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Gas-phase transformations of mercury in coal-fired power plants

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Abstract

Because mercury enters the food chain primarily through atmospheric deposition, exposure models require accurate information about mercury emission rates and mercury speciation from point sources. Since coal-fired power plants represent a significant fraction of the anthropogenic emissions of mercury into the atmosphere, the speciation of mercury in coal-fired power plant flue gas is currently an active topic of research. We have demonstrated that the assumption of gas-phase equilibrium for mercury-containing species in coal-fired power plant exhaust is not valid at temperatures below approximately 800 K (500°C). Chlorine-containing species have been shown to be the most important for oxidation of elemental mercury in the post-combustion gases. The conversion of HCl to Cl₂ in the flue gas of a coal-fired power plant is kinetically limited. Kinetic calculations of the homogeneous oxidation of elemental mercury by chlorine-containing species were carried out using global reactions from the literature. The levels of mercury oxidation, while of comparable magnitude to field observations, are still below the 40% to 80% oxidation typically observed in field measurements. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Mercury; Coal-fired power plant; Flue gas

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1. Introduction

A recent report by the Environmental Protection Agency (EPA) on emission of hazardous air pollutants by electric utilities predicted that emissions of air toxics from coal-fired utilities would increase by 10% to 30% by the year 2010 [1]. Mercury from coal-fired utilities was identified as the hazardous air pollutant of greatest potential public health concern.

Anthropogenic emissions of mercury account for 10% to 30% of the world-wide emissions of mercury [2]. EPA has estimated that during the period 1994–1995 annual emissions of mercury from human activities in the United States were 159 tons [1]. Approximately 87% of these emissions were from combustion sources. Coal-fired utilities in the U.S. were estimated to emit 51 tons of mercury per year into the air during this period.

The form of mercury emitted from point sources is a critical variable in modeling the patterns and amount of mercury deposition from the atmosphere [1,3]. Both elemental and oxidized mercury are emitted to the air from combustion point sources. Elemental mercury has a lifetime in the atmosphere of up to a year, while oxidized forms of mercury have lifetimes of a few days or less [1] as a result of the higher solubility of Hg^{+2} in atmospheric moisture. Elemental mercury can thus be transported over long distances, whereas oxidized and particulate mercury deposit near the point of emission. Once mercury has deposited on land or water, it can transform into methylmercury, an organic form, and thereby enter the food chain. Humans are most likely to be exposed to methylmercury through consumption of fish.

Mercury is present in coal in low concentrations, on the order of 0.1 ppmw. In the combustion zone of a coal-fired power plant, all the mercury in coal is vaporized as elemental mercury, yielding vapor concentrations of mercury in the range of 1 to 20 $\mu\text{g}/\text{m}^3$ (1 to 20 ppbw). At furnace exit temperatures (1700 K), all of the mercury is expected to remain as the thermodynamically favored elemental form in the gas. As the gas cools after combustion, oxidation reactions can occur, significantly reducing the concentration of elemental mercury by the time the post-combustion gases reach the stack. Measurements of the concentration of mercury species taken in the stacks of pilot and full scale coal combustion systems show more than half of the vapor phase mercury as the oxidized form which is likely to be HgCl_2 [4–6]. Current measurement methods cannot identify specific oxidized species of mercury. The range of observed values is broad: one study consisting of mercury speciation measurements from fourteen different coal combustion systems reported anywhere from 30% Hg^{+2} to 95% Hg^{+2} upstream of the air pollution control device (APCD) [4].

Although we can identify the major reaction pathways for mercury in coal combustion flue gas with some degree of confidence, we cannot yet make quantitative predictions of the emissions of specific mercury species from coal-fired power plants. In our work, the goal is to advance the state of knowledge such that a predictive model for emissions of total mercury and specific mercury species can be formulated. Specifically, we want to predict the rate of oxidation of elemental mercury from the furnace exit to the convective air heater, leading to prediction of gas-phase mercury speciation at the

inlet to the APCD. In this paper, we examine methods for calculation of the speciation of mercury in coal combustion flue gas.

2. Equilibrium calculations

As a starting point, the distribution of mercury species in coal combustion flue gas were calculated using equilibrium calculations. Such equilibrium calculations have been carried out before [7]. However, no one has yet explored whether the assumption of equilibrium is valid for mercury species in coal-fired utility flue gas given the time-temperature history in the post-combustion region. If equilibrium is a valid assumption for a particular element, then predicting the fate of the element is relatively straightforward. On the other hand, if equilibrium will not be attained in the flue gas, constrained equilibrium or kinetic models will need to be developed.

Equilibrium calculations were conducted using SOLGASMIX [8]. The thermochemical database in the HSC package provided thermochemical data on the species of interest [9]. Calculations were carried out for four coals using the material balances in Table 1. A stoichiometric ratio of 1.2 was assumed for the combustion process. The species considered in the equilibrium calculation were as follows:

Gas: CO, CO₂, Cl₂, H₂, HCl, H₂O, Hg, HgCl₂, HgO, N₂, NO, NO₂, O₂, SO₃

Condensed: C, Hg, HgO, HgSO₄.

Table 1
Compositions for equilibrium calculations at SR = 1.2

	Elkhorn/Hazard (bituminous)	Pittsburgh (bituminous)	Illinois 6 (bituminous)	Wyodak (sub-bituminous)
<i>Ultimate analysis (wt.%)</i>				
H	4.85	4.98	5.1	7.04
C	74.87	76.62	67.7	52.84
N	1.43	1.48	1.18	0.7
S	0.82	1.64	3.6	0.39
O	10.45	8.19	12.14	34.54
Ash	7.41	7.01	10.26	4.49
<i>Minor species (ppmw)</i>				
Cl	1700	980	340	550
Hg	0.13	0.11	0.11	0.11
<i>Gas composition at SR = 1.2 (in vol.%)</i>				
CO ₂	14.5	14.44	14.26	13.86
H ₂ O	5.7	5.69	6.51	11.13
O ₂	4.13	3.86	4.21	6.27
N ₂	76.49	76.59	75.8	72.17
<i>(in ppmv)</i>				
SO ₂	594	1166	2837	383
HCl	111	62	24	49
Hg	0.0015	0.00124	0.0014	0.00172
SO ₃ ^a	8.2	15.5	39.6	6.5

^aCalculated assuming frozen equilibrium at 1400 K.

Unlike previous calculations [7], the equilibrium between SO_2 and SO_3 was frozen in these calculations. Without this assumption, all of the sulfur is predicted by the equilibrium calculations to exist as SO_3 at low temperatures. This result is contrary to observations from coal-fired power plants in which on the order of 3% of the sulfur is present as SO_3 in stack gases. The formation and destruction of SO_3 is dominated by radical reactions which become slow as the combustion products are cooled below about 1500 K [10]. The concentration of SO_3 in the flue gas was set equal to that predicted by equilibrium at 1400 K for each coal based on these kinetic arguments.

Typical results from 500 to 1100 K are shown in Fig. 1 for the Pittsburgh coal. Below about 425 K (150°C) condensation of HgSO_4 is predicted, but results of the equilibrium calculations are not shown for this temperature in the figure for two reasons. First, below the acid dewpoint temperature (typically 400 K), the simple equilibrium approach employed for this analysis cannot adequately model the formation of multi-component aqueous solutions containing sulfates. Second, heterogeneous reactions appear to be important for oxidation of mercury at temperatures as high as 600 K [11].

Results for the other three coals are qualitatively similar to those shown in Fig. 1. Below 725 K (450°C) all of the Hg is predicted to exist as HgCl_2 . Above about 975 K (700°C) 99% of the Hg is predicted to exist as gaseous Hg. The rest (1%) is predicted to be gaseous HgO . Between 725 and 975 K, the split between HgCl_2 and Hg is determined by the chlorine content of the coal (Fig. 2). The mercury content of the coal has no effect on the equilibrium distribution of mercury species. Equilibrium HCl concentrations in the gas are predicted to be in the range of 24 to 111 ppm for the coals studied here. Even at these low concentrations, the reaction between Hg and HCl dominates the equilibrium chemistry. At temperatures representative of the inlet to the APCD, therefore, all the mercury should exist in the gas phase as HgCl_2 , if equilibrium were attained in the flue gas.

It is unlikely, however, that equilibrium is attained for mercury species in the post-combustion gas of practical combustion systems. Consider Fig. 3, an idealized

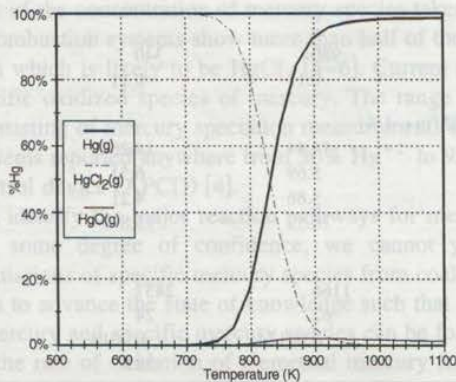


Fig. 1. Equilibrium mercury speciation in flue gas as a function of temperature (Pittsburgh coal).

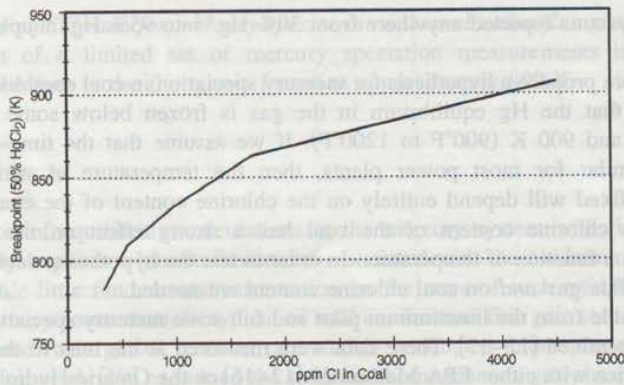


Fig. 2. Equilibrium mercury speciation in flue gas: temperature of 50% HgCl₂ in gas as a function of coal chlorine content.

temperature history for a coal-fired power plant. The flue gas cools rapidly as heat is transferred to water and steam. Observations of kinetic limitations for other species in practical combustion systems and measurements of mercury speciation in coal-fired power plants suggest that equilibrium will not be attained for mercury in coal-fired power plant flue gas. Minor species in the flue gas such as CO and SO₂ do not have time to equilibrate as the gas cools [10]. Similarly for trace species, equilibrium may not be attained as the flue gas cools.

The evidence from pilot-scale and full-scale combustion systems is not consistent with the assumption of equilibrium for mercury species in flue gas at the temperatures corresponding to the location of the APCD. The amount of mercury in the oxidized form when measured at the APCD inlet is almost always less than 100%. For example, one study consisting of mercury speciation measurements from fourteen different coal

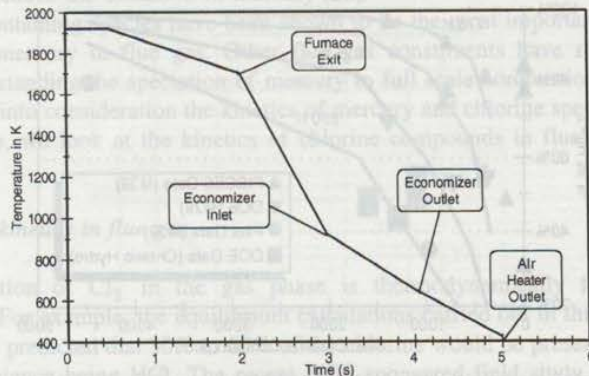


Fig. 3. Time-temperature history for pulverized coal-fired boiler.

combustion systems reported anywhere from 30% Hg^{+2} to 95% Hg^{+2} upstream of the APCD [4].

We therefore propose a hypothesis for mercury speciation in coal combustion flue gas which states that the Hg equilibrium in the gas is frozen below some temperature between 750 and 900 K (900°F to 1200°F). If we assume that the time–temperature history is similar for most power plants, then the temperature at which mercury speciation is fixed will depend entirely on the chlorine content of the coal. As Fig. 2 indicated, the chlorine content of the coal has a strong effect on the equilibrium distribution as a function of temperature. In order to test the hypothesis, data on mercury speciation in flue gas *and* on coal chlorine content are needed.

Data available from the literature on pilot and full scale mercury speciation measurement were assembled [12–17]. These data were measured at the inlet to the particulate collection device with either EPA Method 29 [12–16] or the Ontario Hydro method [17] used to measure mercury speciation. The mercury speciation results are compared with equilibrium predictions in Fig. 4. The percentage of mercury as gaseous Hg^{+2} is plotted as a function of coal chlorine content. The lines indicate hypothetical temperatures at which the equilibrium is frozen. Considerable scatter is seen in the data over a range of frozen equilibrium temperatures. However, the mercury speciation data were obtained using both EPA Method 29 and the newer Ontario Hydro method. The former method may overestimate the amount of Hg^{+2} by as much as 10% to 30% [18]. Such a correction to the Method 29 data would bring them closer to the Ontario Hydro data. The data are consistent with a cut-off temperature for mercury oxidation in the range of 800 to 850 K (980°F to 1070°F). Further work will be required to gather field data that provides a validation of this hypothesis.

In summary, equilibrium predicts complete oxidation of elemental mercury to HgCl_2 in coal-fired combustion flue gas at temperatures below about 725 K. The chlorine content of the coal determines the temperature below which HgCl_2 is thermodynamically stable.

Measurements in full scale combustion systems (circa 400 K) do not show complete oxidation of elemental mercury as predicted by equilibrium. *We conclude that the*

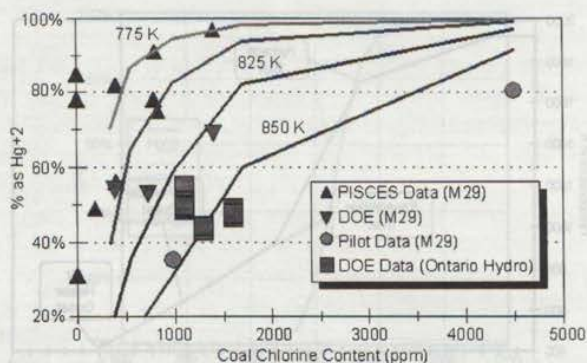


Fig. 4. Fraction of mercury as oxidized in flue gas at APCD inlet conditions as a function of coal chlorine content, comparison of field and pilot data with frozen equilibrium hypothesis.

assumption of equilibrium for mercury species in coal combustion flue gas is not valid. Consideration of a limited set of mercury speciation measurements indicates that mercury equilibrium in the flue gas is frozen at approximately 800 K.

3. Kinetics

Comparison of equilibrium calculations in the mercury system with field measurements strongly implicates kinetic limitations associated with the oxidation of elemental mercury. While little fundamental information on the rates of such oxidation reactions exists for mercury concentrations typical of coal combustion flue gas, some information can be obtained from global reaction rate studies conducted under waste incineration conditions. Hall et al. [19] examined the potential homogeneous gas phase reactions of mercury with Cl_2 , HCl , O_2 , NH_3 , NO , NO_2 , SO_2 , and H_2S at atmospheric pressure and temperatures ranging from ambient to 900°C. Reactions of elemental mercury (Hg^0) were evaluated through measurement of total gaseous Hg and Hg^0 in experiments conducted under both isothermal and decreasing temperature conditions. Reactions with HCl occurred rapidly at temperatures ranging from 500°C to 900°C, with approximately 90% reaction noted in 0.7 s in isothermal measurements at the highest temperature. Reactions with Cl_2 were also rapid, with 70% conversion occurring in 1.1 s at 500°C. Similarly, Gaspar et al. [20] examined the reaction of Hg^0 in simulated incinerator flue gas at temperatures of 400°C to 900°C and concluded that the process was kinetically limited.

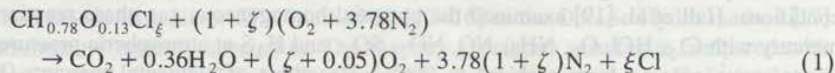
Other components of combustion flue gas also influence mercury oxidation in a minor way. Nitrogen dioxide has been shown to oxidize elemental mercury in the temperature range of 773 to 973 K (500°C to 700°C) [19,21], but the rates are much lower than those for HCl or Cl_2 . High concentrations (~ 1000 ppm) of NO_2 oxidized only 10% of elemental mercury in simulated flue gas at 613 K [19]. Elemental mercury does not react directly with SO_2 [19], but the presence of SO_2 in the gas reduces the amount of elemental mercury oxidized by HCl [21,22]. The presence of water vapor also was noted to reduce the oxidation of mercury [22].

Chlorine-containing species have been shown to be the most important for oxidation of elemental mercury in flue gas. Other flue gas constituents have relatively minor effects. Understanding the speciation of mercury in full scale combustion systems must therefore take into consideration the kinetics of mercury and chlorine species in flue gas. As a first step, we look at the kinetics of chlorine compounds in flue gas at realistic cooling rates.

3.1. Chlorine kinetics in flue gas

The formation of Cl_2 in the gas phase is thermodynamically favored at low temperatures. For example, the equilibrium calculations carried out in this study on four different coals predicted that 30% to 60% of the chlorine would be present as Cl_2 at 423 K with the balance being HCl . The recent DOE-sponsored field study of emission of HAPs from utility boilers reported molecular chlorine levels of 4%, 5%, and 45% of

total chlorine for the three plants reporting such data [23]. The formation of Cl_2 may be kinetically limited in the rapidly cooling flue gas which might reduce the gas-phase oxidation of elemental mercury relative to the equilibrium value. Kinetic calculations for the C–H–O–N–Cl system were carried out using the SENKIN code developed at the Sandia National Laboratories. This code models the time evolution of a homogeneous reacting gas mixture in an open system with a constant flow rate using the system mass balance, energy balance, and reaction rate expressions as the governing equations. Calculations were then carried out for chlorine transformations under conditions similar to those in a coal-fired boiler by using the CH_3Cl mechanism in the standard CHEMKIN-II code. The CH_3Cl mechanism includes 264 elementary reactions (documented in Ref. [24]). The initial composition was calculated according to the overall combustion reaction:



where ζ is the amount of excess air relative to stoichiometric and ξ is the chlorine content of the coal. The code used in this study assumes constant pressure, but allows the temperature to vary as a function of time. Prior to initiating the temperature-variant kinetic calculations, the system is allowed to react at 1925 K for 0.5 s to generate an equilibrium mixture of species and thus convert most of the chlorine to HCl. We then use either an idealized temperature history from furnace exit to APCD inlet for a coal fired power plant (Fig. 3) corresponding to an average cooling rate of approximately 300 K s^{-1} or a constant cooling rate of 200 or 500 K s^{-1} to examine homogeneous chlorine chemistry. The amount of excess air and the coal chlorine content were varied in the calculations in order to investigate their effects on chlorine speciation in the flue gas.

Fig. 5 shows the percentage of total chlorine calculated to be Cl_2 as a function of time. The initial chlorine content of the coal was assumed to be 2000 ppmw and 25% excess air was assumed for the combustion stoichiometry. It can be seen that Cl_2 is produced only when the temperature falls below 1200 K. At the end condition, 0.7% of the total initial chlorine has been transformed into Cl_2 .

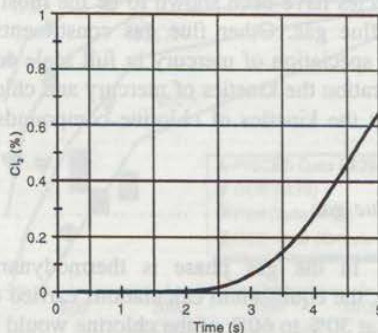


Fig. 5. Percentage of total chlorine in flue gas found as Cl_2 as a function of time assuming 2000 ppm Cl in coal and 25% excess air.

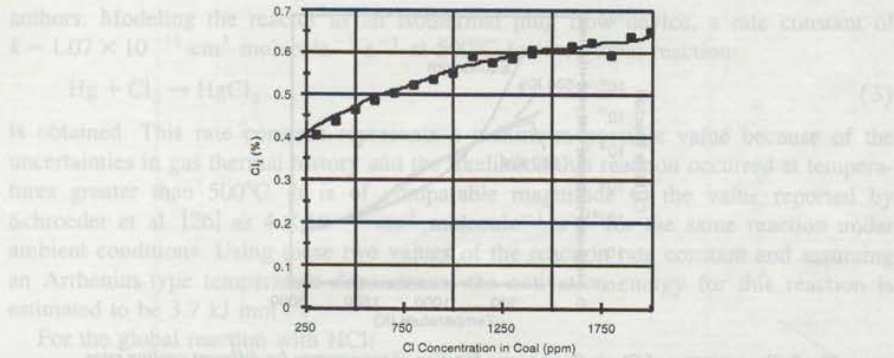


Fig. 6. Final percentage of total chlorine in flue gas found as Cl_2 as a function of chlorine content of coal, assuming 25% excess air.

Fig. 6 shows that as the concentration of chlorine in the coal increases, more is transformed into Cl_2 at the end condition. However, a 10-fold increase in coal chlorine content only increases the amount converted to Cl_2 by a factor of two. This shows that the conversion has a weak dependence on concentration. The effect of changes in excess air is shown in Fig. 7. As the excess air increases, more chlorine will be transformed into Cl_2 , but the increase is very small. At stoichiometric conditions, calculations showed almost no production of Cl_2 . A possible explanation is that the concentration of OH radical is lower for the stoichiometric case. OH is needed to produce significant amounts of atomic Cl, which then forms Cl_2 .

The production of molecular chlorine falls far below equilibrium levels given the high cooling rates in power plant flue gas. This is illustrated in Fig. 8 which compares the concentration of Cl_2 in the flue gas as a function of temperature calculated from reaction kinetics using cooling rates of 200 K s^{-1} and 500 K s^{-1} and from equilibrium.

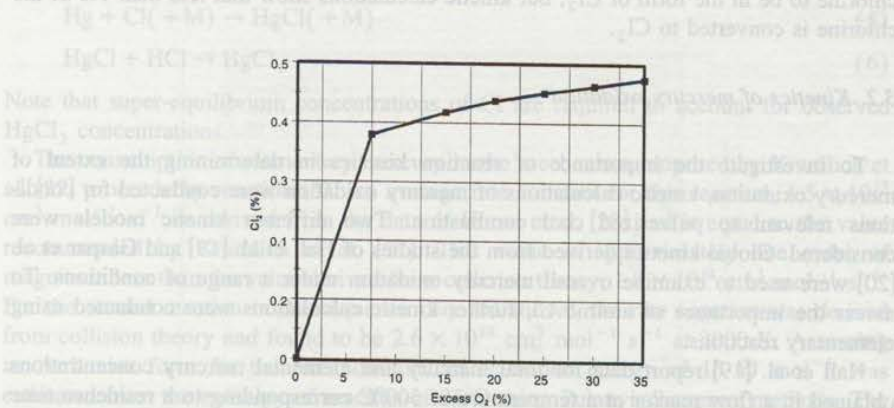


Fig. 7. Final percentage of total chlorine in flue gas found as Cl_2 as a function of excess air, assuming 500 ppm Cl in coal.

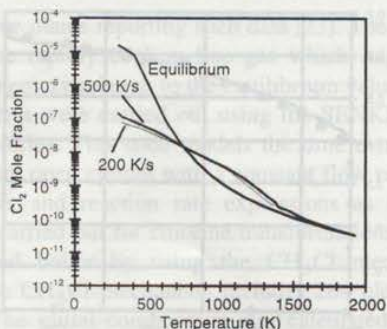


Fig. 8. Concentration of Cl_2 in flue gas as a function of temperature for different cooling rates.

Between 1400 and 750 K, the kinetically calculated concentration of Cl_2 with flue gas cooling is slightly higher than the equilibrium concentration. As the temperature drops below 750 K, the concentration of Cl_2 with flue gas cooling is much lower than the equilibrium value. A more detailed examination of the kinetic mechanism shows the three body reaction:



to be the pathway for production of Cl_2 . For the high cooling rates of practical combustion systems, this reaction is not fast enough at temperatures below 750 K to produce much molecular chlorine. The kinetic model thus predicts super-equilibrium concentrations of the chlorine radical at temperatures below 1500 K.

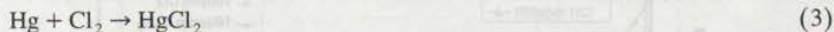
These calculations show that the conversion of HCl to Cl_2 in the flue gas of a coal-fired power plant is kinetically limited. At flame temperatures, chlorine is predicted to be HCl. At APCD inlet temperatures, equilibrium predicts as much as half of the chlorine to be in the form of Cl_2 , but kinetic calculations show that less than 1% of the chlorine is converted to Cl_2 .

3.2. Kinetics of mercury oxidation

To investigate the importance of reaction kinetics in determining the extent of mercury oxidation, kinetic calculations of mercury oxidation were conducted for conditions relevant to pulverized coal combustion. Two different kinetic models were considered. Global kinetics derived from the studies of Hall et al. [19] and Gaspar et al. [20] were used to examine overall mercury oxidation under a range of conditions. To assess the importance of atomic Cl, further kinetic calculations were conducted using elementary reactions.

Hall et al. [19] report data for total mercury and elemental mercury concentrations obtained in a flow reactor at a temperature of 500°C corresponding to a residence time of approximately 1.5 s. Upstream of the sampling point, temperatures are greater than 600°C [25], but peak temperatures and temperature profiles are not provided by the

authors. Modeling the reactor as an isothermal plug flow device, a rate constant of $k = 1.07 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 500°C for the global reaction:



is obtained. This rate constant represents a maximum possible value because of the uncertainties in gas thermal history and the likelihood that reaction occurred at temperatures greater than 500°C. It is of comparable magnitude to the value reported by Schroeder et al. [26] as $4 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the same reaction under ambient conditions. Using these two values of the reaction rate constant and assuming an Arrhenius-type temperature dependence, the activation energy for this reaction is estimated to be 3.7 kJ mol^{-1} .

For the global reaction with HCl:



Gaspar et al. [20] report a rate constant of $k = 2.20 \times 10^7 \exp(-3460/T) \text{ l mol}^{-1} \text{ s}^{-1}$ over the temperature range 400°C to 900°C. This latter rate constant was derived from experiments conducted at HCl concentrations of 300 and 3000 ppmv, mercury concentrations of 0.37 ppmv (approximately 10 to 20 times greater than typical values associated with pulverized coal combustion), and approximate residence times of 1 s.

In considering the global reactions of Hg with Cl_2 and HCl (Eqs. (3) and (4)), we ran both “reactions” simultaneously. The reason for doing this was that the rates were derived from studies in which only Cl_2 or HCl was injected, and thus represent reactions derived from those species alone. Since we believe Cl atom is responsible at the elementary level, this choice (considering both “reactions” simultaneously) ignores interplay between Cl derived from Cl_2 and HCl, and could thus be considered a maximum rate of conversion.

Studies of the mechanism of mercury oxidation at temperatures of 600°C and above by Kramlich et al. [27] suggest that the key oxidizing species is atomic Cl. Kramlich et al. propose a homogeneous pathway, governed by two principal steps:



Note that super-equilibrium concentrations of Cl are required to account for observed HgCl_2 concentrations.

The consumption of elementary mercury in the mechanism proposed by Kramlich et al. [27] proceeds by reaction (5). An average rate constant for this reaction, $1.5 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, is derived from the data of Horne et al. [28] and is equal to the value recommended by Kramlich et al. [27]. This value is approximately one order of magnitude less than the value derived from collision theory, $1.8 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. For the second reaction in the sequence (Eq. (6) above), the rate constant was derived from collision theory and found to be $2.6 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 2000 K. Assuming an Arrhenius form for the rate constant, an activation energy of 15 kJ mol^{-1} was estimated from the enthalpy of reaction at 25°C using Polanyi–Semenov methods. The pre-exponential factor was set equal to the value of the collision limited rate constant at 2000 K since at this temperature the exponential term approaches unity.

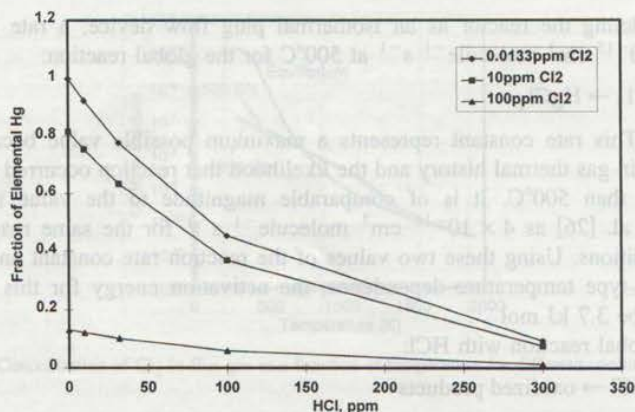


Fig. 9. Hg conversion as a function of HCl concentration at 773 K using global kinetics.

We considered the reverse of reaction (5) in the two-step elementary reaction sequence as well. The reverse rate constant was derived from the equilibrium constant using data from HSC and checked by evaluating free energy of formation values in the JANAF tables. No effect on the results was seen by including the reverse reaction. We did not consider the reverse of reaction (6). We assumed that HgCl levels would not build up in the vapor phase, so that the proposed two-step reaction mechanism converts the HgCl at collision-limited rates to HgCl₂.

3.3. Results of mercury kinetic calculations

Mercury consumption rates were derived from kinetic calculations conducted using the global reaction sequence (both Eqs. (3) and (4)) and the two primary steps of the mechanistic pathway (Eqs. (5) and (6)). Mercury concentrations of 0.15 ppmw in the

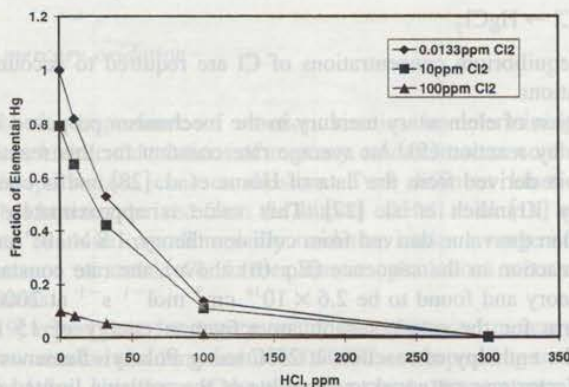


Fig. 10. Hg conversion as a function of HCl concentration at 973 K using global kinetics.

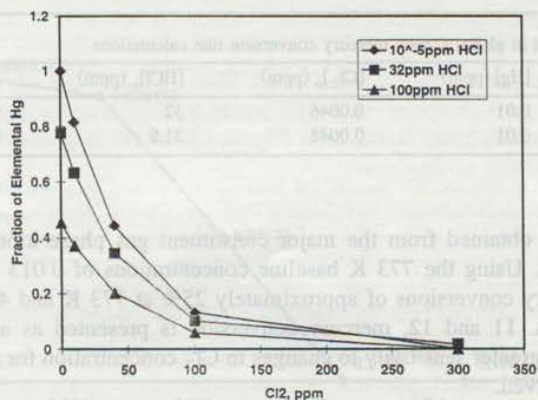


Fig. 11. Hg conversion as a function of Cl_2 concentration at 773 K using global kinetics.

coal, corresponding to 0.01 ppmv in the flue gas, were used. Concentrations of the oxidants HCl, Cl_2 , and Cl were taken from the combustion gas kinetic calculations described above. Reactions were examined at the isothermal conditions of 773 and 973 K as well as under cooling rates of 200 and 500 K s^{-1} , in each case starting from a peak temperature of approximately 973 K. Note that the starting temperature of 973 K is outside of the 300–773 K range used to derive the rate constant for the global reaction involving molecular chlorine (Eq. (3)). We are therefore assuming that the moderate temperature dependence of this reaction rate remains unchanged between 773 and 973 K, an assumption necessitated by a lack of high temperature rate data.

In Figs. 9 and 10, mercury conversion under isothermal conditions is presented as a function of HCl concentrations at temperatures of 773 and 973 K, respectively. A residence time of 2 s was used in these calculations. Baseline Cl_2 and HCl concentra-

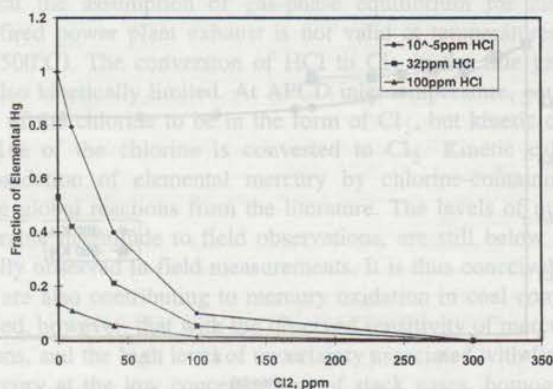


Fig. 12. Hg conversion as a function of Cl_2 concentration at 973 K using global kinetics.

Table 2
Initial conditions used in global kinetic mercury conversion rate calculations

dT/dt	[Hg] (ppm)	$[Cl_2]_0$ (ppm)	$[HCl]_0$ (ppm)	T range (K)
-200 K s^{-1}	0.01	0.0046	32	962.6–300
-500 K s^{-1}	0.01	0.0048	31.9	971.4–300

tions were those obtained from the major constituent gas phase kinetic simulation at each temperature. Using the 773 K baseline concentrations of 0.013 ppm Cl_2 and 32 ppm HCl, mercury conversions of approximately 25% at 773 K and 45% at 973 K are obtained. In Figs. 11 and 12, mercury conversion is presented as a function of Cl_2 concentration. A greater sensitivity to changes in Cl_2 concentration for the global kinetic sequence is observed.

To investigate mercury oxidation under thermal profiles associated with coal combustion, calculations using the combined global reactions were also conducted at cooling rates of 200 and 500 K s^{-1} . Initial conditions for these calculations are presented in Table 2. As shown in Fig. 13, mercury conversion is higher at the slower cooling rate, a result of increased residence time at higher temperatures. For the cooling rate of -200 K s^{-1} , an overall conversion of 24% is achieved in 2 s. At the higher cooling rate, an asymptotic value of 10.5% conversion is reached in 1 s.

Mercury concentration profiles derived from the elementary reaction sequence (5)–(6) at a temperature of 773 K are presented in Fig. 14. Use of this reaction sequence is seen to result in complete conversion of elemental mercury within 1 s. Order of magnitude reductions in the atomic Cl concentration significantly reduced the conversion, however. Mercury conversions of comparable magnitude to the field data were obtained at atomic Cl concentrations of 0.00173 ppm, 100-fold less than those suggested by the major constituent gas phase reaction chemistry. This suggests that accurate prediction of

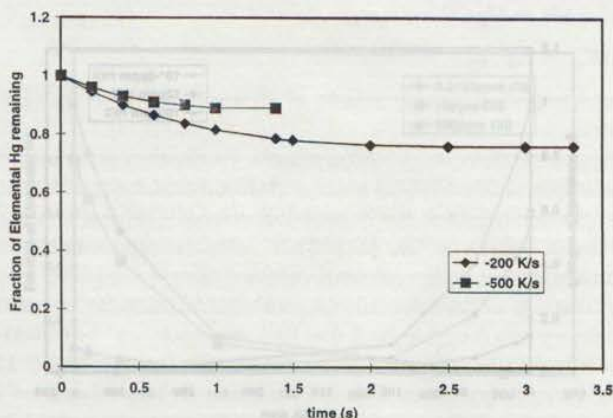


Fig. 13. Hg conversion for two different cooling rates.

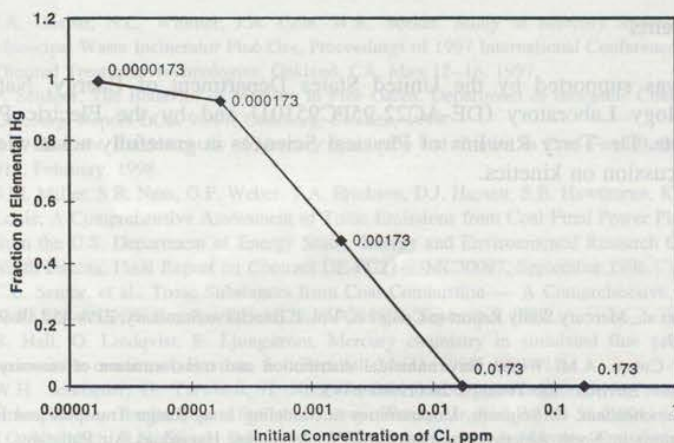


Fig. 14. Hg conversion as a function of Cl atom concentration at 773 K and 1 s residence time.

mercury speciation in coal combustion systems using a mechanistic model will require detailed knowledge of the super-equilibrium chlorine atom concentrations as a function of temperature and cooling rate.

4. Conclusions

Chlorine-containing species have been shown to be the most important for oxidation of elemental mercury in flue gas. Other flue gas constituents (e.g., H_2O , SO_2 , NO_2) may have secondary effects on the rate of homogeneous oxidation of mercury. We have demonstrated that the assumption of gas-phase equilibrium for mercury-containing species in coal-fired power plant exhaust is not valid at temperatures below approximately 800 K (500°C). The conversion of HCl to Cl_2 in the flue gas of a coal-fired power plant is also kinetically limited. At APCD inlet temperature, equilibrium predicts as much as half of the chlorine to be in the form of Cl_2 , but kinetic calculations show that less than 1% of the chlorine is converted to Cl_2 . Kinetic calculations of the homogeneous oxidation of elemental mercury by chlorine-containing species were carried out using global reactions from the literature. The levels of mercury oxidation, while of comparable magnitude to field observations, are still below the 40% to 80% oxidation typically observed in field measurements. It is thus conceivable that heterogeneous reactions are also contributing to mercury oxidation in coal combustion systems. It must be stressed, however, that with the observed sensitivity of mercury conversion to Cl_2 concentrations, and the high level of uncertainty associated with field measurements of oxidized mercury at the low concentrations of stack gases, homogeneous pathways alone may be important.

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Abstract

Trace elements in coal have diverse modes of occurrence that will greatly influence their behavior in many coal utilization processes. Mode of occurrence is important in determining the partitioning during coal cleaning by conventional processes, the susceptibility to oxidation upon exposure to air, as well as the changes in physical properties upon heating. In this study, three complementary methods were used to determine the concentrations and chemical states of trace elements in pulverized samples of four US coals: Pittsburgh #1, Illinois No. 6, Silliman acid Bitum, and Wyodak-seam. Neutron Activation Analysis (NAA) was used to measure the absolute concentration of elements in the parent coals and in the size- and density-fractionated samples. Chemical leaching and X-ray absorption fine structure (XAFS) spectroscopy were used to provide information on the form of occurrence of an element in the parent coals. The compositional differences between size-segregated coal samples of different density mainly reflect the large density difference between minerals, especially pyrite, and the organic portion of the coal. The heavy density fractions are therefore enriched in pyrite and the elements associated with pyrite, as also shown by the leaching and XAFS methods. Nearly all the As is associated with pyrite in the

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