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A Mechanism for Mercury Oxidation in Coal-Derived Exhausts

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ABSTRACT

This paper evaluates an elementary reaction mechanism for Hg⁰ oxidation in coal-derived exhausts consisting of a previously formulated homogeneous mechanism with 102 steps and a new three-step heterogeneous mechanism for unburned carbon (UBC) particles. Model predictions were evaluated with the extents of Hg oxidation monitored in the exhausts from a pilot-scale coal flame fired with five different coals. Exhaust conditions in the tests were very similar to those in full-scale systems. The predictions were quantitatively consistent with the reported coal-quality impacts over the full range of residence times. The role of Cl atoms in the homogeneous mechanism is hereby supplanted with carbon sites that have been chlorinated by HCl. The large storage capacity of carbon for Cl provided a source of Cl for Hg oxidation over a broad temperature range, so initiation was not problematic. Super-equilibrium levels of Cl atoms were not required, so Hg was predicted to oxidize in systems with realistic quench rates. Whereas many fundamental aspects of the heterogeneous chemistry remain uncertain, the information needed to characterize Hg oxidation in coalderived exhausts is now evident: complete gas compositions (CO, hydrocarbons, H₂O, O₂, NO₂, SO₂), UBC properties (size, total surface area), and the ash partitioning throughout the exhaust system are required.

IMPLICATIONS

The extent of Hg oxidation determines the portion of Hg in furnace exhausts that is water-soluble and, therefore, amenable to removal with SO_2 scrubbers. This paper introduces a reaction mechanism that interprets the extents of Hg oxidation reported for five coals in a laboratory-scale furnace within useful quantitative tolerances. Chemistry both in the gas phase and on UBC particles is essential for accurate simulations of Hg oxidation in coalderived exhausts under utility exhaust conditions.

INTRODUCTION

The Hg emissions from coal-fired power plants are highly dependent on Hg speciation, because the predominant oxidized species, HgCl₂, is water-soluble and therefore dissolves in scrubbing solutions, whereas Hg⁰ is insoluble and passes into the smokestack, unless it is captured by a sorbent. Unfortunately, all the Hg leaving a furnace is elemental, and its subsequent oxidation under typical exhaust-flue conditions is kinetically limited, so the abundance of oxidized Hg expected under thermochemical equilibrium does not materialize in actual exhaust systems.

We would like to be able to predict the speciation of Hg in utility exhaust streams to manage the coal-quality impacts and to evaluate competing control strategies. Recently, marked strides have been made in unraveling the reaction mechanism for homogeneous Hg oxidation,14 including reasonable evaluations with all the laboratoryscale test data recorded with synthetic exhausts in which HCl is the main Cl species,³ as it is in coal-derived exhausts. This paper significantly broadens the scope of such evaluations by using data on coal-derived exhausts, in which inorganic and carbonaceous particles were present at the typical loadings for utility exhaust systems. The added complexity could not be depicted with the formerly satisfactory homogeneous reaction mechanism, so a skeletal heterogeneous reaction scheme involving unburned carbon (UBC) particles was developed and introduced to satisfy the evaluation.

TEST FACILITY AND EVALUATION DATA

This brief overview of the facility and test procedures are supported by a separate, more detailed description.⁵ The pulverized coal flame (PCF) was fired in a heated 30-cm tube through a single swirl burner with both primary and secondary air streams, as seen in Figure 1. Overfire air was added about halfway down the furnace. The firing rate was fixed for all coals at 200,000 kcal/m³-hr. The entire



Figure 1. The PCF test facility.

exhaust stream was first diverted into the branch of a tee to eliminate bottom ash, then passed through a cyclone at 480–500 °C to remove most of the fly ash. An air-cooled sampling probe extracted 20 SLPM of the exhaust through one of nine ports downstream of the cyclone into the line to a heated silica thimble filter. Another line beyond the final filter moved the particle-free exhaust into impingers for detection of Hg vapors.

The data sets contained the feed rates of coal and total (wet) exhaust, plus the exhaust concentrations of O_{γ} NO_x, SO_y, and, in a few cases, CO. The total recovered ash was apportioned to bottom ash, cyclone ash, and filter ash. Similarly, the loss-on-ignition (LOI) and percentages of total Hg in each of these three residues were reported. Each test was run for 2-4 hr to recover the solid samples and complete the various analyses. A total Hg balance for each run was formulated by incorporating the vapor-Hg fraction into the solids distribution. Based on the dimensions of the furnace outlet and an assumed furnace exit gas temperature of 1000-1100 °C, we used an inlet temperature of 700 °C for the sidearm in all simulations. Temperatures at the sampling probe inlet, and at the inlet and outlet to the final filter housing, were reported for each case. All dimensions were specified; therefore, nominal residence times could be estimated from plug-flow velocities and the temperature profiles across each unit in the exhaust system, assuming that they were linear. For the range of sampling port locations used in the tests, the total estimated residence times increased from 0.44 to 1.03 sec, and the temperatures at the probe inlet fell from 310 to 123 °C. As seen in Figure 2, the nominal quench rates in the tests were several hundred degrees per second, which is consistent with estimates for full-scale utility exhaust systems.



Figure 2. Assigned profiles of temperature and residence time (top), and predicted profiles of the concentrations of Cl atoms (solid curve) and Cl_2 (dotted curve) for the simulations of Case 3, with Coal E based on the homogeneous/heterogeneous mechanism (bottom). The predicted extent of Hg oxidation appears in the lower panel (dashed curve).

The coal properties are reported in Table 1. This suite of samples represents high volatile bituminous coals, except for Coal E, which is borderline subbituminous. The Cl and Hg contents cover broad ranges, whereas the other properties are typical for coals of these ranks. Note the unusually high Cl content of Coal D.

REACTION MECHANISMS AND COMPUTER SIMULATIONS

The total amount of Hg in coal-derived exhausts is typically less than 10 ppbv.6 Consequently, Hg cannot possibly affect the concentrations of any of the species that participate in its own oxidation, because all are present at much higher concentrations. In other words, chemistry that does not involve Hg sets the concentrations of Cl, Cl₂, O, OH, and HO₂, which subsequently participate in the Hg oxidation. As explained elsewhere,^{3,7} the homogeneous mechanism includes eight reactions for Hg oxidation that involve Hg⁰, HgCl, HgCl₂, Cl, Cl₂, HCl, HOCl, H, and OH. This submechanism represents a Cl atom recycle, whereby the Cl atom consumed in the partial oxidation of Hg⁰ into HgCl is regenerated in the subsequent oxidation of HgCl by Cl₂ into HgCl₂. All supporting kinetic submechanisms were taken directly from the literature and used without modification. The Cl oxidation

Table 1. Coal properties.

	Coal A	Coal B	Coal C	Coal D	Coal E
Proximate Analysis, as	rec'd wt. %				
Moisture	1.7	2.3	4.2	4.6	3.1
Ash	9.8	12.6	8.2	10.6	14.5
Volatiles	33.1	27.4	27.6	26.0	40.9
Fixed Carbon	55.4	57.7	60.0	58.8	41.5
Ultimate Analysis, daf	wt %				
C	82.8	85.4	82.9	81.1	78.2
H	5.3	5.2	4.8	4.4	5.9
0	9.8	7.3	10.0	12.0	13.6
N	1.6	1.9	2.0	1.8	1.3
S	0.6	0.3	0.3	0.7	1.1
CI, ppm	233	408	176	2304	176
Hg, ppb	114	49	29	44	119

submechanism^{8,9} accounts for a broad range of HCl concentrations and incorporates additional coupling of Cl chemistry and NO_x chemistry.⁸ The moist CO oxidation submechanism¹⁰⁻¹² is an update of previous efforts by Dryer and coworkers and describes the kinetics of moist CO oxidation at low to moderate temperatures, allowing for perturbations from NO_x conversion¹¹ and interactions with NO_x and SO_x conversion chemistry.¹¹ The H/N/O submechanism^{12,13} describes the kinetics of NO_x conversion at low to moderate temperatures. In total, 102 elementary chemical reactions are included in the homogeneous Hg⁰ oxidation mechanism.

As shown later, the homogeneous Hg oxidation mechanism was unable to interpret the dynamics and coal-quality impacts in the reported data sets, so a skeletal heterogeneous reaction scheme was added with the following steps:

$$StSA(s) + HCl \rightarrow StCl(s) + H$$
 (1)

$$StCl(s) + Cl \rightarrow Cl_2 + StSA(s)$$
 (2)

$$StCl(s) + Hg \rightarrow StSA(s) + HgCl$$
 (3)

There are two types of carbon sites in the mechanism: StSA(s) denotes an unoccupied site, and StCl(s) denotes a chlorinated site. Unoccupied sites may be chlorinated by deposition of HCl with release of H atoms into the gas phase, according to eq 1. Chlorinated sites are freed either by recombination with a Cl atom, to generate Cl₂ vapor (eq 2), or by partial oxidation of Hg into HgCl on a chlorinated site (eq 3). Competitive adsorption and chemistry among many other exhaust species, particularly SO_x and NO_x, were omitted for lack of kinetic information.

A preliminary regression analysis of the reported extents of Hg oxidation indicated that the most important test variables were the carbon mass flow rate in the fly ash and the percentage of Hg recovered in the filter ash. Multivariate regressions improved the regression coefficients but did not identify any other parameters with distinctive roles in the data sets, provided that the carbon mass flow rate in the fly ash was included in the regression. Also, HCl does adsorb onto carbon at low temperatures, although the only data available¹⁴ are for activated carbon fibers with no structural similarities to UBC from a coal-fired furnace. Based on these tendencies, the proposed heterogeneous chemistry was restricted to only the carbon in the various ash fractions. That is, in the simulations, the surface areas for

heterogeneous chemistry were based on a

mean size for only the suspended carbon in the entrained ash. Inorganic components of the ash did not participate. This premise is consistent with reports of Hg oxidation over beds of carbon particles¹⁵ but would be unable to depict the distinctive Hg oxidation behavior of fly ashes with elevated levels of iron oxides^{16,17} or, perhaps, from subbituminous coals with high Ca levels.¹⁸ Calcium compounds can be chlorinated by HCl adsorption.¹⁹

To evaluate the heterogeneous reaction scheme, three rate constants plus the participating surface area of the carbon particles in the system must be specified. Rate constants have not been reported for the proposed steps, and the sizes of UBC were not monitored in the tests. Accordingly, a procedure that reduced the unknowns to a single adjustable parameter was devised: the kinetics in the simulations were based on sticking coefficients, which are factors between zero and unity that multiply the collision rate among the gas-phase species and the surface reaction sites. Physically, they represent the probability that a specific collision will form the products indicated in that particular reaction channel. Sticking coefficients for all three reactions in the heterogeneous submechanism were set to unity, and the size of UBC in the final filter ash was regarded as a single adjustable parameter in the heterogeneous analysis. This parameter value was assigned by matching the prediction for Case 3 with Coal E to the reported extent of oxidation. The assigned size of filter-ash UBC was applied to all other cases, so that no model parameters were adjusted in the simulations of the other 19 test cases.

The reaction mechanisms were incorporated into a simulator for the testing system with the Plug routine in Reaction Design's Chemkin III software. The feed rates of coal and air were adjusted to match the reported exhaust gas flow rate and excess O_2 level. The initial exhaust composition was based on an equilibrium calculation at 700 °C, the assumed sidearm inlet temperature, except that

the reported CO and NO levels were imposed in the inlet gas composition. Temperature and residence time were specified as functions of distance along the 1-D reactor coordinate from the system geometry, the reported exhaust flow rates, and the reported temperatures at various points along the system. The simulations were terminated when the exhaust was cooled to 100 °C, which was cooler than the temperature range in which the oxidation kinetics reached their ultimate extent of Hg oxidation. The area for heterogeneous chemistry per unit reactor length was assigned from

Sample	Case	Time (sec)	т _s (°С)	0 ₂ (%)	CO (ppm)	NO (ppm)	LOI (wt %)	(LOI) _{FA} (wt %)	Hg-Bal (%)	X _{ox} (%)
Coal A	1	0.44	305	4.1	nmª	nm	4.2	5.0	87.1	39.6
	2	0.44	255	4.6	nm	nm	4.8	21.2	77.1	17.1
	3	0.78	150	4.3	nm	nm	4.4	12.2	85.7	23.3
	4	1.03	120	4.5	nm	nm	4.9	22.8	55.6	11.2
Coal B	1	0.44	270	nm	nm	nm	1.9	7.3	82.7	35.2
	2	0.59	203	4.1	115	320	4.0	9.7	71.8	36.7
	3	0.78	150	4.0	90	335	3.2	8.9	71.5	50.6
	4	0.89	124	4.0	70	305	3.7	9.4	60.3	72.4
Coal C	1	0.44	310	nm	nm	nm	2.8	6.6	36.9	60.0
	2	0.59	223	4.1	80	370	4.2	13.1	42.8	34.2
	3	0.78	157	4.2	110	370	4.7	14.7	66.6	40.5
	4	0.89	124	4.1	50	390	3.4	7.9	88.7	29.1
Coal D	1	0.59	244	4.1	nm	380	4.9	7.0	89.8	94.7
	2	0.78	168	4.2	nm	280	5.5	7.2	102.8	88.6
	3	0.89	138	4.2	nm	375	4.2	6.7	128.1	96.2
Coal E	1	0.44	290	4.2	nm	280	1.3	4.6	57.9	45.1
	2	0.59	240	4.4	nm	295	1.1	3.9	73.4	24.5
	3	0.78	169	4.2	nm	280	1.1	4.4	69.2	53.4
	4	0.89	169	4.3	nm	235	0.7	3.7	65.8	49.7
	5	1.03	123	4.3	nm	295	1.0	4.7	52.2	59.6

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^anm means not measured.

Table 2. Exhaust conditions.

the mean diameter of filter-ash UBC particles that was assigned in the calibration for Case 3 with Coal E. This value was entered into Surface Chemkin to obtain solutions from the heterogeneous reaction mechanism.

The density of UBC was assigned as 0.45 g/cm³, and the initial density of carbon sites was assigned as 6×10^{-9} mol/cm², based on the site density of a graphitic lattice. The baseline size specifications for the UBC were 86.5 µm up to the cyclone, then 9.3 µm for the filter-ash UBC. The assumed size of the initial UBC of 86.5 µm is larger than the mean size of the coal, consistent with characterization work.20 The impact of carbon collection at the cyclone and final filter, and also the impact of temperature and gas velocity variations throughout the various components in the PCF exhaust system, were incorporated into the simulations. Whereas the carbon surface per unit reactor length increases in direct proportion to the flow area, it is inversely proportional to the falling gas temperature, through a dependence on exhaust gas density. Once the flow passed into the final filter, the area for heterogeneous reaction was set to zero.

RESULTS

Operating conditions for each test case are collected in Table 2. The data sets contain the percentages of the coal-Hg recovered in bottom ash, cyclone ash, and filter ash, as oxidized vapor species, and as elemental Hg vapor. As seen in Table 2, the closures on the Hg balances based on these independent determinations were widely variable with a median value of 70%. It was assumed that the extent of Hg oxidation was independent of the deficit in the Hg balance, which is equivalent to assuming that Hg speciation did not affect the delivery or detection of oxidized or elemental Hg at the impingers. Accordingly, the extents of oxidation were assigned as

$$X_{\rm OX} = \frac{100 \frac{O}{E}}{1 + \frac{O}{E}}$$
(4)

where X_{0x} is the extent of homogeneous Hg oxidation, and O and E are the reported percentages of oxidized and elemental Hg from the PCF tests. The assigned extents of oxidation are collected in Table 2. Coal D has uniformly high extents of Hg oxidation, whereas the other coals have extents that are roughly half as large. The spread in the assigned extents of Hg oxidation is very significant, and the ratio of the greatest to the least values is at least 2 for all samples except Coal D. These variations do not correlate with breaches in the Hg balances. Indeed, the regression of the extents of Hg oxidation on the Hg balance closures had an r² correlation coefficient of only 0.247. Note also that the measured extents of oxidation do not increase for progressively longer residence times or correlate with variations in the sampling temperatures. There also were variations in the levels of CO, NO, excess O₂,

bottom ash fraction, and cyclone collection efficiency among the data sets for each coal. These variations account for some of the variability among the reported extents of Hg oxidation in Table 2 and were factored into the simulations, as explained previously.

The measured extents of oxidation are compared with two sets of predictions in Table 3: one based on only the homogeneous reaction mechanism, and one based on the combined homogeneous/heterogeneous mechanism. Predictions based on only the homogeneous mechanism show complete oxidation at the longest residence time for all coals except Coal D. In contrast, only the measured extents for Coal B show more oxidation for progressively longer residence times, which is probably coincidental. Coal D is the only coal whose reported extents of oxidation approach 100%, exactly opposite to the coal-quality impacts predicted by the homogeneous reaction mechanism.

The predictions based on the heterogeneous/homogeneous mechanism cover only four coals, because the partitioning of the fly ash into bottom, cyclone, and filter ash was not monitored with Coal A, so the surface area of UBC could not be assigned. The combined mechanism does depict the distinctive behavior of Coal D, in terms of extents of oxidation that are much greater than those for the other coals and only slightly lower than the reported values. Moreover, the predictions do not increase

Table 3. Evaluation of model prediction	٦S.
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Sample	Case	Time (sec)	Hg-Bal (%)	Hg Oxidation (%)			
				Mes'd	Homo.	Ho/Het	
Coal A	1	0.44	87.1	39.6	58.5	Na	
	2	0.44	77.1	17.1	58.5	Na	
	3	0.78	85.7	23.3	100.0	Na	
	4	1.03	55.6	11.2	100.0	Na	
Coal B	1	0.44	82.7	35.2	19.3	27.4	
	2	0.59	71.8	36.7	53.7	52.1	
	3	0.78	71.5	50.6	100.0	64.6	
	4	0.89	60.3	72.4	98.9	56.7	
Coal C	1	0.44	36.9	60.0	21.4	42.3	
	2	0.59	42.8	34.2	5.3	46.3	
	3	0.78	66.6	40.5	87.6	60.7	
	4	0.89	88.7	29.1	100.0	52.1	
Coal D	1	0.59	89.8	94.7	47.8	78.4	
	2	0.78	102.8	88.6	24.7	68.9	
	3	0.89	128.1	96.2	80.5	88.9	
Coal E	1	0.44	57.9	45.1	2.5	37.9	
	2	0.59	73.4	24.5	60.8	39.8	
	3	0.78	69.2	53.4	51.2	53.5	
	4	0.89	65.8	49.7	57.2	48.6	
	5	1.03	52.2	59.6	99.4	78.3	

The dynamics in the simulations in Figure 2 indicate where the Hg is oxidized in the PCF exhaust system. The profiles of temperature and residence time for Case 3 with Coal E appear in the top panel, including the locations of the cyclone, sampling probe inlet, and final filter. These profiles begin at the sidearm inlet and end at the inlet to the impingers. Oxidation of Hg began at 6 m and continued through 13 m, where the temperature decreased from 370 to 130 °C. The quench rate across these positions was 600 °C/sec. Flow velocities decreased after the cyclone, then remained constant to the inlet of the final filter, where there was a significant deceleration. Consequently, the residence time profile is uniform across the entire system, except for the final filter. The profile of UBC surface area per unit reactor length (not shown) was also uniform at 2×10^{-5} cm²/cm until it surged to 1.1×10^{-3} in the final filter. Downstream of the final filter there were no carbon particles to sustain heterogeneous chemistry.

As seen in the lower panel of Figure 2, nearly all the Hg oxidation occurred in the delivery lines from the cyclone to the final filter, although the excessive UBC surface area in the final filter caused the extent of oxidation to surge from 40 to 53.5%. There was no oxidation through the cyclone outlet, even though the Cl atom concentration surged to its maximum value of 70 ppb in this re-

gion. Cl atoms were produced primarily by the decomposition of COCl and were eliminated by the homogeneous attack of COCl and by the heterogeneous recombination on chlorinated carbon sites, according to eq 2. Both destruction channels produced Cl_2 , so the decay in the Cl atom level coincided with the accumulation of Cl_2 to its steady-state value of just less than 0.4 ppm. Once established, the level of Cl_2 remained constant throughout. All the partial oxidation of Hg^0 into HgCl occurred on chlorinated carbon sites, according to eq 3. The subsequent oxidation of HgCl by Cl_2 into HgCl₂ was homogeneous and essentially instantaneous.

The homogeneous mechanism predicted significantly different dynamics for the same operating conditions, as seen in Figure 3. The initial surge in the Cl atom and Cl_2 concentrations before 1 m was followed by a much larger surge at 7.7 m, which brought the Cl atom level to 430 ppb and the Cl_2 level to 3.6 ppm, both of which are almost 10 times larger than in Figure 2. The much higher Cl atom level sustained homogeneous partial oxidation of Hg into HgCl,



Figure 3. Predicted profiles of the concentrations of CI atoms (solid curve) and Cl_2 (dotted curve) for the simulations of Case 3, with Coal E based on the homogeneous mechanism only. The predicted extent of Hg oxidation is shown by the dashed curve.

which was subsequently oxidized by Cl_2 into HgCl_2 . In addition, HgCl_2 was destroyed by Cl atoms and OH, producing HgCl plus Cl_2 and HOCl, respectively. Production of Cl atoms from the decomposition of HOCl continued to sustain Hg oxidation, until the exhaust was cooled to the lowest temperature in the simulations, 100 °C.

Based on the reasonably accurate predictions from the homogeneous/heterogeneous mechanism, sets of parameters related to coal quality, the combustion conditions, and ash partitioning were evaluated in parametric sensitivity studies. The baseline parameters were assigned from Case 3 with Coal E, and the coal and airflow rates were adjusted to maintain the same overall stoichiometric ratio for all parameter variations. Among the coal-quality parameters, variations over the practical ranges of coal-C, coal-H, and coal-Hg changed the predicted extent of Hg oxidation by less than 10%. As seen in Figure 4, the extent of oxidation increased in proportion to increases in coal-Cl, up to 0.07 dry-ash-free (daf) wt %, then the effect began to saturate. It increased from 50 to 62% when the coal-Cl content was increased from 0.01 to 0.10 daf wt %. However, the level of coal-Hg had little impact.

The impact of variable combustion conditions was evaluated in terms of the levels of CO, NO, and O_2 in the exhaust and of the overall LOI level. Predicted extents of oxidation increased from 28 to 54% for CO levels from 1 to 100 ppm but were constant thereafter. Extents of oxidation fell by 15% when the excess O_2 level was increased from 0 to 6%. The extent of oxidation passed through a maximum at 70 ppm NO, but remained uniform for NO levels greater than 300 ppm. However, the maximum was only 5% greater than the asymptotic value; therefore, the homogeneous/heterogeneous mechanism does not predict the acute sensitivity to NO seen with only the homogeneous mechanism.³



Figure 4. Predicted impact of variations in coal-Cl (solid curve) and coal-Hg (dashed curve) based on the homogeneous/heterogeneous mechanism for Case 3 with Coal E.

The predicted extent of oxidation is essentially independent of the overall LOI level in the PCF system, because no Hg oxidizes before the cyclone outlet.

All the parameters related to ash and UBC partitioning are very important, except for the level of bottom ash removal. Indeed, the predicted extent of Hg oxidation is directly proportional to the surface area of UBC in the flow downstream of the cyclone, according to the rate associated with eq 3. Consequently, the predicted extents increased from 18 to 80% when the cyclone collection efficiency was reduced from 99 to 92% and when the LOI in the filter ash was increased from 1 to 10%. The extents also were inversely proportional to the square of the size of the filter ash UBC and nearly proportional to the LOI of the ash from the final filter, as seen in Figure 5.

DISCUSSION

This evaluation shows that a heterogeneous reaction mechanism was needed to initiate Hg oxidation under utility exhaust conditions and also to sustain the partial oxidation of Hg into HgCl. The heterogeneous Hg mechanism introduced here represents the chlorination of carbon in the ash by HCl, with subsequent recombination of Cl atoms and partial oxidation of Hg into HgCl on the chlorinated sites. In conjunction with the original homogeneous reaction mechanism, it depicted the observed coal-quality impacts in the PCF tests within useful quantitative tolerances without heuristic adjustments to the kinetic parameters or operating conditions.

The same homogeneous mechanism previously interpreted four data sets on Hg oxidation in synthetic exhausts. The predictions for these tests generally were



Figure 5. Predicted impact of variations in size of UBC particles (solid curve), and the LOI in the filter ash (dashed curve) based on the homogeneous/heterogeneous mechanism for Case 3 with Coal E.

within experimental uncertainty across a broad domain of gas compositions,^{3,7} corroborating a Cl atom recycle process whereby Cl atoms partially oxidize Hg⁰ into HgCl, which is then subsequently oxidized by Cl₂ into HgCl₂. This interpretation has no explicit role for HCl and requires super-equilibrium levels of Cl atoms to sustain the partial Hg oxidation. The very rapid quenching imposed in the tests with synthetic exhausts was responsible for the excessive Cl atom concentrations.

When the homogeneous reaction mechanism was applied to the conditions in the exhaust systems of coalfired furnaces, where quench rates are much slower, several problems surfaced. Without rapid quenching, Cl atom concentrations usually remained below the threshold for initiation of Hg oxidation. Also, in cases with appreciable Hg oxidation, the oxidation persisted through the lowest temperatures in the simulations, because the rate of Cl atom recombination is slow. In the evaluation of the PCF data, this problem became apparent as essentially complete Hg oxidation for the longest residence times with four of the five coals, which was contradicted by the data and by the reported coal-quality impacts.

Adding the heterogeneous submechanism rectified these problems by supplanting Cl atoms with a chlorinated carbon surface. The surface is chlorinated by HCl, the most abundant Cl species in coal-derived exhausts, and the large storage capacity of carbon for Cl ensures that a source of Cl will be present to oxidize Hg over a broad temperature range, so initiation is not problematic. Super-equilibrium levels of Cl atoms are no longer necessary, so Hg is predicted to oxidize for systems with realistic quench rates. The predicted concentrations of both Cl atoms and Cl_2 were almost an order of magnitude less than those with the homogeneous mechanism only. Most important, the predicted extents of Hg oxidation for the longest residence times were not excessive, and the complete mechanism identified the distinctive behavior of Coal D. In addition, recent studies with X-ray absorption fine structure spectroscopy revealed Hg-Cl bonds on carbon surfaces after sorption by either Hg⁰ or Hg²⁺ in synthetic flue gases that contained moisture, SO₂, and HCl.²¹

Of course, this implementation of a heterogeneous submechanism for Hg oxidation has not yet extended beyond the phenomenological. Many other species, including S and N species, compete for the available adsorption sites on UBC particles in coal-derived exhausts. So the real heterogeneous chemistry is undoubtedly more complex than proposed. It also is likely that other forms of particulates participate with some coals, particularly fly ash, with elevated levels of iron oxide and calcium. Notwithstanding such basic unresolved aspects in the mechanism, the information needed to characterize Hg oxidation in coalderived exhausts is now evident: complete gas compositions (CO, hydrocarbons, H₂O, O₂, NO_x, SO_x), UBC properties (size, total surface area), and the ash partitioning throughout the exhaust system, including LOI levels at every collection unit, are required. Tests with synthetic gas mixtures are much less relevant than those with coalderived exhausts, because they do not sustain the same chemistry. And tests in which various particulate forms can be introduced at will are needed to confirm the essential role for heterogeneous chemistry proposed here.

CONCLUSIONS

Under realistic coal-derived exhaust conditions, the analysis of the PCF data sets supports the following conclusions:

- Extents of Hg oxidation did not increase for progressively longer residence times in the PCF exhaust system; therefore, homogeneous oxidation mechanisms are not sufficient to describe them. The determining factor in the reported extents of oxidation is the UBC level, suggesting an essential role for heterogeneous chemistry.
- (2) A heterogeneous reaction mechanism was needed to initiate Hg oxidation under utility exhaust conditions and also to sustain the partial oxidation of Hg into HgCl. In conjunction with the original homogeneous reaction mechanism, it depicted the observed coal-quality impacts in the PCF tests within useful quantitative tolerances without heuristic adjustments to the kinetic parameters or operating conditions.

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