis base and reacts with acid

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[4] Carbene is a molecular structure of carbon with two unshared valence electrons, comprising of a reactive diradical species.

gas components thereby serving as a potential adsorption site for oxidized Hg (Huggins et al., 1999; Radovic and Bockrath, 2005). A recent DFT study (Liu et al., 2011) on the effect of chemical functional groups on Hg adsorption on carbon surfaces supports this suggestion. The study indicates that an embedded halogen atom promotes chemisorption on the neighboring site, which is consistent with experimental results, and indicative of Hg oxidation. Results also indicate a varying effect of organic groups on Hg adsorption, with lactone, carbonyl, and semiquinone groups promoting Hg chemisorption while phenol and carboxyl functional groups promote physisorption and reduce overall Hg capture. A mechanistic study of Hg oxidation due to halides on carbon materials proposes that the interactions of microcrystalline graphitic structures with halide ions result in the withdrawal of electrons from the graphitic structure, producing a strong Lewis acid site (Qu et al., 2010), with Hg adsorption combined with the electron transfer results in Hg oxidation.

To date, little work has been conducted on the effect of Br on Hg-activated carbon interactions. Wilcox et al. (2011) investigated the binding mechanism of Hg on brominated activated carbon sorbents with a combination of experimental work, as discussed previously, and quantum mechanical modeling using a nine-benzene-ring-wide graphene ribbon. Consistent with Padak and Wilcox's (2009) results for Hg adsorption in the presence of chlorine, it was found that HgBr species are more stable on the carbon surface than $HgBr_2$ species. Furthermore, DFT and density of states (DOS) calculations indicated that Hg is more stable when it is bound to the edge C atom interacting with a single Br atom bound atop of Hg. However, while the form of Hg adsorbed on the activated carbon surface is known to be oxidized, the exact speciation of the adsorbed Hg remains in question. Furthermore, the Hg adsorption mechanism on the carbon surface and the effects of the flue gas components are not well understood. Additional work, including closely coupled experimental and theoretical investigations, is required to determine the binding mechanism of Hg on activated carbon sorbents in various flue gas environments and to further elucidate the adsorption mechanism of Hg on activated carbon.

3.3. Mercury adsorption on precious metals

In general, precious metal adsorption of Hg has been applied to Hg capture from fuel gases of coal gasification processes since these metals, in contrast to carbon-based sorbents, can withstand the high temperatures of gasification processes. For gasification applications the exhaust is termed a fuel gas and consists primarily of H_2, CO_2, and CO, while in the case of traditional coal combustion, the exhaust gas is termed a flue gas and is comprised primarily of N_2 and CO_2, and water vapor.

Precious metals, including palladium (Pd), platinum (Pt), gold (Au), iridium (Ir), and rhodium (Rh), have traditionally been used as modifiers for graphite-tube atomic absorption or emission analysis of solid and liquid samples. Among them, Pd has been identified as the best modifier for the adsorption of Hg (Granite et al., 2006). Jain et al. (2010) theoretically screened potential high-temperature metal sorbents for Hg capture in syngas streams. Using DFT predictions, the enthalpy of amalgamation and oxidation for metals was evaluated to predict the capability of Hg sorption and oxidation in the gas stream, demonstrating that Pd has the highest amalgamation enthalpy of all metals. Fig. 6 shows the Hg amalgam formation enthalpy versus the binary oxide formation enthalpy to clarify the tendency of various metals for amalgamation and oxidation. Metals above the O_2 gas chemical potential line (i.e., dashed horizontal line) are estimated to form oxides and metals to the right of the Hg gas chemical potential (i.e., dashed vertical line) are estimated to form amalgams in the syngas stream. Metals satisfying both criteria (i.e., Section (II) in Fig. 6) were found to form oxides rather than amalgams according to the grand canonical potential predictions. An
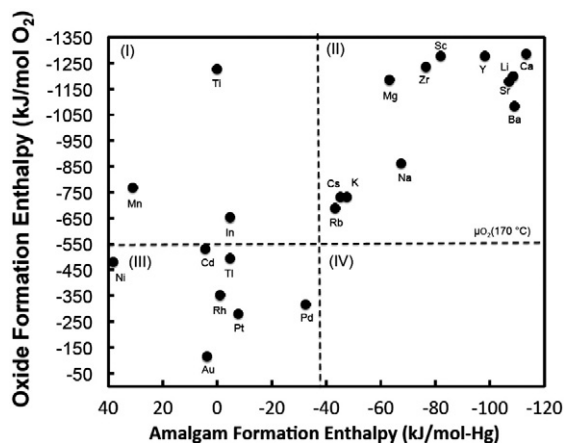
Fig. 6. Estimated amalgam formation enthalpies of binary Hg amalgam versus binary oxide, normalized per mol of Hg and per mol of O_2, respectively. Dashed horizontal and vertical lines represent the O_2 gas and Hg gas chemical potentials, respectively (Jain et al., 2010).

ideal metal, which amalgamates without oxidizing, will be located in Section (IV) of Fig. 6. No metals are available in the most desirable area, but Pd is the closest to the area, indicating that Pd is the most promising metal for Hg capture.

In a study carried out by Steckel (2008), DFT is used to carry out electronic structure calculations on slab models representing the (001) and (111) surfaces of silver (Ag), Au, copper (Cu), nickel (Ni), Pd, and Pt. Relatively strong binding for all of the metals was noted, with binding energies of ~1 eV for Pt and Pd. However, the DFT method used appears to underestimate the adsorption energy when compared directly to experimental results. Mercury has been predicted to have a stronger bond with the (001) surface, where four-fold hollow sites exist, in contrast to the three-fold hollow sites on (111) surfaces. Aboud et al. (2008) performed a density functional theory study of Pd alloyed with small amounts Au, Ag, and Cu and found that doping of the Pd surface increased the overall binding energy of Hg, which is beneficial for a sorption process. Furthermore, the binding energy increased the most when the dopants remained sub-surface. In a continuation of the work, Sasmaz et al. (2009) showed that Pd is primarily responsible for interacting with Hg in both alloys and overlays and that the interaction is a result of overlap between the s- and p-states of Pd and the d-state of Hg.

For example, Baltrus et al. (2008, 2010) showed some evidence of Hg amalgamation on Pd/Al$_2$O$_3$. Maximum Hg adsorption on Pd/Al$_2$O$_3$ occurs at 204 °C and at low loadings of Pd (<8.5 wt.% Pd). An interesting finding is that Hg adsorption is suppressed by an excess of As; however, H$_2$S in fuel gas can improve this imbalance by moderately inhibiting the As adsorption while enhancing the Hg adsorption (Baltrus et al., 2010). Poulston et al. (2007) compared the Hg removal capacities of Pd and Pt sorbents supported on alumina and found that Pd is superior to Pt sorbents for Hg removal. This trend is supported by Fig. 6, which indicates that Pt is located farther from the Section (IV) than Pd. The Hg removal capacity of both Pd and Pt sorbents increases with metal loading but decreases with sorbent temperature. Although most metal sorbent candidates exhibit poor capacities for Hg at temperatures greater than 204 °C, Pd proves to be an attractive sorbent for the Hg removal at elevated temperatures (Granite et al., 2006). Fuel-gas substances that can affect the Hg adsorption on metal sorbents may include moisture, H$_2$S, CO, and H$_2$ (Granite et al., 2006). Baldeck et al. (1974) presented the use of Au for the quantitative fuel-gas separation of Hg in the form of an amalgam of Au$_2$Hg$_3$. It was demonstrated that Hg removal on Au is not affected by corrosive substances such as SO$_2$, H$_2$S, and organic compounds that may be present in flue gas.

Adsorption of Hg on noble (or precious) metals has been explored experimentally since the early 1970s with Anderson et al. (1971) proposing the use of Au as a collector for Hg. High temperature capture of Hg has particular application in coal-derived gasification, where overall plant efficiency can be maintained by keeping the fuel gas at high temperatures. Granite et al. (2000) demonstrated that a 40 wt.% Pt/quartz-wool sorbent was capable of adsorbing Hg from an Ar gas stream, with a demonstrated capacity of 5 mg Hg/g of sorbent at 140 °F. Furthermore, the Pt sorbent maintained adsorption of Hg at a temperature of 410 °C for a period of 70 min.

A number of metals were studied by Granite et al. (2006) In particular, Ir, Pt, Ag, Pd, Rh, titanium (Ti), and ruthenium (Ru) were exposed to Hg in a N$_2$ atmosphere at three temperatures relevant to high-temperature gas cleanup (204 °C, 288 °C, and 371 °C). In general, Hg removal was greatest at 288 °C, with a significant decrease in capture at 371 °C, which is thought to be the result of deamalgamation. Platinum, Pd, Ir and Ru demonstrated the strongest ability to capture Hg in N$_2$. Platinum and Pd continued to show high capacity for Hg over the same range of temperatures in a simulated fuel gas (H$_2$, CO, CO$_2$, H$_2$O, and N$_2$), with Pd chosen for further study due to its proven high-temperature capture of Hg. Palladium supported on alumina (1 wt.% and 5 wt.%) was tested at 204 °C and 288 °C, with an increased mean loading capacity on 5 wt.% Pd/alumina and no discernible differences due to temperature.

This Hg adsorption on precious metals work was continued by Poulston et al. (2007), where it was observed that Hg removal increased with Pt loading and had no apparent dependence on metal dispersion. X-ray diffraction (XRD) was used to show that a Pd–Hg solid solution (amalgam form) at the lower temperatures, with a more crystalline structure appearing as a result of higher temperatures. Baltrus et al. (2008), based on the work by Poulston et al. (2007), concluded that metal dispersion does have an impact on Hg capacity once the metal loading reaches higher than 5 wt.%, suggesting an optimal loading of 8.5 wt.% Pd. Sulfur was also shown to have a positive impact on Hg adsorption, interacting with Hg in the Pd solution. Poulston et al. (2010) further looked into the dependence of the support on adsorption of Hg by Pd using XRD and EXAFS, demonstrating that 5 wt.% Pd/Al$_2$O$_3$ and 5 wt.% Pd/SiO$_2$ have significantly different Hg capacities (11.2 at.% and 16.2 at.%, respectively). Mercury and Pd formed a single homogeneous phase on Al$_2$O$_3$, which is consistent with previous results (Baltrus et al., 2008; Poulston et al., 2007), while on SiO$_2$, both Pd and Hg formed multiple alloys of varying composition. The difference was attributed, in part, to the wider dispersion of Pd on Al$_2$O$_3$, which results in smaller Pd particles dispersed across the support. Mercury is capable of fully diffusing in and alloying with small Pd particles, where larger particles may continue to have pure Pd cores. Baltrus et al. (2011) continued to investigate Pd dispersion by altering the Al$_2$O$_3$ support in order to increase or decrease Pd dispersion. Using a combination of breakthrough experiments and analytical techniques (e.g., XPS, XRD, scanning electron microscopy (SEM), hydrogen chemisorption, and pore volume measurements), they concluded that increased Pd dispersion decreased Hg capture while increasing resistance to catalyst poisoning by sulfur.

Palladium nanoparticles supported on a range of carbon substrates (e.g., carbon nanotubes, expanded graphite, carbonized chicken litter, and AC from chicken litter and coal combustion ash) at 2, 10, and 20 wt.% Pd theoretical loading showed 90% removal efficiency in laboratory air, but only 60% in real flue gas, which is comparable to benchmark Darco Hg-LH, a brominated PAC (Lineberry et al., 2009). In general, an increase in Hg capture over unmodified carbon substrates was noted. Other supported metals studied include Au-impregnated commercial AC (Rodriguez-Perez et al., 2011), which exhibits increased Hg capture in N$_2$/O$_2$ atmospheres over similar unamended AC, and a carbon nanotube–Ag composite (Luo et al., 2010), which completely captured Hg at 150 °C and released it at 330 °C, restoring the original Hg adsorption capacity. The Ag–CNT composite showed a higher capacity for Hg than Ag- or Au-coated quartz

beads, and minimal memory effect and was negligibly impacted by SO_2, NO_x, CO_2, and O_2, indicating potential use in combustion flue gas.

3.4. Mercury adsorption on other materials

While fly ash, AC, and precious metals have been the primary research focus for Hg adsorption, researchers have used the information derived from this work to suggest other low-cost materials as alternatives. Many of these studies have looked at using the metal oxide components of fly ash, rather than the fly ash itself. The use of metal oxides for Hg removal in syngas was reported by Portzer et al. (2004). Numerous metal oxides (e.g., cuprous sulfide or oxide powder, cupric sulfide or oxide powder, cupric oxide on alumina, etc.) were exposed to 50-ppm Hg concentrations for 30 min at 300 °C in a dry nitrogen atmosphere, with capture percentages ranging from 5 to 37%. Cupric oxide on alumina and a mixed metal oxide (metals not provided) on alumina produced the highest capture percentages. In the same study, six proprietary oxides were tested, showing much higher (60–100%) Hg capture in the same conditions.

Wu et al. (2006, 2008) studied the use of iron oxides to remove Hg from synthetic fuel gases (Ozaki et al., 2008; Wu et al., 2006, 2008). Initially, two oxides, Fe_2O_3 and 1 wt.% Fe_2O_3 on TiO_2, were tested in the temperature range of 60 to 100 °C. After initially higher rates, 5 ppb Hg was removed from the fuel gas at a constant rate of about 60% for both sorbents. The presence of H_2S promoted the removal of Hg, while H_2O slowed Hg removal caused by H_2S (Wu et al., 2006). Wu et al. (2008) expanded upon the sorbents investigated (FeS_2 and Fe_2O_3–$Ca(OH)_2$) and added 1 ppm HCl to the synthetic fuel gas. It was found that HCl inhibited the removal of Hg on Fe_2O_3, possibly due to a non-regenerable deactivation process. The presence of calcium hydroxide appeared to prevent HCl inhibition, but was not proposed as a solution to the deactivation problem. An attempt was made to identify the adsorbed species using temperature programmed decomposition desorption (Ozaki et al., 2008). Though the adsorbed species were not identified, it was observed that Hg is completely removed from the iron oxide by 400 °C, with maximum adsorption capacity occurring around 200 °C.

Lee et al. (2009d) proposed the use of a paper-derived, mineral-based sorbent, referred to as MinPlus. The primary components of MinPlus are limestone, lime and meta-kaolinite. The sorbent was tested in the range of 600 to 1100 °C, showing increased capture of Hg with increasing temperatures due to two different mechanisms: an in-flight sorption and sorption on the wall-deposited sorbent. Chemisorption was postulated as the primary removal mechanism, due to the formation of gehlenite, which was not present in the sorbent prior to deactivation. The Hg capture experiments were performed in an atmosphere with more resemblance to a combustion environment (i.e., CO_2, CH_4, N_2, other mixture gases, exact values not given) and at a temperature which suggests possible use as an injected sorbent immediately downstream of the boiler.

4. Heterogeneous mercury oxidation

4.1. Mercury oxidation across SCR catalysts

Many coal-based power plants installed SCR units to satisfy NO_x emission regulations. Selective catalytic reduction technology reduces NO_x emissions by catalytically reducing NO_x to N_2 and H_2O by injecting NH_3 as a reducing agent. A co-benefit of SCR implementation is that it is also effective at oxidizing Hg to Hg^{2+} (Afonso and Senior, 2001; Gutberlet et al., 2000; Kilgroe and Senior, 2003). Mercury oxidation is beneficial because Hg^{2+} has a higher solubility in water than its elemental form, allowing easier removal in downstream flue gas desulfurization units (FGD) (Carey et al., 1996; Niksa and Fujiwara, 2005b).

Commercial SCR catalysts employ the anatase phase of TiO_2 as a support material for the active catalyst (Alemany et al., 1995; Lietti

et al., 1996), which consists of less than 2 wt.% V_2O_5 and 10 wt.% WO_3. The content of V_2O_5 is limited to less than 2 wt.% not only to avoid the formation of SO_3, but also because high loadings of vanadia oxide reduced the temperature at which the TiO_2 anatase-to-rutile phase transformation occurs (Saleh et al., 1986). This phase transformation leads to a decrease in the catalyst surface area and a subsequent reduction in catalytic activity. The addition of tungsten oxide, WO_3, has been shown to stabilize the anatase, preserving surface characteristics (Alemany et al., 1995; Djerad et al., 2004), and increasing the number of Brønsted acid sites that play an important role in NO_x reduction as the increase in surface acid sites enhances the interaction with NH_3 with the surface (Alemany et al., 1995; Chen and Yang, 1992). The influence of the addition of tungsten to Hg oxidation is not yet well understood.

The detailed mechanism for Hg oxidation across the SCR catalyst is still unknown, although V_2O_5 is known to be the active component. Studies carried out by Senior and Linjewile (2004) suggest that the reaction follows an Eley–Rideal mechanism, in which Hg adsorbs to the surface of V_2O_5 and is later oxidized by HCl present in the gas phase. However, Niksa and Fujiwara (2005b) suggest that the oxidation of Hg to Hg^{2+} takes place through a Langmuir–Hinshelwood mechanism where gas-phase Hg reacts with HCl that has previously been adsorbed onto the V_2O_5 catalyst. The Langmuir–Hinshelwood mechanism for Hg oxidation through the interaction of adsorbed HCl and Hg is described in Fig. 7.

The degree of Hg oxidation across the SCR unit varies with factors such as coal rank, halogen and flue gas species concentrations (i.e., HCl, NH_3, SO_2, and SO_3), temperature, and age and composition of the catalyst formulation. In this review, the effect of each of these factors on Hg oxidation is discussed.

The effectiveness of SCR catalysts on Hg oxidation is highly dependent upon coal composition. The rank of the coal determines the content of carbon as well as the concentration of HCl, sulfur, and inorganic metal oxides, such as CaO or MgO (Cao et al., 2007). Low-rank coal, such as subbituminous or lignite, has a lower concentration of Cl and higher concentrations of Hg and CaO, which lead to higher concentrations of Hg in the flue gas (Eswaran and Stenger, 2008; Srivastava et al., 2006). In a pilot-scale study carried out by Gutberlet et al. (2000), three bituminous coals and one subbituminous Powder River Basin (PRB) coal were combusted, revealing that the high-sulfur bituminous coal has a significant increase in Hg^{2+} at the exit of the SCR unit, while the PRB coal with low-sulfur and low-chlorine content did not affect Hg speciation. Another reason bituminous coals can
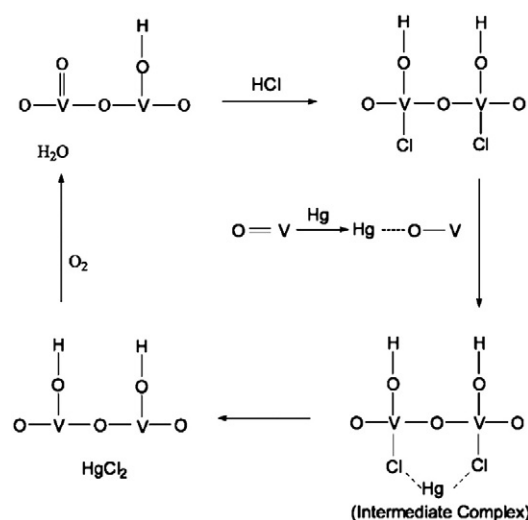

Fig. 7. Description of the Hg oxidation based upon the Langmuir–Hinshelwood mechanism (He et al., 2009).

increase Hg capture is the higher content of unburned carbon, which can adsorb and oxidized Hg (Srivastava et al., 2006).

The major oxidized Hg species in a flue gas environment is $HgCl_2$, which makes it important to study the effect of chlorine in the Hg oxidation. Although homogeneous oxidation due to the interaction of Hg and Cl_2 takes place relatively fast at room temperature (Sliger et al., 2000), the extent of Hg oxidation observed in SCR units cannot be explained by the kinetics of the reaction and Cl_2 concentrations (Niksa and Fujiwara, 2005b; Presto and Granite, 2006). For this reason, numerous studies have examined the heterogeneous reaction between Hg, HCl, and the SCR surface. From these studies, bench-scale SCR reactors show no significant Hg oxidation in the absence of HCl (Lee et al., 2003; Zhuang et al., 2007). Straube et al. (2008) studied the effect of HCl, SO_2, NO, and NH_3 on Hg and $HgCl_2$ adsorption and oxidation on a commercial SCR-DeNOx catalyst (2.5 wt.% V_2O_5) and results of adsorption analysis show that $HgCl_2$ and Hg adsorb on the surface of the SCR in the absence of HCl and that both adsorption processes decrease with temperature. In contrast, Hg is oxidized with a negative temperature dependence in the presence of HCl, suggesting that the critical step during Hg oxidation involves an adsorption process. Zhuang et al. (2007) also observed that 87.2% of Hg adsorbs on the surface of fresh SCR catalyst in the absence of acid gases (HCl, SO_2, and SO_3). Smaller adsorption levels were obtained by Lee et al. (2003), who observed that 50 to 58% of Hg is adsorbed when 500 ppm of SO_2 is present in flue gas. Eom et al. (2008) and He et al. (2009) confirmed negligible Hg oxidation activity on the SCR catalyst when HCl is not present in a bench-scale system. The effect of HCl on the Hg oxidation across the SCR unit studied by He et al. (2009) can be seen in Fig. 8. He et al. (2009) concluded that HCl has a higher affinity for the active sites in the V_2O_5 catalyst than Hg, due to Hg desorption upon the injection of HCl into the reactor. Eom et al. (2008) suggested that Hg and HCl compete for the same V_2O_5 adsorption sites, supporting the Langmuir–Hinshelwood mechanism. The study of a pilot-scale SCR slipstream by Cao et al. (2007) indicated that HCl enhances Hg oxidation, but this effect is not seen when Cl_2 is injected. The larger concentration of SO_2, NO, or H_2O may inhibit Hg oxidation by Cl_2.

Fluorine, bromine, and iodine are also present in coal, but in lower concentrations than chlorine (Vassilev et al., 2000; Wang et al., 2005). The effect of those gas species on Hg oxidation and the nature of the reaction have been analyzed in several studies. Cao et al. (2007) tested Hg oxidation with 0 to 300 ppm HCl, 0 to 9 ppm HBr, 0 to 20 ppm HF, and 0 to 15 ppm HI, in the presence and absence of an SCR slipstream reactor. They found that small concentrations of HBr and HI (i.e., <5 ppm) led to a higher degree of Hg oxidation (i.e., >60% Hg oxidation) than in the case of HCl (i.e., 300 ppm for 40% Hg oxidation). This seems to be a homogeneous oxidation since it did not depend on the availability of sites on the SCR catalyst. The increased eff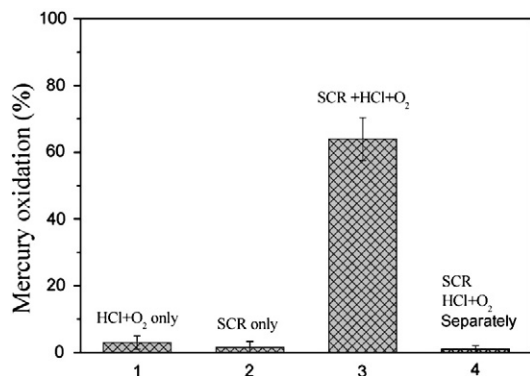ect of HBr on Hg oxidation, when compared to HCl, is explained by Vosteen et al. (2006) as being due to the larger production of Br_2 from HBr than Cl_2 from HCl, which later follows the Deacon reaction to generate $HgBr_2$. However, as Niksa et al. (2009) suggested, the Vosteen et al. (2006) estimation is based on thermodynamics without including reaction kinetics. Niksa et al. (2009) measured Hg, Hg^{2+}, and Hg^p (Hg adsorbed on particulate matter) at the inlet and outlet of a SCR unit in two experimental runs: a baseline without Br injection and a second run with Br injection. Their study suggests that NH_3 competes with HBr/Br_2 species for adsorption sites but, since the concentration of NH_3 decreases significantly due to adsorption in the first part of the SCR monolith, Br species have more opportunities to adsorb on the second part of the SCR monolith surface and oxidize Hg. Furthermore, it was shown that Br loadings of 78 ppmw increase Hg oxidation in both a back-end exchanger (through homogeneous oxidation) and across a SCR unit (through heterogeneous oxidation). The concentration of Hg at the exit of the heat exchanger decrease from 87% to 50%, and the SCR unit oxidizes nearly all Hg, with an oxidation efficiency of 97%.

The effects of adding HCl, HBr, and HI on Hg oxidation across SCR catalyst were also studied by Eswaran and Stenger (2008) in a lab-scale reactor testing both Honeycomb and Plate type catalyst. It was shown that adding 2 ppm HBr has the ability to oxidize 87% of inlet Hg while almost 50% is adsorbed on the catalyst. In the case of HI, the addition of 2 ppm leads to an oxidation extent of 85%, in the same order as HBr, but also promotes Hg desorption. The inability to carry out the experiments for long periods of time (>40 h) means that the conclusions cannot be applied to steady-state conditions, which would provide more accurate estimations of oxidation and adsorption capacities.

The composition of the flue gas varies significantly during NOx reduction due to the upstream injection of NH_3. The effect of NH_3 on Hg speciation has been analyzed several times with different results. At lab-scale, Thorwarth (2007) found that not only does Hg oxidation not occur when ammonia is present, but that ammonia can reduce oxidized Hg to its elemental form. Straube et al. (2008) also suggested that Hg adsorption is slightly decreased by NH_3 and increased with V_2O_5 loading on SCR catalyst. However, Hocquel et al. (2002) indicated that the oxidation rate of Hg at the outlet of the SCR unit is not influenced by the injection of stoichiometric amounts of NO and NH_3.

While many of these studies have used small-scale pilot experiments, there are problems associated with drawing conclusions about Hg oxidation using the results for several reasons: the small diameter size of the reactor can lead to different surface area-to-volume ratios; different flue gas chemistries may have an impact on the extent of Hg oxidation across the SCR unit; and different temperature and time profiles may result from variations in reactor dimensions (Laudal et al., 2002). For that reason, the U.S. Department of Energy's National Energy Technology Laboratory and EPA published a report in 2002 on the effect of SCR on Hg speciation and removal efficiency for a variety of coals (Feeley et al., 2003). Among the control technologies used were SCR, SNCR, ESPs, wet scrubber, and a Venturi scrubber. The overall results indicate that Hg oxidation across a SCR reactor is coal dependent but that the injection of NH_3 does not appear to have any effect on Hg speciation.

The presence of sulfur leads to the formation of stable metal sulfates that displace the Hg chlorides and, occasionally, Hg oxides. At high temperatures, volatile sulfites may appear, but at oxidizing conditions they do not play a significant role in Hg oxidation (Thorwarth, 2007). Cao et al. (2007) showed that the presence of SO_2 may displace Hg oxidation while SO_3 enhanced Hg oxidation through a homogeneous reaction, since the availability of SCR sites did not affect this reaction. The increase in the Hg oxidation with SO_3 was also observed by Eswaran and Stenger (2008) in their lab-scale SCR system, where SO_3 was mimicked by adding H_2SO_4. The individual effects of SO_3 and HCl in these experiments could not be determined since temperature, concentration, and space velocity were not kept

Fig. 8. The effect of HCl on the heterogeneous oxidation of Hg across the SCR unit (He et al., 2009).

constant. Zhuang et al. (2007) analyzed the individual effects of HCl, SO_2, and SO_3 in Hg oxidation. They found that 7% of the Hg was oxidized through the addition of 2000 ppm of SO_2, while 20% was oxidized by the addition of 50 ppm of SO_3, and only 4% of the Hg was oxidized with the addition of both SO_2 and SO_3. By adding 50 ppm of HCl, 71% oxidation was obtained, and is decreased when SO_2 (2000 ppm) and/or SO_3 (50 ppm) were added. This result indicates that sulfur species compete with HCl for adsorption sites on the SCR surface, lowering its capacity for Hg oxidation.

The shape of the catalyst may influence the mass-transfer rates that influence the Hg–Cl reaction. Senior (2004) predicted larger Hg oxidation for Plate-type SCR catalyst than Honeycomb type at the same operation conditions. However, those results do not agree with Eswaran and Stenger (2008), who found better Hg oxidation rates for Honeycomb-type catalyst and suggested that higher internal and external mass-transfer rates for Honeycomb catalysts, compared to the Plate type, could explain the results. Similar results to Eswaran and Stenger (2008)were predicted by Tronconi and Beretta (1999).

Catalyst formulation affects Hg speciation. For instance, while V_2O_5 is the active component for Hg oxidation, other oxides present either in the SCR unit or in the fly-ash such as CaO, MoO_3, or WO_3 can oxidize Hg but also potentially reduce $HgCl_2$ to Hg (Hocquel, 2004). Lee et al. (2004) studied the effect of aging and residence time on catalyst performance by comparing the degree of Hg oxidation across a fresh SCR catalyst and an aged catalyst (after 8000 h). Aging did not significantly affect the catalyst efficiency for Hg oxidation with a space time of 2263 h^{-1}, but did decrease Hg oxidation from 85% to 69% for increased space time (3031 h^{-1}). The observed that a decrease in Hg oxidation with a decrease in contact time between Hg and SCR catalyst surface indicates that the process is heterogeneous. Eswaran and Stenger (2008) showed different Hg oxidation levels in an aged catalyst (3300 h) and a young catalyst (1030 h), although the difference decreased as higher concentrations of HCl were injected.

Some studies suggest that increasing temperature reduces the Hg oxidation across the SCR unit. For example, Bock et al. (2003) observed a decrease in Hg oxidation from 78% at 290 °C to 50% at 410 °C under flue gas conditions with 10 ppm HCl. A similar trend was observed by Straube et al. (2008) who observed 43% oxidation at 260 °C but only 8% at 320 °C, with a flue gas composition of 0.3 ppm HCl, 70 ppm SO_2, 400 pm NO, and 300 ppm of NH_3.

4.2. Mercury oxidation across activated carbon

Activated carbon has been used to support a number of catalysts in order to promote the oxidation of Hg. Metal oxides, particularly Co_3O_4, MnO_2, and $CuCoO_4$, were demonstrated to increase the oxidation rate of Hg as the temperature increased to 250 °C, which offsets the decrease in overall capture efficiency due to desorption of physisorbed Hg at the higher temperatures (Mei et al., 2008). The Co- and Mn-promoted AC is deactivated in the presence of SO_2, removing any utility in industrial applications, while the CuCo AC is unaffected. Multiple studies have tested AC impregnated with CeO_2, which is most effective at 100 °C in a N_2-only atmosphere, but still effective over a range of temperatures, with both physisorption and chemisorption playing a role in Hg removal (Tian et al., 2009). A later study showed that Hg capture on CeO_2-promoted AC is much higher than that of AC alone, and that the presence of SO_2 significantly increases the Hg removal efficiency (Hua et al., 2010). Mercury was oxidized in the presence of HCl and was a good potential candidate for Hg removal from high-sulfur coals. The capture capacity of LOI carbon present in fly ash was investigated in combustion flue gas, gasification fuel gas, and an inert (N_2) atmosphere (Lopez-Anton et al., 2007) and it was concluded that any capture on fly ash must be directly related to Hg oxidation due to the difference in behavior in a combustion

atmosphere versus the gasification and inert atmospheres. They also noted that oxidation does not occur in the absence of HCl.

A kinetic study of Hg oxidation across commercial activated carbon and Thief carbon treated with HCl was performed by Presto et al. (2006). The ACs were tested in flue gas from a pilot-scale combustor using two different pulverized coals. A kinetic model was proposed, assuming that Hg oxidation is first-order in both Hg and HCl, while noting the difficulty in separating the impact of Hg adsorption (both Hg and Hg^{2+}) from direct oxidation of Hg on the surface. Using experimentally determined reaction rates, they concluded that, while the AC and the Thief carbon are effective in catalytically oxidizing Hg, when normalized for catalyst mass, a noble metal, Ir, is a far more effective catalyst. The study also could not determine whether an Eley–Rideal mechanism or a Langmuir–Hinshelwood mechanism is the dominant mechanism. A series of studies by Lee at al. (Lee et al., 2008, 2009a, 2009b, 2009c) looked at $CuCl_2$-impregnated carbonaceous surfaces. Using a bench-scale entrained-flow reactor, two different $CuCl_2$-impregnated ACs demonstrated equivalent adsorption capabilities and increased oxidation extent over commercial ACs. However, Hg adsorption was largely dependent on the carbon content of the sorbent. The results indicate that there is a potential maximum for $CuCl_2$ doping. As $CuCl_2$ increases, the amount of Hg oxidized increases, due to the increasing surface area of AC available for the adsorption. The formation of $HgCl_2$ was proposed to occur at different sites on the $CuCl_2$-impregnated AC surface. A downstream filter demonstrated that even if oxidized Hg is not captured on the original sorbent/catalyst bed, it is easily captured downstream in a second AC filter, indicating persistence of oxidation. Murakami et al. (2010) proposed that the presence of Cl_2 is more beneficial for Hg removal than HCl, so that the promotion of the Deacon reaction (2 HCl + 1/2 O_2 = Cl_2 + H_2O) has a beneficial effect on the overall Hg removal. Similar to other experimental results, they suggest that $HgCl_x$ is formed on the surface. The impact of SO_2 on Hg is proposed to be negative due to the prevention of the Deacon reaction, unless the O_2 concentration is sufficient.

4.3. Mercury oxidation across precious metal catalysts

The overall reaction of the catalytic oxidation of Hg to $HgCl_2$ due to precious metals is assumed to involve the overall pathway, Hg + 2HCl → $HgCl_2$, based on the large HCl concentration, as compared to the concentration of Cl_2, in the flue gas (Presto and Granite, 2008). Hg oxidation across a precious-metal surface can occur via one of three possible mechanisms (Presto and Granite, 2008): a Langmuir–Hinshelwood mechanism, an Eley–Rideal mechanism, or a Mars–Maessen mechanism. In a Langmuir–Hinshelwood mechanism (Pilling and Seakins, 1995), each gas species (Hg and HCl) is separately adsorbed on a catalyst surface, then the adsorbed species react to form an adsorbed product of $HgCl_2$, which is ultimately desorbed into the gas phase. In an Eley–Rideal mechanism (Niksa and Fujiwara, 2005a, 2005b), one of two species (Hg or HCl) is adsorbed while the other remains in the gas-phase, and they react with each other to produce $HgCl_2$ in the gas phase. Lastly, in a Mars–Maessen mechanism (Granite et al., 2000), adsorbed Hg reacts with a lattice oxidant (either Cl or O) that is replenished from the gas phase. An adsorbed product, $HgCl_2$ or HgO, desorbs into the gas phase.

Precious metals, such as Au, Pd, Pt, Cu, Ag, and Ir have been used as potential Hg oxidation catalysts. Mercury adsorbs to Au, Pd and Pt surfaces (Presto and Granite, 2008) and Hg appears to react from an adsorbed state (Presto and Granite, 2006). Gold, Pd, and Ir have traditionally been used as modifiers to improve Hg capture (Hladky et al., 1990; Matousek et al., 2002; Yan et al., 1993). The precious metals used for the Hg oxidation are supported by various materials, including aluminas, silica, aluminosilicates, zirconias, cerates, stainless steels, titanias, carbons, and zeolites, in order to maximize specific surface areas of the catalysts (Presto and Granite, 2006). For example, a mass loading of 1% Ir supported by 99% alumina can oxidize 75% of

Hg at approximately 140 °C. Various coating methods to impregnate catalysts onto fabric filters include dip coating, rod coating, blade or air knife coating, spray coating, curtain or slide coating, gravure coating, reverse roll coating, and extrusion coating. Among them, a simple spray-coating process appears to be the simplest and most effective technique for the highest initial loading and the lowest losses (Hrdlicka et al., 2008; Seames et al., 2007). The catalyst-coated filters with Au/TiO_2 and Pd/Al_2O_3 showed Hg oxidation ranges of 40 to 60% and 50 to 80%, respectively.

Zhao et al. (2006) have reported that the elemental Hg catalytic oxidation by Cl_2 on the Au catalyst surfaces reached 40 to 60% at temperatures between 175 and 225 °C. Hydrogen chloride has weaker oxidizing capability compared to Cl_2, but appreciably inhibits the Hg oxidation by Cl_2 due to competition between HCl and Cl_2 for active sites. Additionally, NO may serve as a promoter to enhance Hg adsorption on Au surfaces, while H_2O is regarded to inhibit Hg adsorption. Despite a previous kinetics modeling study suggesting that NO is capable of inhibiting homogeneous Hg oxidation by eliminating OH radicals (Niksa et al., 2001), the simultaneous addition of NO and H_2O had little effect on Hg oxidation by Cl_2 on Au surfaces.

Ghorishi et al. (2005) tested Hg oxidation in the presence of CuO-containing model fly ashes, showing that CuO exhibits significant catalytic Hg oxidation greater than 90% at a bed temperature of 250 °C in the presence of HCl. It was presumed that Hg oxidation is preceded by the Deacon process, where Cl_2 is produced via the catalytic oxidation of HCl on the CuO surface. The flue gas SO_2/HCl ratio significantly affects Hg oxidation in the presence of H_2O while having negligible impact on Hg oxidation in the absence of H_2O. Changing the SO_2/HCl ratio from 10:1 to 1:4 in the presence of H_2O results in Hg oxidation increasing from 60 to 90%. This trend is attributed to a scavenging effect of SO_2 and H_2O on Cl_2 ($Cl_2 + SO_2 + 2H_2O \rightarrow 2HCl + H_2SO_4$), which results in more Cl_2 available for Hg oxidation.

Field testing of Hg oxidation on Pd catalysts has been conducted at power plants (Sites 1, 2, and 3) with a wide range of flue gas compositions and coal types: Site 1 used a medium-sulfur lignite with a relatively high Hg concentration (United States Environmental Protection Agency, 1999); Site 2 used a low-sulfur subbituminous coal with a substantial Hg concentration ($\sim$8 to 9 μg/N m^3) (Blythe et al., 2000); and Site 3 used a medium-sulfur bituminous coal with a relatively low Hg concentration ($\sim$1 to 7 μg/N m^3) (Blythe et al., 2001). Palladium catalysts showed high Hg conversion to Hg^{2+} on Site 1 (3.5 month test) with 82%, Site 2 (5 month test) with 96%, and Site 3 (6 month test) with 85% of Hg oxidized. Seames et al. (2007) compared the Hg oxidation on Al_2O_3, TiO_2, and Pd/Al_2O_3 in bench-scale tests under temperatures ranging 150 to 350 °C, demonstrating that Pd/Al_2O_3 was the most attractive catalyst with elemental Hg oxidation rates on the order of 90%. Titania also showed possible potential with oxidation on the order of 70% while Al_2O_3 was completely ineffective.

Presto and Granite (2008) measured Hg oxidation on precious-metal catalysts (1 wt.% Au, Pd, and Pt supported on 2-mm alumina beads) in the flue gas conditions using a bench-scale packed bed reactor. The overall reaction rates of the catalysts for Hg^{2+} formation were compared with changing HCl and O_2 concentrations. As shown in Fig. 9, the Au catalyst showed no apparent catalyst deactivation over a period of seven experiments (the catalyst samples were tested for approximately 6 h/day for several days), while the Pd catalyst was deactivated over time. When the HCl concentration increases from 50 to 75 ppm for the Au catalyst and to 100 ppm for the Pd catalyst, little impact on the Hg oxidation rate was observed in both catalysts. In the absence of gas phase HCl, however, it was observed that Hg oxidation still continues on the catalysts, but with a declining reaction rate. From this observation, it was concluded that Hg reacts with HCl that is bound to the catalyst surface; the lack of a chlorine source to replenish the catalyst surface is responsible for the reduced reaction rate. Removing O_2 on the Au catalyst also showed very similar effect
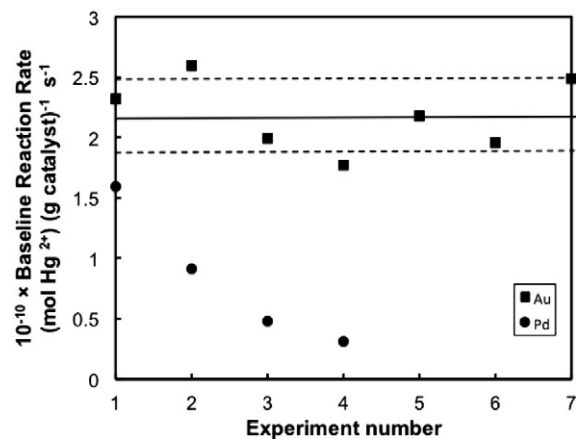

Fig. 9. Baseline Hg oxidation reaction rates across the Au (square) and Pd (circle) catalysts. One 6-hour experiment is conducted per day. Solid and dashed lines indicate the mean baseline reaction rate and one standard deviation for the Au catalyst, respectively (Presto and Granite, 2008).

as shown in removing the HCl concentration. The apparent activation energy for the Hg oxidation reaction on the Au catalyst by HCl ($Hg + 2HCl \rightarrow HgCl_2$) measured under temperatures ranging from 138 to 160 °C was calculated as 40 kJ/mol, which is comparable with the apparent activation energy of approximately 30 kJ/mol for the Hg oxidation by Cl_2 (Zhao et al., 2006). It was also assumed that surface-bound chlorine should be available for the Hg oxidation on the Au and Pd surface, based on the facts that Cl_2 can chemisorb to Au surfaces (Spencer and Lambert, 1981) and HCl dissociatively adsorbs to Pt surfaces (Wagner and Moylan, 1989). On the Au surface, chlorine binds preferentially on steps, vacancies, and Au adatoms[5] (Baker et al., 2008). At high coverage of chorine (>0.33 monolayer), Au atoms are released to the Au surface and incorporated with chlorine atoms (Baker et al., 2009); at low coverage, chlorine binds to the top of the Au surface (Gao et al., 2008).

Like the Pd catalyst, the Pt catalyst was deactivated over the test period (Presto and Granite, 2008). While no impact on Hg oxidation was observed when increasing the HCl concentration to 75 and 100 ppm, reducing the HCl concentration to 0 ppm immediately stopped Hg oxidation on the Pt catalyst, which is in contrast to both Au and Pd catalysts. Based on this observation, Presto and Granite (2008) suggested that adsorbed Hg on the Pt catalyst may react with gas phase HCl in accordance with an Eley–Rideal mechanism. The apparent activation energy for the Hg oxidation across the Pt catalyst measured under temperature ranging 140 to 157 °C was $\sim$120 kJ/mol. The Hg oxidation on a Pt catalyst may initially form HgO species in the absence of chlorine and sulfur due to strong affinity of Pt toward oxygen (Irfan et al., 2007; Mulla et al., 2006), and then $HgCl_2$ may be yielded when a chlorine source like HCl is available (Schofield, 2004, 2005). This may indicate that the Hg conversion to $HgCl_2$ requires an intermediate of HgO species in the presence of O_2 (Presto and Granite, 2008).

Presto et al. (2006) tested four Hg oxidation catalysts, including Ir (e.g., 1 wt.% Ir deposited on 4-mm γ-Al_2O_3), HCl-treated Ir (Ir/HCl), Darco FGD activated carbon (Darco), and HCl-treated Thief carbon (Thief/HCl) in a flue gas obtained from a pilot-scale pulverized coal combustor. Elemental Hg oxidation was 40, 30, 50, and 60–70% for Ir, Ir/HCl, Darco, and Thief/HCl, respectively; however, the higher percentages of two carbon-based materials (Darco and Thief/HCl) were due to larger catalyst mass. The rates of Hg oxidation normalized for catalyst mass revealed that the Ir catalyst is actually the best of the four catalysts tested: Ir (25 ± 6) > Ir/HCl (12 ± 3) > Darco

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[5] Adatoms are defined as atoms that are singularly bound or bound in small clusters to a surface.

$(3.6 \pm 0.9) >$ Thief/HCl (3.3 ± 0.8) $(m^3 \, mol^{-1} \, s^{-1}) \cdot (m^3$ of catalyst$) \cdot (g$ catalyst$)^{-1}$ at 141 °C. The HCl treatment that increases the surface Cl concentration leads to the decreased activity of Ir/HCl relative to Ir. The deactivation of Ir due to HCl might be because the HCl treatment reduced the number of surface sites available for the Hg reaction. This also might be interpreted as chlorine preventing elemental Hg from adsorbing on the Ir catalyst surface, which is the opposite behavior of Hg shown on carbon sorbents where chlorine serves as a promoter for the removal of Hg (Granite et al., 2000).

In addition to bench-scale experiments, pilot-scale tests have been carried out in which elemental Hg oxidation tests in coal-combustion flue gas using Pd and carbon-based catalysts and SCR-type catalysts were conducted for 21 months to compare elemental Hg oxidation percentages and to conduct economic comparisons (Blythe et al., 2006). Palladium and carbon-based catalysts showed initial elemental Hg oxidation percentages of 95 and 98%, respectively. Their high activities declined to 67% oxidation for the Pd-based catalyst after 21 months in service and 79% oxidation for the carbon-based catalyst after 13 months in service. On the other hand, an SCR-type catalyst (Ti/vanadium (V)) and an experimental fly-ash-based catalyst showed significantly less elemental Hg oxidation activity. Sorbent regeneration capabilities were tested by flowing heated air through the catalysts overnight, the Pd-based and SCR-type catalysts were effectively regenerated while the carbon-based catalyst was not observed to regenerate after the long-term tests. Regeneration can significantly improve the cost effectiveness of the Hg oxidation catalyst technology; for example, if the Pd-based catalyst can be regenerated to double its operation life to four years, a 50% reduction in Hg control cost would be expected compared to conventional AC injection methods, provided that a plant sells its fly ash. Although precious-metal catalysts (Pd or Au) have a high cost of installation, a minimal difference in cost can be expected between the precious metal catalysts and the "low cost" carbon-based catalyst due to the larger catalyst volume (44% more) required for the carbon-based catalysts. The pilot tests also evaluated the catalyst performance of a Au-based catalyst compared to the Pd-based catalyst. After eight months of service, both showed elemental Hg oxidation greater than 90% and declined to 51 and 47% for the Pd and Au-based catalysts after 18 months, respectively, which were more active than carbon-based and SCR-type catalysts.

5. Current challenges and future work

- Effective sorbent design relies upon accurate speciation knowledge from both homogeneous and heterogeneous oxidation mechanisms. Direct Hg speciation measurements may provide insight into material modifications for enhanced oxidation and subsequent capture.
- Understanding the mechanism of Hg capture and its interaction with flue gas components may be useful for determining the optimal location of the sorbent/catalyst. Although close, there are still enough questions to prevent this determination from being made.
- In the case of activated carbon sorbents, first-stage oxidation intermediates such as HgCl and HgBr are found to adsorb readily. The extent at which these intermediates are formed across the surface versus in the gas-phase is still to be determined. In its elemental form, Hg acts as a base, willing to donate electrons, thereby leading to interactions with surface acid sites (electron acceptors). However, in its oxidized form, it acts as an acid leading to interactions with surface basic sites. These properties of elemental and oxidized Hg are generally accepted, but have been explored in more detail in the activated carbon literature.
- For precious-metal sorbents/catalysts, the mechanism of regeneration must be determined due to economic considerations. In addition, further insight into the material properties mechanisms of adsorption and oxidation using computational modeling may

lead to the replacement of these rare-earth elements with earth-abundant materials.
- An economic analysis of precious metal sorbents may be beneficial to determine the feasibility of such a high-priced sorbents with potentially fluctuating costs.
- Further investigations may be useful regarding the stability of Hg on sorbents and fly ash, i.e., what is the likelihood of Hg leaching into the environment post capture and how might the leachability be influenced by particle size? For instance, do the extent and mechanism of Hg adsorption and oxidation change in the case of nanoparticles?
- Although it is currently well known that the organic portion of fly ash (as unburned carbon) acts as a strong sorbent of Hg, little is known of the adsorptive properties and related adsorption mechanisms for Hg binding on the inorganic portion of fly ash. Currently, it is known that Fe oxides, such as maghemite and magnetite, are abundant within the inorganic portion of fly ash and can act as oxidants of Hg, and laboratory experiments have demonstrated strong sorption of Hg^{2+} on goethite (α-FeOOH) forming a bidentate corner-sharing surface complex; however, the mechanism through which Hg^{2+} adsorbs on metal oxides within the multicomponent matrix of fly ash, along with the extent of Hg adsorption, has yet to be elucidated.
- Hg adsorbs on the surface of the SCR in the absence of HCl and this adsorption process decreases with temperature. In contrast, Hg is oxidized with a negative temperature dependence in the presence of HCl, suggesting that the critical step during Hg oxidation involves an adsorption process. Further investigations need to be carried out in developing a detailed mechanism to explain the heterogeneous reaction between Hg, HCl and the SCR surface.
- Since other trace, toxic elements have been considered for regulation by the US EPA, the interaction of arsenic (As) and selenium (Se) is a needed area for future work, not only in the interactions of As and Se with the sorbents, but their effect (positive or negative) on Hg reactivity.

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