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Mercury Speciation in Coal Combustion and Gasification Flue Gases

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Coal combustion and gasification are an anthropogenic source of mercury emission to the atmosphere. Effectively minimizing the emission and understanding the atmospheric fate and transport of mercury require knowledge of its speciation in flue gases. $Hg^0(g)$ is the thermodynamically stable form in the highest temperature regions of combustors and gasifiers. $Hg^0(g)$ remains as the dominant form in the relatively reducing conditions of a gasification flue gas, but with decreasing temperature in a combustion flue gas $Hg^0(g)$ will react to form Hg^{2+} compounds. Current mercury speciation analysis results suggest that generally >50% of the $Hg^0(g)$ reacts with oxidants in coal combustion flue gases; results for gasification conditions are lacking. Oxidation is beneficial because Hg^{2+} compounds are generally water-soluble and are therefore more effectively captured by wet scrubber pollution control systems and are more apt to deposit locally or regionally. Conversely, $Hg^0(g)$ is difficult to control and is likely to enter the global atmospheric cycle because of its high vapor pressure and low water solubility. The physical and chemical processes governing the interactions of mercury species with flue gas components are poorly known.

Introduction

Recent reviews have addressed mercury (Hg) emissions resulting from coal combustion and gasification, Hg partitioning among the various effluents of coal combustion and gasification systems, and the effects of anthropogenic Hg emission on the environment (*1–8*). These reviews, however, do not consider in-depth the speciation of Hg in combustion and gasification flue gases. Speciation describes the range of physicochemical forms of an element that collectively composes its total concentration in a sample. The identification and quantification of individual Hg forms is imperative for addressing questions concerning

Hg emission control, toxicity, mobility, bioaccumulation, and atmospheric fate and transport because each has distinctive physical, chemical, and biological properties. Until recently, only total mercury (Hg[tot]) concentration was measured in combustion and gasification flue gases. Significant improvements and developments in modeling, sampling, analytical, and experimental methods have enabled the elucidation of Hg speciation. A review of the available information relevant to Hg flue gas chemistry is timely because of the recent (since about 1990) increase in Hg research activity that has been spurred by environmental concerns and the resulting potential for stringent Hg emission regulations in the United States and abroad (*2, 8, 9*).

In contrast to most trace metals in coal, Hg is highly volatile (boiling point of 357 °C) and therefore exists almost exclusively in the vapor phase of combustion and gasification flue gases (*10, 11*). It has been reported that Hg can be volatilized from coals at temperatures as low as 150 °C (*12*). The very low concentrations of Hg in the bottom ash and slag deposits of boilers and gasifiers also attest to the volatility of Hg (*3*). As flue gases cool, it is possible for a significant fraction of the vaporized Hg to adsorb on residual carbon particles or on other particles with a large surface area to volume ratio (*13–17*). Consequently, the speciation of Hg in flue gas involves both gaseous (g) and solid (s) phases. The three oxidation states of Hg, elemental (Hg^0), mercurous (Hg_2^{2+}), and mercuric (Hg^{2+}), must also be considered in determining speciation. The properties and reactivity of Hg depend strongly on its oxidation state. Hg^0 possesses a relatively high vapor pressure, 2.46×10^{-1} Pa or 1.85×10^{-3} Torr at 25 °C (*18*), and low water solubility, 6×10^{-5} g/L at 25 °C (*19*). The Hg_2^{2+} and Hg^{2+} cations compose numerous inorganic and organic compounds; however, the Hg_2^{2+} compounds are generally unstable in flue gas and atmospheric conditions. In contrast to Hg^0, the inorganic Hg^{2+} compounds are generally reactive and water-soluble. The organic Hg^{2+} (organomercuric) compounds are characterized by covalent C–Hg bonding and high volatility.

The physicochemical forms of the elemental and inorganic Hg^{2+} phases have been predicted as functions of temperature, pressure, and flue gas composition based on thermochemical equilibrium calculations. The predictions

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TABLE 1

Thermochemical Equilibrium Models of Hg Speciation

conversion process	no. of elements	no. of Hg species	ref
AFBC,[a] PFBC[b]	14		20
gasification	21	189	21
AFBC, PFBC	26		22
combustion	17	500	23
AFBC, PFBC, gasification	4	76	24
combustion, gasification	29	400	25
combustion	9	200	26
combustion, gasification	33	800	27

[a] Atmospheric fluidized-bed combustion. [b] Pressurized fluidized-bed combustion.

TABLE 2

Mercury Measurement Methods

method	form(s)	ref
EPA 101A	Hg(tot), $Hg^{2+}X$(s)	34
sorbent	Hg(tot), Hg^0, $Hg^{2+}X$(g)	30
denuder	Hg(tot), Hg^0, $Hg^{2+}X$(g)	31, 32
EPA Method 29	Hg(tot), Hg^0, $Hg^{2+}X$(g), $Hg^{2+}X$(s)	35, 36
diffusion screen	Hg(tot)	33
MIT solid sorbent	Hg(tot)	37, 38
HEST[a]	Hg(tot), $Hg^{2+}X$(s)	39
MESA[b]	Hg(tot), Hg^0, $Hg^{2+}X$(g), CH_3Hg(g)	40
MM101A[c]	Hg(tot), Hg^0, $Hg^{2+}X$(g), $Hg^{2+}X$(s)	41

[a] Hazardous element sampling train. [b] Mercury speciation adsorption method. [c] Modified Method 101A.

indicate that Hg^0(g), $HgCl_2$(g), HgO(s,g), and $HgSO_4$(s) are the predominant forms. The actual forms can be empirically classified as Hg^0(g), inorganic mercuric compounds ($Hg^{2+}X$[s,g], where X is Cl_2, O, SO_4, etc.), and monomethylmercury, CH_3Hg(g). These classifications are based primarily on the capabilities of currently available analytical methods for determining Hg speciation. Measurements indicate that the proportions of the different Hg forms in flue gases vary widely. The variability may be attributable to a number of factors, including the concentration of Hg and its mode of occurrence in the feed coal; flue gas temperature and composition; concentration and physical characteristics of the entrained ash; and the length of time that Hg and its compounds are entrained in the flue gas. Carefully controlled experiments are required to establish the relative importance of these factors in controlling Hg speciation. Furthermore, such experiments are crucial for elucidating the behavior and fate of Hg released into air pollution control systems (APCS) and the atmosphere.

This review examines the available predictive and empirical methods and their corresponding results that pertain to the speciation of Hg in combustion and gasification flue gases. Information published within about the last 5 years is emphasized. The current understanding of Hg speciation is discussed, and research needs are identified.

Predictions of Mercury Speciation

Many researchers have developed thermochemical equilibrium models to predict the physicochemical forms of Hg as functions of temperature, pressure, and total composition in various coal combustion and gasification systems (20−27). The results of these predictions depend largely on the number of Hg species considered and the quality of their corresponding thermochemical data. The predictions also depend on the total chemical composition of the system (i.e., total number of elements) considered because of possible interelement reactions. In addition, thermodynamic predictions do not account for any kinetic or mixing limitations that may control species formation. Despite these limitations, equilibrium modeling predictions may provide a reasonable approximation of Hg speciation in various flue gas compositions.

Table 1 summarizes the thermochemical equilibrium models that have been developed to predict Hg speciation. The main components of coal conversion flue gases (C, H, O, S, N, Br, Cl, F) are considered in most of the models. In addition to the studies indicated in Table 1, results of

thermodynamic equilibrium analyses for Hg in waste incineration processes have been presented by Wu and Biswas (28) and Linak and Wendt (29).

The recent model developed by Frandsen et al. (27) is the most comprehensive, based on the number of elements and Hg species considered (Table 1). They predict that, in conventional coal combustion systems at low temperatures, $HgSO_4$(s) or HgO(s) are the stable forms of Hg. The maximum temperatures of stability for these solid phases range widely, from about 270 to 100 °C, because of the effects of chlorine on the system. Chlorine enhances the vaporization of Hg and inhibits the nucleation and condensation processes. At higher temperatures, Hg is predicted to react with flue gases, producing three forms: $HgCl_2$(g), HgO(g), and Hg^0(g). The $HgCl_2$(g) phase is dominant at temperatures of less than about 450 °C, but with increasing temperature, $HgCl_2$(g) reacts with H_2O(g) to produce HgO(g):

$$HgCl_2(g) + H_2O\ (g) \rightleftharpoons HgO(g) + 2HCl(g)$$
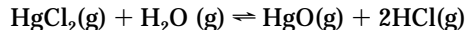
and HgO(g) gradually decomposes according to the reaction

$$HgO(g) \rightleftharpoons Hg^0(g) + 1/2O_2(g)$$
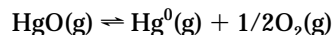
Consequently, the formation of Hg^0(g) is favored with increasing temperature at the expense of $HgCl_2$(g) and HgO(g). The relative proportion of HgO(g) is minor in comparison to $HgCl_2$(g) and Hg^0(g).

Mojtahedi (24) predicted the speciation of Hg in atmospheric fluidized-bed combustion (AFBC) and pressurized fluidized-bed combustion (PFBC) systems. His results are in general agreement with those predicted for conventional combustion systems. At low temperatures, however, the $HgSO_4$(s) phase is predicted to be unstable because of the removal of sulfur from the flue gas caused by introducing limestone or dolomite into the bed. The effect of pressure (10 bar) in PFBC systems is to increase the temperature stability range of $HgCl_2$(g) and HgO(g) at the expense of Hg^0(g).

The thermodynamic calculations predict that in the reducing conditions of a coal gasification flue gas, only Hg^0(g) is stable. Gasification conditions generally reduce the ferric iron (Fe^{3+}) in minerals, and therefore the reduction of Hg^{2+} in coal is expected; the redox potential for Hg^{2+} reduction to Hg^0, 0.85 V, is similar to that for the $Fe^{3+}-Fe^{2+}$ couple, 0.77 V (10).

Flue Gas Mercury Measurement Methods

Table 2 provides a listing of several methods that are used for sampling and quantifying Hg in flue gas. The U.S.

Environmental Protection Agency (EPA) Method 29, EPA Method 101A, and the Modified Method 101A (MM101A) employ glass fiber filters and acidic impinger solutions for sampling and cold-vapor atomic absorption spectroscopy (CVAAS) for measuring Hg. The Hg speciation adsorption (MESA), hazardous element sampling train (HEST), and Massachusetts Institute of Technology (MIT) methods use solid sorbents for sampling and cold-vapor atomic fluorescence spectroscopy (CVAFS), energy-dispersive X-ray fluorescence spectrometry, and instrumental neutron activation analysis, respectively, for quantification. Metzger and Braun (30) use CVAAS in their sorbent method. The methods of Larjava et al. (31−33) require KCl and Ag denuder tubes or a gold-coated screen for sampling and an analyzer that measures Hg concentrations in solution based on the adsorption of Hg on a gold plate and the resulting change in resistance. EPA Method 29 is the most widely used of the methods. Most were originally designed for determining Hg(tot) in flue gas, and none of them have been validated for determining Hg speciation. Nevertheless, several of the methods are being used in research for identifying various Hg forms, as indicated in Table 2. The speciation determination is based on the physical entrapment of particulate forms in a filter and the chemically selective absorption or adsorption of gaseous forms in impinger solutions and on solid sorbents, respectively (30, 42). The method of Larjava et al. (31, 32), however, is based on the selective amalgamation and diffusion of gaseous Hg forms onto reactive denuder surfaces. Most of these methods require that the collected Hg species be recovered and then converted to Hg^0 before quantification. Therefore, the methods in Table 2 are not definitive in that the Hg species determination is an operational classification rather than a true species identification. Uncertainties in the selectivity and collection efficiencies of the sampling media and analyte recovery efficiencies are currently being investigated by several U.S. research organizations.

Miller and Laudal (43) demonstrated in a bench-scale system that $Hg^0(g)$ and $HgCl_2(g)$ can be accurately measured in an inert $N_2(g)$ atmosphere using EPA Method 29. Preliminary testing results indicate that $Hg^0(g)$ and $HgCl_2(g)$ can also be determined with reasonable accuracy in a simulated combustion flue gas consisting of O_2, H_2O, CO_2, SO_2, and N_2 (44). The Hg(tot) measurements obtained by EPA Method 29 and EPA Method 101A during pilot-scale testing on a Pittsburgh no. 8 coal compared very favorably (44). Nott (45) reported the results of a study to evaluate and compare EPA Method 29, EPA Method 101A, MESA, HEST, and MIT methods. The results indicated "reasonably good agreement" among the Hg(tot) measurements for the different methods. However, the oxidized Hg concentrations measured by EPA Method 29 were generally greater than those measured by MESA method, indicating a sampling or measurement problem with one or both of the methods (45, 46). Hargrove et al. (47) noted that during their pilot-scale testing, EPA Method 29 and MESA provided comparable results in measuring spiked $HgCl_2(g)$ concentrations in combustion flue gas but not $Hg^0(g)$. Bush et al. (48) compared Hg measurements obtained using EPA Method 29 and MM101A at a coal-fired power plant. Their results indicated "good agreement" between the Hg(tot) measurements for the different methods, but the measured proportions of $Hg^0(g)$ and $Hg^{2+}X(g)$ differed substantially. Miller et al. (49) presented Hg speciation results obtained via EPA Method 29 as a function of the sampling filter temperature for two Powder River Basin subbituminous coals and a bituminous coal burned in a pilot-scale combustion system. Their results suggested that the amounts of $Hg^0(s)$ and $Hg^{2+}X(s)$ in the fly ash collected on the Method 29 sampling filter are indirectly proportional to filter temperature for the Powder River Basin coals and bituminous coal, respectively.

In addition to the batch sampling and manual testing methods indicated in Table 2, several on-line Hg analysis instruments are being developed based on the well-established techniques of atomic absorption spectroscopy (50, 51), CVAAS (52, 53), and CVAFS (53) as well as on the emerging technology of chemical microsensors (54). The instruments can be used to directly measure $Hg^0(g)$ in flue gas. The instruments can also be equipped with converters for reducing oxidized Hg forms into $Hg^0(g)$ so that Hg(tot) can be determined, and the oxidized Hg concentration can be estimated by difference [$Hg^{2+}X(s,g) = Hg(tot) − Hg^0(g)$]. These instruments, with continued development and validation testing, may enable the continuous monitoring of Hg forms in flue and stack gases.

Mercury Speciation Measurements

Estimates of the relative proportions of $Hg^0(g)$, $Hg^{2+}X(g)$, $Hg^{2+}X(s)$, and $CH_3Hg(g)$ have been made recently for several coal combustion pilot- and full-scale systems, as indicated in Table 3. Most of the values are averages of several measurements for a given coal and in some cases for different coals and combustion systems. The measurements were conducted at various sampling locations relative to APCS.

The estimates in Table 3 indicate that, before APCS, gaseous and particulate Hg^{2+} compounds, $Hg^{2+}X(s,g)$, generally compose greater than half of the total Hg present in combustion flue gas. The other dominant form of Hg in combustion flue gas is $Hg^0(g)$. The presence of $CH_3Hg(g)$ reported by Chow et al. (56) may be an artifact of a digestion procedure used in the MESA method, as discussed by Prestbo and Bloom (40). Ballantine and Zoller (58), however, found elevated concentrations of atmospheric $CH_3Hg(g)$ in the vicinity of coal combustion plants using a very sensitive gas chromatography method.

Lindqvist et al. (2) suggested that the oxidized Hg species are relatively easy to collect in APCS because of their relatively high water solubilities and surface reactivities, while $Hg^0(g)$ is difficult to isolate from the flue gas because of its volatility and low water solubility. Based on the speciation results determined after APCS (Table 3), it appears that electrostatic precipitation (ESP) systems are ineffective in removing the $Hg^{2+}X(s,g)$ forms, but the flue gas desulfurization (FGD) systems are effective, as evidenced by the relatively high proportions of $Hg^0(g)$ downstream of the FGD. The apparent effectiveness of FGD systems in removing oxidized Hg, however, may be misrepresented by the results in Table 3. Fahlke and Bursik (57) noted that Hg^{2+} dissolved in a scrubber suspension can be reduced by SO_2 to form Hg_2^{2+}, which may then disproportionate to Hg^{2+} and Hg^0 as a function of chloride concentration and pH. The release of $Hg^0(g)$ from the scrubber suspension may actually produce a flue gas downstream of the FGD that is even more enriched in $Hg^0(g)$ than that originally produced by combustion. Hargrove et al. (47) have recently discounted this mechanism, based on bench-scale tests, and suggest that some other mechanism must account for

TABLE 3

Proportions of Hg Species in Coal Combustion Flue Gases (%)

method	location[a]	Hg^0	Hg^{2+}X(g)	Hg^{2+}X(s)	CH$_3$Hg	ref
sorbent	before APCS	50	50			55
denuder	before APCS	50	30	20		5
MESA	before APCS	30	60		10	56
MESA	after ESP and FGD	100				56
sorbent	before APCS	23	77			57
sorbent	after ESP and FGD	76	24			57
MESA	before APCS	33	67			40
MESA	after ESP	45	55			46
Method 29	after ESP	30	70			46
MESA	after FGD	75	25			46
Method 29	after FGD	55	45			46
MM101A	before FGD	52	48	<1		48
Method 29	before FGD	26	74	<1		48
MM101A	after FGD	91	9	<1		48
Method 29	after FGD	79	21	<1		48
Method 29	before FGD		95			47

[a] APCS = air pollution control system(s); ESP = electrostatic precipitation; FGD = flue gas desulfurization.
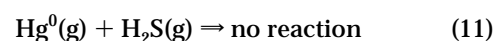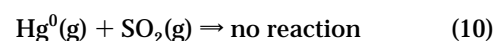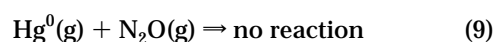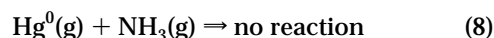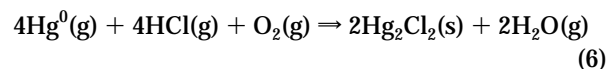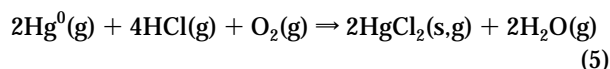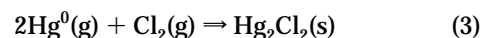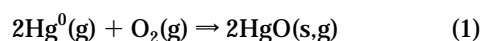
the commonly observed increases in Hg^0(g) concentration downstream of FGD systems. They have also proposed the existence of an "alternate form" of Hg to account for the poor performance of FGD in removing oxidized Hg for some coals.

Published results of speciation measurements for gasification systems are lacking. In the relatively reducing conditions of a gasification flue gas, the proportion of Hg^{2+}X(s,g) relative to Hg^0 is expected to be considerably less than in combustion flue gas, but the presence of CH$_3$-Hg(g) is more likely because methane concentrations are much greater. Although the oxidation of Hg^0(g) by methylation in a flue gas to form CH$_3$Hg(g) may be possible, organic forms of Hg are primarily produced through biogenic transformation mechanisms (7). Zygarlicke et al. (59) investigated the effects of gas temperature and oxygen/carbon on the speciation of Hg by converting an Illinois no. 6 coal in a pressurized drop-tube furnace using simulated gasification conditions. They found that the concentration of Hg^0(g) increased with increasing gas temperature and decreasing oxygen/carbon. This relationship is in agreement with thermochemical equilibrium predictions (Table 1).

Mercury Reaction Chemistry

Equilibrium calculations indicate that the Hg in coal is initially converted to Hg^0(g) during combustion and gasification. Subsequent oxidation−reduction reactions with flue gas and APCS components in the cooler regions of a coal conversion system ultimately determine the forms of Hg emitted to the atmosphere. Experiments in laboratory-scale systems have been conducted to identify the oxidation−reduction reactions that are relevant to Hg speciation.

Mercury Oxidation Reactions. Schager (60) and Hall et al. (61) investigated the reactivity of Hg^0(g) in combustion flue gas components (O$_2$, HCl, Cl$_2$, SO$_2$, NO$_2$, N$_2$O, NO, NH$_3$, H$_2$S) at temperatures ranging from 20 to 900 °C. They found that Hg^0(g) reacted slowly with NO$_2$(g) but rapidly with HCl(g) and Cl$_2$(g) and with O$_2$(g) in the presence of activated carbon. The Hg^0(g) was unreactive with the NH$_3$(g), N$_2$O(g), SO$_2$(g), and H$_2$S(g) components. The following reactions between Hg^0(g) and flue gas components were proposed:

$$2Hg^0(g) + O_2(g) \rightleftharpoons 2HgO(s,g) \tag{1}$$

$$Hg^0(g) + Cl_2(g) \rightleftharpoons HgCl_2(s,g) \tag{2}$$

$$2Hg^0(g) + Cl_2(g) \rightleftharpoons Hg_2Cl_2(s) \tag{3}$$

$$Hg^0(g) + 2HCl(g) \rightleftharpoons HgCl_2(s,g) + H_2(g) \tag{4}$$

$$2Hg^0(g) + 4HCl(g) + O_2(g) \rightleftharpoons 2HgCl_2(s,g) + 2H_2O(g) \tag{5}$$

$$4Hg^0(g) + 4HCl(g) + O_2(g) \rightleftharpoons 2Hg_2Cl_2(s) + 2H_2O(g) \tag{6}$$

$$Hg^0(g) + NO_2(g) \rightleftharpoons HgO(s,g) + NO(g) \tag{7}$$

$$Hg^0(g) + NH_3(g) \rightleftharpoons \text{no reaction} \tag{8}$$

$$Hg^0(g) + N_2O(g) \rightleftharpoons \text{no reaction} \tag{9}$$

$$Hg^0(g) + SO_2(g) \rightleftharpoons \text{no reaction} \tag{10}$$

$$Hg^0(g) + H_2S(g) \rightleftharpoons \text{no reaction} \tag{11}$$

Heidt et al. (44) also investigated the effect of HCl(g) on Hg speciation and found that Hg^0(g) did not readily react with the HCl(g) component of a simulated combustion flue gas at temperatures of ≤180 °C. Reaction 4 is strongly temperature dependent, a relatively rapid reaction at temperatures of ≥500 °C (60, 61), and is unlikely to occur except in the presence of an oxidant, such as O$_2$(g) (reactions 5 and 6). Hall et al. (62) investigated reaction 7 in detail and concluded that NO$_2$(g) has a negligible effect on the oxidation of Hg in combustion processes. The reaction, however, may be important in a stack plume during stable meteorological conditions where high concentrations of NO$_2$(g) can react with Hg^0(g) for long periods.
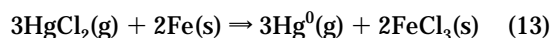
In a review of the atmospheric chemistry of Hg, Seigneur et al. (63) tabulated rate constants for several Hg oxidation reactions that are pertinent to coal conversion flue gases, including reactions 1, 2, 4, and 8−11. The reaction rates, however, were determined at ambient temperature. Nevertheless, the kinetic data indicate that the reaction rate of Hg^0(g) with Cl$_2$(g) is about 3 orders of magnitude greater

than for the reaction of $Hg^0(g)$ with HCl, $\leq 4.1 \times 10^{-16}$ versus $\leq 1.0 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1}. The reactions of $Hg^0(g)$ with $NH_3(g)$, $N_2O(g)$, $SO_2(g)$, and $H_2S(g)$ are expected to proceed at rates intermediate between the $Hg^0(g)-Cl_2(g)$ and $Hg^0(g)-HCl$ reactions, with values ranging from 1.0×10^{-17} to $\leq 6 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}. The reaction of $Hg^0(g)$ with $O_2(g)$ proceeds at a relatively slow rate of $\leq 1 \times 10^{-23}$ cm^3 molecule^{-1} s^{-1}. The applicability of these reaction rates to combustion conditions is suspect because of the temperature dependence for many of the reactions and also because of differences in the concentrations of reactant gases actually present in a flue gas. Therefore, the relative rankings of these reaction rates at high temperatures are probably very different.

Mercury Reduction Reactions. The principal oxidized forms of Hg in coal conversion flue gases are generally assumed to be Hg^{2+} compounds because of the instability of Hg_2^{2+} compounds. Hg^{2+} compounds, such as HgO(s) and $HgCl_2(g)$, may undergo reduction to form $Hg^0(g)$. Schager (60) reported evidence for the reduction of oxidized Hg species by reaction with $SO_2(g)$ and hot steel surfaces according to the following reactions:

$$HgO(s,g) + SO_2(g) \rightrightarrows Hg^0(g) + SO_3(g) \qquad (12)$$

and

$$3HgCl_2(g) + 2Fe(s) \rightrightarrows 3Hg^0(g) + 2FeCl_3(s) \qquad (13)$$

respectively. Stevens et al. (64) calculated a rate constant of 3×10^{-12} cm^3 molecule^{-1} s^{-1} for the homogeneous gas-phase reaction between HgO(g) and $SO_2(g)$ (reaction 12). The reaction rate is, to a first approximation, temperature-independent. Zacharewski et al. (65) investigated the heterogeneous reaction between HgO(s) and $SO_2(g)$ at ambient temperature. They identified solid Hg sulfation reaction products using Fourier transform infrared spectroscopy. The reaction products, however, required several weeks to form. HgO(s) can also be reduced according to the established reaction

$$HgO(s) + CO(g) \rightrightarrows Hg^0(g) + CO_2(g) \qquad (14)$$
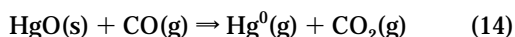
at ambient and elevated temperatures (18). In summary, the experimental evidence indicates that the formation and subsequent condensation of HgO (reaction 1) is catalyzed by the presence of residual carbon, but is repressed by the presence of $SO_2(g)$ and CO(g) (reactions 12 and 14, respectively).

Perspective

A considerable amount of work has been performed in developing methods to sample and measure various Hg forms in coal combustion and gasification flue gases. Although significant progress has been made, no validated method currently exists for determining Hg speciation. A major limitation of the available methods is that the forms, especially the oxidized forms, are not measured independently of each other. The continued development and validation of methods are required before the exact forms of Hg present in coal conversion flue gases can be identified.

The experimental results from laboratory-scale systems reveal many homogeneous and heterogeneous reactions that may oxidize or reduce Hg species. The proposed reactions suggest that Hg speciation is cyclic in coal conversion systems, whereby the $Hg^0(g)$ that is released from coal during conversion and then oxidized, via reactions such as 1–7, may be reduced again through reactions such as 12–14. The applicability of the published experimental results, however, is suspect primarily because of the uncertainties of extrapolating laboratory-derived information to utility-scale systems. Nonetheless, additional experimental work is required to identify potential reactions and to determine their relative importance and environmental significance.

Literature Cited

(1) Nriagu, J. O.; Pacyna, J. M. *Nature* **1988**, *333*, 134–139.
(2) Lindqvist, O.; Johansson, K.; Aastrup, M.; Anderson, A.; Bringmark, L.; Hovsenius, G.; Håkanson, L.; Iverfeldt, Å; Meili, M.; Timm, B. *Water, Air, Soil Pollut.* **1991**, *55*, 1–261.
(3) Clarke, L. B.; Sloss, L. L. Report IEACR/49. International Energy Agency Coal Research: London, U.K, 1992.
(4) Clarke, L. B. *Fuel* **1993**, *72*, 731–736.
(5) Munthe, J. Report No. 1110. Swedish Environmental Protection Institute: Göteborg, Sweden, 1993.
(6) Carlson, C. L.; Adriano, D. C. *J. Environ. Qual.* **1993**, *22*, 227–247.
(7) Mason, R. P.; Fitzgerald, W. F.; Morel, F. M. M. *Geochim. Cosmochim. Acta* **1994**, *58*, 3191–3198.
(8) Sloss, L. L. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **1995**, *40*, 793–797.
(9) Provisions for Attainment and Maintenance of National Ambient Air Quality Standards. Public Law 101-549, 1990.
(10) *CRC Handbook of Chemistry and Physics,* 64th ed.; Weast, R. C., Ed.; CRC Press, Inc.: Boca Raton, FL, 1983.
(11) Otani, Y.; Emi, H.; Kanaoka, C.; Matsui, S. *Environ. Sci. Technol.* **1984**, *18*, 793–796.
(12) Finkelman, R. B.; Palmer, C. A.; Krasnow, M. R.; Aruscavage, P. J.; Sellers, G. A.; Dulong F. T. *Energy Fuels* **1990**, *4*, 755–766.
(13) Otani, Y.; Kanaoka, C.; Usui, C.; Matsui, S.; Emi, H. *Environ. Sci. Technol.* **1986**, *20*, 735–738.
(14) Zintl, F. M.; Pedersen, J. R. *VGB Kraftwerkstech.* **1992**, *72*, 906–914.
(15) Krishnan, S. V.; Gullett, B. K.; Jozewicz, W. *Environ. Sci. Technol.* **1994**, *28*, 1506–1512.
(16) Gullett, B. K.; Ragnunathan, K. *Energy Fuels* **1994**, *8*, 1068–1076.
(17) Bool, L. E.; Helble, J. J. *Energy Fuels* **1995**, *9*, 880–887.
(18) Schroeder, W. H.; Yarwood, G.; Niki, H. *Water, Air, Soil Pollut.* **1991**, *56*, 653–666.
(19) Schuster, E. *Water, Air, Soil Pollut.* **1991**, *56*, 667–680.
(20) Alvin, M. A.; O'Neill, E. P.; Keairns, D. L. *Abstracts of Papers*, 5th International Conference on Fluidized-Bed Combustion, Washington, DC, Dec 1977; Abstract 526.
(21) Kalfadelis, C. D.; Magee, E. M. *Ind. Eng. Chem.* **1977**, *16*, 489.
(22) Alvin, M. A. Final Report No. Pb 82-240219. Westinghouse Research and Development Centre: Pittsburgh, PA, 1982.
(23) Moberg, P. O.; Westermark, M.; Noläng, B. Technical Report No. KHM TR 28. The Wedish State Power Board: Vällingby, Sweden, 1982.
(24) Mojtahedi, W. *Combust. Sci. Technol.* **1989**, *63*, 209–227.
(25) SRI International. Vaporization of Trace Element Species from Coal Under Gasification and Combustion Conditions. Final report to the U.S. Department of Energy under Contract No. DE-AC21-86MC23261; Report No. DE89 011687; Morgantown Energy Technology Center: Morgantown, WV, 1989.
(26) Linak, W. P.; Wendt, J. O. L. *Fuel Process. Technol.* **1994**, *39*, 173–198.
(27) Frandsen, F.; Dam-Johansen, K.; Rasmussen, P. *Prog. Energy Combust. Sci.* **1994**, *20*, 115–138.
(28) Wu, C. Y.; Biswas, P. *Combust. Flame* **1993**, *93*, 31–40.

(29) Linak, W. P.; Wendt, J. O. L. *Prog. Energy Combust. Sci.* **1993**, *19*, 145−185.

(30) Metzger, M.; Braun, H. *Chemosphere* **1987**, *16*, 821−832.

(31) Larjava, K.; Reith, J.; Klockow, D. *Int. J. Environ. Anal. Chem.* **1990**, *38*, 31−45.

(32) Larjava, K.; Laitinen, T.; Vahlman, T.; Artmann, S.; Siemens, V.; Broekaert, J. A. C.; Klockow, D. *Int. J. Environ. Anal. Chem.* **1992**, *149*, 73−85.

(33) Larjava, K.; Laitinen, T.; Kiviranta, T.; Siemens, V.; Klockow, D. *Int. J. Environ. Anal. Chem.* **1993**, *52*, 65−73.

(34) U.S. Environmental Protection Agency. Determination of Particulate and Gaseous Mercury Emissions from Sewage Sludge Incinerators, Method 101A. *Code of Federal Regulations* **1992**, *40* (61), Appendix B.

(35) U.S. Environmental Protection Agency. Methodology for the Determination of Metals Emissions in Exhaust Gases from Hazardous Waste Incineration and Similar Combustion Processes. *Code of Federal Regulations* **1992**, *40* (266), Appendix IX, Section 3.1.

(36) Ward, T. E. *Fuel Process. Technol.* **1994**, *39*, 259−263.

(37) Olmez, I.; Ames, M.; Aras, N. K. Presented at the Annual Meeting of the American Nuclear Society, San Diego, CA, June 1993.

(38) Olmez, I.; Huang, X.; Ames, M. R. Presented at the 88th Annual Meeting & Exhibition of the Air & Waste Management Association, San Antonio, TX, June 1995; Paper 95-MP21.02.

(39) Cooper, J. A. *Fuel Process. Technol.* **1994**, *39*, 251−258.

(40) Prestbo, E. M.; Bloom, N. S. *Water, Air, Soil Pollut.* **1995**, *80*, 145−158.

(41) Curtis, K. E.; Eagleson, K. E. Report No. A-F-95-22-Con. Ontario Hydro Technologies: Toronto, Ontario, Canada, 1995.

(42) Meij, R. *Water, Air, Soil Pollut.* **1991**, *56*, 117−129.

(43) Miller, S. J.; Laudal, D. L. Presented at the 87th Annual Meeting of the Air & Waste Management Association, Cincinnati, OH, June 1994; Paper 94-RA114A.02.

(44) Heidt, M. K.; Laudal, D. L.; Nott, B. Presented at the EPRI/DOE International Conference on Managing Hazardous and Particulate Air Pollutants, Toronto, Ontario, Canada, Aug 1995.

(45) Nott, B. R. *Water, Air, Soil Pollut.* **1995**, *80*, 1311−1314.

(46) Chu, P.; Porcella, D. B. *Water, Air, Soil Pollut.* **1995**, *80*, 135−144.

(47) Hargrove, O. W., Jr.; Peterson, J. R.; Seeger, D. M.; Skarupa, R. C.; Moser, R. E. Presented at the EPRI/DOE International Conference on Managing Hazardous and Particulate Air Pollutants, Toronto, Ontario, Canada, Aug 1995.

(48) Bush, P. V.; Dismukes, E. B.; McCain, J. D.; Fowler, W. K. Presented at the EPRI/DOE International Conference on Managing Hazardous and Particulate Air Pollutants, Toronto, Ontario, Canada, Aug 1995.

(49) Miller, S. J.; Laudal, D. L.; Dunham, G. E.; Chang, R.; Bergman, P. D. Presented at the EPRI/DOE International Conference on Managing Hazardous and Particulate Air Pollutants, Toronto, Ontario, Canada, Aug 1995.

(50) Durham, M. D.; Schlager, R. J.; Hyatt, D. E. *Fuel Process. Technol.* **1994**, *39*, 285−299.

(51) Sappey, A. D.; Wilson, K. G.; Schlager, R. J.; Anderson, G. L.; Jackson, D. W. *Prepr. Pap.−Am. Chem. Soc., Div. Fuel Chem.* **1995**, *40*, 818−822.

(52) Wang, J.; Xiao, Z.; Lindqvist, O. *Water, Air, Soil Pollut.* **1995**, *80*, 1217−1226.

(53) Norton, G. A.; Eckels, D. E. Presented at the EPRI/DOE International Conference on Managing Hazardous and Particulate Air Pollutants, Toronto, Ontario, Canada, Aug 1995.

(54) Sorensen, I.; Bao, Q.; Glaunsinger, W. Presented at the 88th Annual Meeting & Exhibition of the Air & Waste Management Association, San Antonio, TX, June 1995; Paper 95-MP21.05.

(55) Gutberlet, H.; Spiesberger, A.; Kastner, F.; Tembrink, J. *VGB Kraftwerkstech.* **1992**, *72*, 586−591.

(56) Chow, W.; Miller, M. J.; Torrens, I. M. *Fuel Process. Technol.* **1994**, *39*, 5−20.

(57) Fahlke, J.; Bursik, A. *Water, Air, Soil Pollut.* **1995**, *80*, 209−215.

(58) Ballantine, D. S.; Zoller, W. H. *Anal. Chem.* **1984**, *56*, 1288−1293.

(59) Zygarlicke, C. J.; McCollor, D. P.; Benson, S. A. Presented at the Pacific Rim International Conference on Environmental Control of Combustion Processes, Maui, HI, Oct 1994.

(60) Schager, P. Report No. FBT-91-20. Statens energiverk, National Energy Administration: Sweden, 1990.

(61) Hall, B.; Schager, P.; Lindqvist, O. *Water, Air, Soil Pollut.* **1991**, *56*, 3−14.

(62) Hall, B.; Schager, P.; Ljungström, E. *Water, Air, Soil Pollut.* **1995**, *81*, 121−134.

(63) Seigneur, C.; Wrobel, J.; Constantinou, E. *Environ. Sci. Technol.* **1994**, *28*, 1589−1597.

(64) Stevens, R. D. S.; Reid, N. W.; Schroeder, W. H.; McLean, R. A. N. Presented at the 2nd Symposium on Combustion and the Nonurban Troposphere, Williamsburg, VA, May 1982.

(65) Zacharewski, T. R.; Cherniak, E. A.; Schroeder, W. H. *Atmos. Environ.* **1987**, *21*, 2327−2332.