Predicting Complete Hg Speciation Along Coal-Fired Utility Exhaust Systems

Paper # 45

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ABSTRACT

This paper introduces a comprehensive mechanism to predict the proportions of elemental and oxidized Hg vapors and particulate-Hg while flue gas moves through the heat exchangers and particle collection devices in utility exhaust systems, with or without sorbent injection. The central premise is that heterogeneous chemistry on carbon or any other active sorbent governs both oxidation and sorption. The predictions are evaluated with Hg oxidation data from several coals from a 1 MW_{th} pilot-scale flame, and with lab-scale data on simultaneous Hg oxidation and sorption on an accumulating filter cake with unburned carbon (UBC) alone and granulated activated carbon (GAC) injection.

The predicted coal quality impacts in the 1.0 MW_{th} flame were within measurement uncertainty in four of five cases. All the bit. coals were predicted and observed to have substantially more Hg^{2+} than a PRB subbituminous, as expected, even though their Cl-levels were similar. The mechanism attributes the large variations among these coals to the substantial UBC variations. Cases with Cl_2-injection into PRB-derived flue gas that had much higher percentages of Hg^{2+} were also accurately predicted, and the negative impact of H_2O injection with a bit. coal is also apparent in the predictions. The predictions for a high-Cl bit. coal are also accurate. The analysis also accurately interprets the reported concentration histories for Hg^0 and Hg^{2+} on UBC alone and GAC in an accumulating filtercake. In-flight contributions governed the oxidation and sorption behavior with UBC alone. In-flight transformations were also significant with GAC, and determined the sorption capacity at the coolest sampling temperature. But at the hotter sampling temperatures, GAC filter cakes determined the sorption capacities.

INTRODUCTION

For the past 7 years, Niksa Energy Associates (NEA) has been developing simulation mechanisms intended to (1) quantitatively interpret a station's baseline Hg test data in terms of the major stages and locations of Hg oxidation and sorption; (2) generalize baseline Hg data for variations in coal quality, furnace operation, and flue gas conditions; and (3) enable operators to select the most effective Hg control strategies, both at individual plants and in regional planning. For these applications, all input requirements must be readily available. The predictions must accurately describe the transient oxidation of Hg vapors and the dynamic partitioning into particulate-Hg at all locations from the superheater to the smokestack. Submodels must also describe Hg transformations and retention in superheaters, economizers, and air heaters, SCRs, ESPs and baghouses, and wet and dry FGDs, plus Hg recovery on injected sorbents. Collectively, such a family of modeling mechanisms would cover the vast majority of exhaust system configurations in the U. S. utility industry.

This paper introduces the backbone of NEA's family: a comprehensive reaction mechanism for simultaneous Hg oxidation and Hg sorption on unburned carbon (UBC), injected sorbents, and selected mineral components. This mechanism predicts complete Hg speciation while flue gas moves through the heat exchangers and particle collection devices, with or without injected sorbents. The predictions are evaluated with Hg oxidation data from several coals from a 1 MW_{th} pilot-scale flame, and with lab-scale data on simultaneous Hg oxidation and sorption on an accumulating filter cake, with and without sorbent injection.

REACTION MECHANISMS

The widespread dissemination of EPA's ICR data spawned several regressions on Hg retention in specific APCDs.[1-4] None are statistically significant[2] (except for systems with spray dryer absorbers), due to omissions in the ICR database and inadequacies in the regression functions, among many other reasons. We are not alone in our belief that Hg transformations in coal-derived flue gases are too complex to model with standard statistical correlations. Moreover, thermodynamics alone cannot be used to predict Hg partitioning because no Hg is ever predicted to be in flyash.[5] At this point, detailed reaction mechanisms offer the strongest potential for predicting Hg speciation in full-scale exhaust systems.

The first elementary chemical reaction mechanisms for Hg oxidation were introduced in 2000.[6,7] More chemistry was added to quantitatively interpret the lab database on systems without particles in 2001, including inhibition by moisture and by NO under some, but not all, conditions.[8] In 2002, they were expanded with chemistry on UBC particles to interpret the data from coal-derived exhausts from lab-scale flames, [9] and with chemistry on inorganics to generate Cl_2 from HCl.[10] They are now being expanded for the impact of sulfur species,[11] and being used to predict behavior in pilot-scale coal flames,[12] as the final prerequisite for full-scale applications.

Hg Oxidation

NEA's homogeneous Hg oxidation mechanism quantitatively interpreted all the published lab studies of Hg oxidation in synthetic flue gases.[8,13] We then introduced a heterogeneous oxidation pathway from Hg^0 to HgCl and, for the first time, quantitatively interpreted reported coal quality impacts from tests on lab and pilot-scale coal flames.[9,12] The homogeneous mechanism has eight reactions for Hg oxidation involving Hg^0, HgCl, $HgCl_2$, Cl, Cl_2, HCl, HOCl, H, and OH. There is a Cl-atom recycle whereby the Cl-atom consumed in the partial oxidation of Hg^0 into HgCl is regenerated in the subsequent oxidation of HgCl by Cl_2 into $HgCl_2$. The supporting kinetic submechanisms for wet CO oxidation;[14-16] Cl-chemistry;[14,15] NO_X chemistry;[17] SO_X chemistry;[18,19] and NO_X/SO_X interactions[19] were developed by Yetter and Dryer at Princeton, and fully validated with an extensive database of flow reactor data. These submechanisms are used without modification. The homogeneous Hg oxidation mechanism alone quantitatively interprets all the available datasets with synthetic flue gases.[6,7,20,21]

The following heterogeneous reaction subset was combined with the homogeneous mechanism to predict Hg oxidation in coal-derived flue gases:[9]

$$\mathrm{StSA(s)+HCl \rightarrow StCl(s)+H} \quad (1)$$
$$\mathrm{StCl(s)+Cl \rightarrow Cl_2+StSA(s)} \quad (2)$$
$$\mathrm{StCl(s)+Hg \rightarrow StSA(s)+HgCl} \quad (3)$$

StSA(s) and StCl(s) denote unoccupied and chlorinated sites, respectively, on UBC. Sites are chlorinated by HCl (eq. 1), the most abundant Cl-species, and carbon's large storage capacity maintains a Cl-source to oxidize Hg over a broad temperature range. Chlorinated sites either recombine with a Cl-atom to generate Cl_2 vapor (eq. 2), or partially oxidize Hg into HgCl (eq. 3). They have much more robust activity than Cl-atoms in the gas phase, as in established chemistry for dioxin production under comparable conditions.

Hg Sorption

Predictive mechanisms for Hg capture on sorbents have also developed rapidly,[22] but have not yet been reduced to elementary reaction mechanisms. UBC is the most effective Hg sorbent within flyash from hv bit. coals. Particulate-Hg tends to increase in proportion to flyash LOI with an acute temperature dependence, and increases for higher inlet Hg concentrations. Both these aspects have been used to assert that Hg sorption on carbon is driven by physical adsorption, rather than chemisorption. This simple phenomenology is sufficient for hv bit. coals, but only for two reasons. First, the speciation of Hg vapors from hv bit. coals tends toward an abundance of Hg^{2+}, which masks the ways that Hg speciation and other acid gases generally affect Hg sorption. Second, the inorganic components in the flyashes from hv bit. coals have negligible sorption capacities,[23] whereas selected inorganic flyash components that mostly appear in the ashes from subbit. coals can retain substantial amounts of Hg.

Other observations, however, indicate that a physical adsorption is inconsistent with the ways that HCl, NO_X, SO_2, and H_2O affect Hg sorption on carbon.[24-27] Removing HCl completely eliminates Hg^0 sorption and retards the initial sorption of $HgCl_2$ without affecting the equilibrium sorption capacity.[24] SO_2 inhibits sorption of both Hg^0 and Hg^{2+} on carbon.[25-27] NO_2 inhibits Hg^0-sorption but has little effect on Hg^{2+}-sorption. The sorption characteristics are significantly different in systems with and without the acid gases, but not among systems that have typical flue gas levels. Moreover, XAFS spectroscopy[28,29] reveals Hg-Cl bonds on the surface of carbons after adsorption of either Hg^0 or Hg^{2+}. At the very least, these findings indicate that adsorbed acid gases play a critical role in Hg capture, either by directly determining the sites for Hg adsorption or by significantly attenuating the sites' sorption properties.

Models for Hg sorption[30-33] circumvented such uncertainties with a variety of limiting approximations. The simplest ones assumed that Hg adsorption rates were limited by film mass transfer,[30,32] which always becomes limiting as the concentration of a sorbing species approaches zero, as it does for typical Hg concentrations in coal-derived flue gases. Rostam-Abadi et al. also showed that intraparticle transport resistances can be neglected when pore sizes are larger than 3 Angstroms,[30,32] which is always satisfied with UBC and granulated activated carbon (GAC); flyash particles have no pore structure to sustain intraparticle transport. These analyses were expanded by addition of adsorption isotherms based on Henry's Law;[32] Langmuir isotherms;[31] and Freundlich isotherms.[31,33] The parameters in the isotherms were assigned by fitting laboratory "breakthrough curves," including cases that contained either Hg^0 or Hg^{2+} plus HCl, SO_2, NO_X, and H_2O at typical levels.[31]

A Unified Mechanism for Simultaneous Oxidation and Sorption

NEA's comprehensive modeling framework for simultaneous speciation, sorption, and retention of Hg comprises three mechanisms: (1) A single, unified elementary reaction mechanism for Hg oxidation and sorption on UBC and GAC, with adaptations for low-rank flyashes and Ca-sorbents; (2) An Hg oxidation mechanism in SCRs; and (3) Hg retention mechanisms in wet and dry FGD scrubbers. The mechanism for oxidation in SCRs has been formulated and is now been evaluated with test data. The FGD retention mechanism is described separately.[34] This paper introduces the unified mechanism for oxidation and sorption, which is called Uni-Hg.

The two primary components of Uni-Hg are the oxidation mechanism and the adsorption mechanism. It is not coincidental that good sorbents for Hg are generally good oxidizing media as well, and carbon is both the best oxidizing medium and most effective sorbent. The connection is clearly apparent in sorption capacity tests with GAC, in which Hg^{2+} alone appears in the effluent once the bed has reached its equilibrium sorption capacity. At unusually high loadings, certain minerals may enhance Hg oxidation rates or supplement sorption capacities. But chlorinated carbon is the most effective oxidizing medium for Hg, and also has the highest sorption capacity.

This connection is readily elaborated at the mechanistic level. Mercury transformations occur while flue gases are cooled along an exhaust system. At the superheater section, only Hg^0 is present and the carbon is oxidized but otherwise clean. The process begins when temperatures are cooled into the range where HCl chlorinates some of the carbon sites in a reversible reaction. With further cooling, Hg^0 adsorbs at appreciable rates onto the chlorinated sites. Since desorption remains relatively fast, the HgCl rapidly desorbs into the gas phase, where it oxidizes into $HgCl_2$. In this temperature range, there is little sorption but extensive oxidation. As the particles are cooled further, the desorption rate becomes controlling, which implies that surface coverage increases, ultimately, to the equilibrium sorption capacity. There is little additional oxidation in the low temperature range, because the HgCl cannot leave the carbon surface.

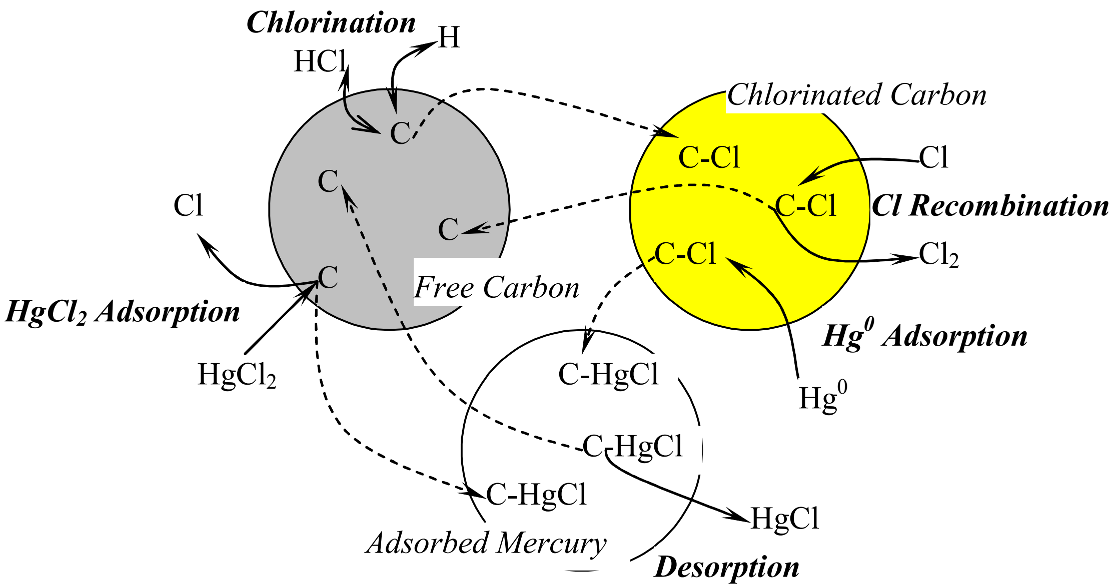
Hg oxidizes via adsorption of Hg^0 on chlorinated carbon sites, as NEA originally proposed. Whereas the original mechanism omitted finite-rate desorption kinetics, Uni-Hg contains them. This addition is crucial because, as desorption becomes rate-limiting at low temperatures, the surface coverage increases. And HgCl on the carbon surface constitutes sorbed or "particulate" Hg. We also include a reverse adsorption step for $HgCl_2$ into adsorbed-HgCl, to depict the different sorption rates of Hg^0 and Hg^{2+}. Note that the surface at the inlet to the exhaust system is assumed to be clean.

Dynamic rate equations for the surface coverages describe the accumulation on clean surfaces to an ultimate sorption capacity. The ultimate capacity will equal the equilibrium sorption capacity only if the kinetics reach their equilibrium rates. But no equilibrium adsorption isotherms are postulated or incorporated into Uni-Hg. Uni-Hg is sketched in Fig. 1. The carbon surface contains three pools: open or clean sites; chlorinated sites; and sites with adsorbed HgCl. There are 5 reactions. Open sites are reversibly chlorinated by HCl, or they may directly adsorb $HgCl_2$ to generate adsorbed HgCl. The chlorinated sites sustain 2 reactions: Cl-atoms recombine into Cl_2, regenerating an open site, and Hg^0 adsorbs onto chlorinated sites to form adsorbed HgCl. The HgCl desorbs into the vapor phase, where it is oxidized further by Cl_2 into $HgCl_2$. Uni-Hg has been formulated for both mean sizes and Rosin-Rammler PSDs, and incorporates NEA's homogeneous Hg oxidation mechanism as well as finite-rate film transport resistances. Intraparticle transport may be included in terms of effectiveness factors, if necessary.

INPUT DATA REQUIREMENTS

The input data needed to characterize Hg oxidation in coal-derived exhausts with these mechanisms is as follows: The fuel properties consist of a proximate analysis and an ultimate analysis expanded with the Hg- and Cl-contents. The heating value is also needed whenever a furnace rating and S. R. value are used to estimate the exhaust composition leaving the economizer. Alternatively, total coal and air flowrates will also specify the moisture and CO_2 levels in the exhaust. Measured exhaust O_2 levels are much better than estimates. Complete emissions levels are required, including HCl, CO, NO_X, and SO_X. Measured values of HCl are much more reliable than estimates, due to the uncertainties on coal-Cl levels. The partitioning of flyash among bottom ash, economizer ash, and flyash is required, along with LOI data on the flyash. UBC properties (size, total

Figure 1: Schematic of the proposed heterogeneous reaction mechanism in Uni-Hg.



surface area) are used in the analysis, but can usually be estimated from characterization data in the literature. The same properties are required for injected sorbents.

The essential operating conditions consist of the unit configurations, and the time-temperature history from the economizer outlet to the stack. It is best to formulate a time-temperature history with temperatures at the inlet and outlet to each unit, and the nominal residence times (which can be estimated from total gas flows and unit cross sections). Finer resolution within the air heater is helpful but not usually available.

DATA EVALUATIONS

Validation With a 1.0 MW_{th} Pilot-Scale Furnace

This Hg oxidation mechanism's most thorough validation comes from Southern Research Institute's Combustion Research Facility (CRF)[35]. The CRF consists of fuel handling and feeding systems, a vertical refractory lined furnace with a single up-fired burner, a horizontal convective pass, several heat exchangers in series and a baghouse filter. Emissions from this system have been qualified against those from full-scale, tangential-fired furnaces for the operating conditions imposed in this work[36]. The 8.5 m by 1.07 m (i.d.) cylindrical furnace handles gas velocities from 3 to 6 m/s, and residence times from 1.3 to 2.5 s. The nominal firing rate is 1.0 MW_t, which was fixed for all cases. A single burner generates a core of pulverized fuel and primary air surrounded by weakly swirled secondary air. Overfire air (OFA) was injected through 4 off-radius ports located 4.6 m down the furnace. The gas temperature history along the exhaust system compares very well with the histories assigned from temperature profiling on full-scale systems.

Table 1. Evaluation with flue gas from 1.0 MW_t furnace.

Table 1.1. Evaluations from SoRI's 1 MW_{th} CRF.

Coal	Coal-Cl	LOI	% Hg^{2+} Pred.	% Hg^{2+} Mes'd.
Bit. #1	0.010	4.8	74.8	76.0
Bit. #1/H_2O	0.010	4.8	72.0	63.0
Bit. #2	0.013	4.2	50.0	52.0
Bit. #3	0.058	1.9	63.0	38.0
	0.058	9.8	99.0	55.0
Bit. #4	0.280	1.7	51.0	46.0
PRB	0.013	0.2	18.9	18.7
PRB	0.013	0.2	29.0	30.0

Mercury speciation was monitored with a PS Analytical Hg detector using samples extracted from the flue gases with an Apogee Scientific QSIS probe. Two sampling positions were used to monitor the speciation at 163 and 280°C. In addition, all major flue gas species were measured, including HCl, SO_2, CO_2, CO, NO_X, SO_X, and O_2. Both LOI and UBC levels were determined for the flyash. LOI was used in all calculations, for consistency with the other evaluations with data completed to date. The test procedures are more completely described elsewhere.[35]

Five coals were fired, including three Eastern bit., an Ill. Bit., and a PRB subbit. Steam injection into the burner was applied with one of the bit. coals, and the combustor was deeply staged to obtain very high LOI with a second bit. coal. In a test series with PRB, Cl_2 was injected at two concentrations at 573°C, upstream of the heat exchangers.
As seen in Table 1, the predictions are remarkably accurate for four of the five coals. All the bit. coals have substantially more Hg^{2+} than the PRB, as expected. But Bit. #1 also has significantly more oxidized Hg than Bit. #2, despite similar coal-Cl and LOI levels. Both of these bit. coals had unusually low Cl-levels comparable to the PRB's so, clearly, coal-Cl is not the determining factor in Hg oxidation. The mechanism depicts large variations among these three coals within experimental uncertainty throughout, based primarily on the substantial LOI variations. Cases with Cl_2-injection into PRB-derived flue gas (not shown) that had much higher percentages of Hg^{2+} were also accurately predicted. The negative impact of H_2O injection with Bit. #1 is also apparent in the predictions. The prediction for Bit. #4, which has a high Cl-content, is also accurate; here, the abundance of Cl is counteracted by the relatively low availability of UBC sites, so the extents of Hg oxidation are moderate.

The predictions for both cases with Bit. #3 are too high, which probably reflects a missing process for higher UBC levels. One possibility is a HgCl desorption step that becomes rate limiting at lower flue gas temperatures. The other is a reverse adsorption step for $HgCl_2$, which eliminates $HgCl_2$ vapors via adsorption on UBC as HgCl. Both steps appear in Uni-Hg, but were not included in the simulations for this evaluation. The very high SO_2 level with Bit. #3 (ca. 1750 ppm) may also inhibit Hg oxidation.

Evaluations for Simultaneous Hg Oxidation and Sorption

This section evaluates predictions from an abridged version of Uni-Hg (without homogeneous chemistry and film transport) with the measured concentration histories for Hg^0 and Hg^{2+} on UBC alone and GAC in accumulating filtercakes at different sampling temperatures. In the tests, coal-derived flue gas with flyash was deposited on an initially clean filter to simulate Hg oxidation and sorption in a baghouse filtercake. Hg speciation was monitored across the accumulating filtercake for 30 min. The tests were especially informative because in-flight transformations determine the early behavior, while filter cake transformations make progressively greater contributions throughout a run.

All test data were recorded with an hv bit. coal, whose proximate and ultimate analyses are as follows: 33.1as rec'd wt. % volatiles, 55.4 % fixed carbon, 1.7 % moisture, and 9.8 % ash; 82.8 daf wt. % C, 5.3 % H, 9.8 % O, 1.6 % N, and 0.68 % S. The Cl- and Hg-contents are 0.023 daf wt. % and 0.114 ppm. 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. Overfire air was added about half-way down the furnace. The firing rate was fixed for all tests at 200,000 kcal/m^3-hr. The flue gases were first diverted into the branch of a tee to eliminate bottom ash, then passed through a cyclone at 460 - 500°C to remove most of the flyash. An air-cooled sampling probe extracted 16 SLPM of the flue gas through one of nine ports downstream of the cyclone. The sampled portion then passed through an air-cooled probe into a connecting line to a heated final filter before it was sent to the impingers in a Hg detection system. More details on this facility are available.[37]

Model predictions are compared to the reported Hg speciation histories for UBC alone in Fig. 2. The sums of the measured Hg vapor species are uniform throughout both runs, at 3 $\mu g/Nm^3$ with sampling at 127°C and at 8.2 $\mu g/Nm^3$ with sampling at 227°C. So sorption only occurs in-flight with UBC alone. The predicted speciation histories are within experimental uncertainly thoughout the tests at both sampling temperatures. The only possible exception is the slightly underpredicted Hg^{2+} level during the first half of the test that sampled from 127°C. For the sampling temperature of 127°C, 10 % Hg^0 and 26 % Hg^{2+} are present in the flue gas at the end of the test, and 64 % of the inlet Hg has been retained on the sorbent. For 227°C, 11 % is retained on UBC and 60 % is oxidized. These sorption capacities and extents of oxidation are entirely determined in-flight at the coolest sampling temperature. At the hottest temperature, the sorption capacity is still determined in-flight, whereas an additional 8 % of the Hg^0 oxidizes across the filter cake.

Model predictions are compared to the reported Hg speciation histories for GAC in Fig. 3. For the sampling temperature of 127°C, only Hg^{2+} is present in the flue gas at the end of the test, and 80 % of the inlet Hg has been retained on the sorbent. The predicted values are the same. The predictions depict within experimental uncertainty the rapid initial decay in the Hg^0 concentration; its complete elimination on the accumulating filter cake by 200 ms; and the gradual increase in the Hg^{2+} concentration throughout the test. Even the inlet speciation is predicted within experimental uncertainty.

Figure 2: Predicted (solid curves) and measured histories of elemental (○) and oxidized (●) Hg vapors with UBC alone for sampling temperatures of (top) 127 and (bottom) 227°C.

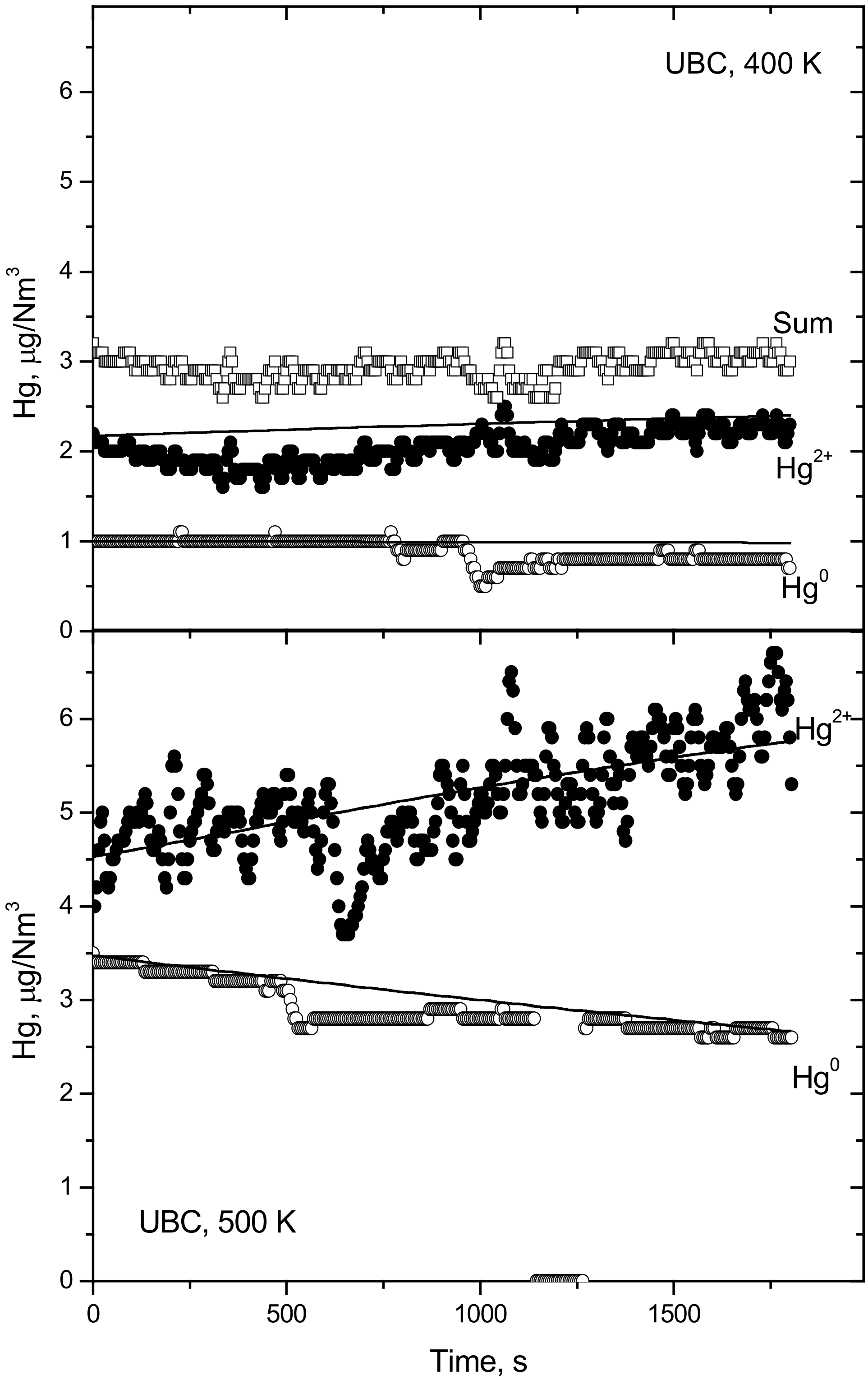
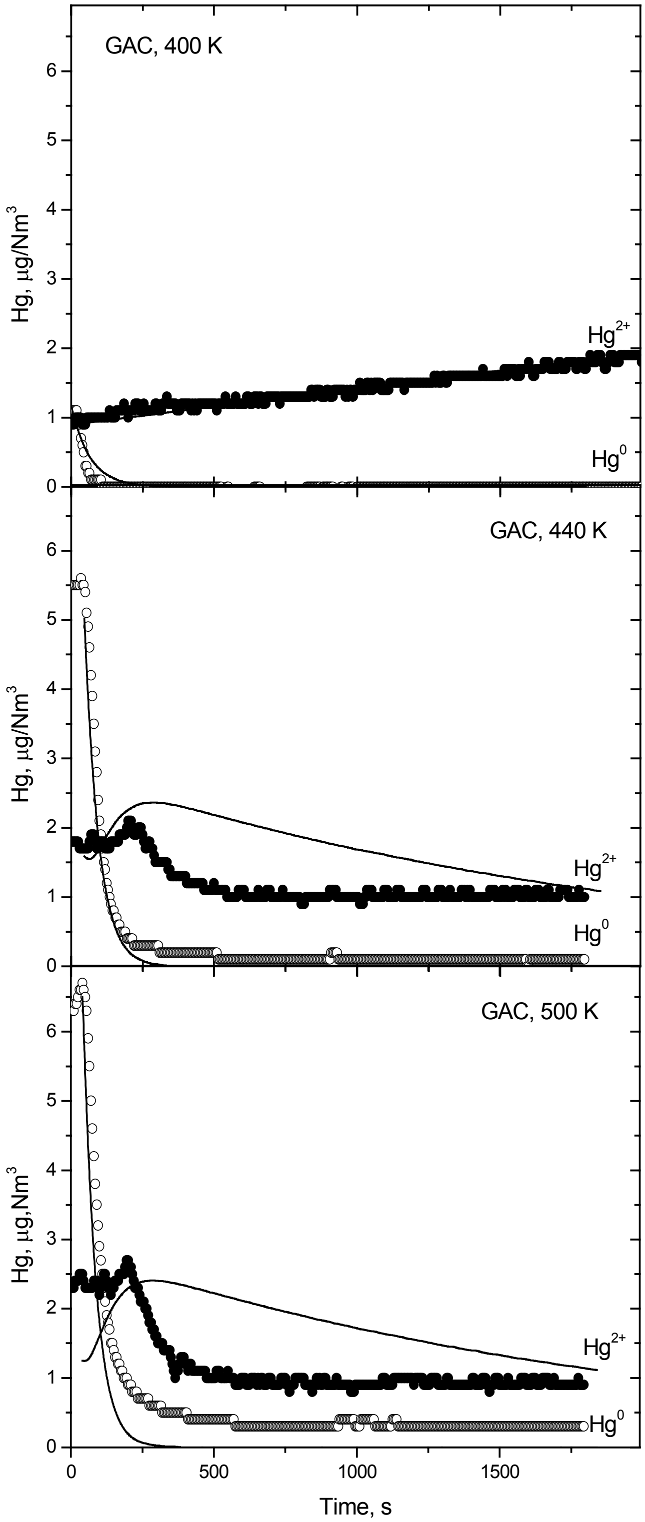


Figure 3: Predicted (solid curves) and measured histories of elemental (○) and oxidized (●) Hg vapors with GAC injection for sampling temperatures of (top) 127, (middle) 167, and (bottom) 227°C.



The interpretation of the test with sampling at 167°C is almost as accurate. The ultimate speciation is 1 % Hg^0, 12 % Hg^{2+}, and 87 % particulate-Hg versus respective predicted values of 0, 12, and 88 %. The predicted proportions of Hg^0 and Hg^{2+} at the inlet are also accurate. The predictions depict within experimental uncertainty the rapid initial decay in the Hg^0 concentration; its complete elimination on the accumulating filter cake by 400 ms; and the sharp initial increase in the Hg^{2+} concentration to a maximum value at 250 ms. Whereas the Hg^{2+} concentration then abruptly decays, the predictions diminish much slower to the same ultimate value. The interpretation of the test with sampling at 227°C is essentially the same, except the quantitative discrepancies are slightly greater, particularly the underprediction of the Hg^{2+} level at the inlet.

The in-flight oxidation contributions are fairly uniform for all runs, whereas the sorption contribution dominates at the coolest sampling temperature, as expected. The filter cake contributions are the same at both of the hottest sampling temperatures for both oxidation and sorption. But, inexplicably, this oxidation contribution increases by 8 % at the expense of the sorption contribution at the coolest sampling temperature.

SUMMARY

This paper introduces a comprehensive mechanism to predict the proportions of Hg^0 and Hg^{2+} vapors and particulate-Hg in coal-derived flue gases. The central premise is that heterogeneous chemistry on carbon or any other active sorbent governs both oxidation and sorption. Mercury transformations occur while flue gases are cooled along an exhaust system. At the inlet to the exhaust system, all the Hg is elemental and the carbon surfaces are relatively clean. According to NEA's five-step heterogeneous mechanism, the process begins when temperatures are reduced into the range where HCl chlorinates some of the carbon sites in a reversible reaction. With further cooling, adsorption of Hg^0 occurs at appreciable rates on the chlorinated carbon sites. Since desorption remains relatively fast, the HgCl intermediate rapidly desorbs into the gas phase, where it is subsequently oxidizes into $HgCl_2$. In this temperature range, there is little sorption but extensive oxidation. As the particles are cooled further, the desorption rate assumes control, which implies that surface coverages increase, ultimately, to the equilibrium sorption capacity. There is little additional oxidation in the low temperature range, because the intermediate partial oxidation product cannot leave the carbon surface.

An abridged version of the analysis, without homogeneous chemistry and finite-rate transport, accurately interprets the reported concentration histories for Hg^0 and Hg^{2+} on UBC alone and GAC, at three different sampling temperatures. These tests were especially informative because the data represent Hg transformations in-flight through the exhaust and sampling systems and on the filter cake in the final filter; in fact, in-flight transformations determine the early behavior, while filter cake transformations make progressively greater contributions as the filter cake accumulates throughout a run. In-flight contributions governed the oxidation and sorption behavior with UBC alone. In-flight transformations were also significant with GAC, and determined the sorption capacity at the coolest sampling temperature. But at the hotter sampling temperatures, GAC filter cakes determined the sorption capacities.

Based on the satisfactory performance, we are now staging evaluations with test data from full-scale exhaust systems.

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KEY WORDS

Mercury Emissions, Mercury Speciation, Oxidized Mercury, Mercury Sorption, Reaction Mechanism, Emissions Prediction