

# **A Computational and Experimental Study of Mercury Speciation as Facilitated by the Deacon Process**

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# A Computational and Experimental Study of Mercury Speciation as Facilitated by the Deacon Process

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## ABSTRACT

It is known that fly ashes that contain trace CuO or Fe<sub>2</sub>O<sub>3</sub> are effective catalysts for elemental mercury conversion to HgCl<sub>2</sub> in the presence of HCl, even at low reactor temperatures (less than 250 °C). As these same trace metals promote chlorine gas formation through the Deacon process, it is possible that this process, combined with gas-phase mercury chlorination pathways, can explain such speciation trends. In support of this hypothesis, experiments are conducted to determine whether direct reactions of mercury with chlorine gas are possible at low temperatures and whether appreciable mercury is captured onto the model fly ash surface. These results are used to develop and refine a chemical kinetics model for mercury speciation as driven by chlorination induced by the Deacon process.

## INTRODUCTION

Much recent attention has been focused toward explaining observed gas-phase mercury speciation trends through the use of detailed kinetics mechanisms.<sup>1-3</sup> Such mechanisms combine elemental mercury chlorination pathways with reactions describing interactions of chlorine-containing compounds with other flue-gas constituents. The dominant path for elemental mercury conversion to HgCl<sub>2</sub> has been identified as:<sup>1</sup>



with the production of atomic chlorine being the controlling factor. Studies have shown that such mechanisms do explain high temperature (> 500 °C) speciation trends quite well, but at lower temperatures (< 500 °C), they tend to underpredict observed conversion trends quite significantly.<sup>2,3</sup> The reason is that, without the introduction of arbitrary concentrations of trace radical species, the proposed pathways do not produce enough

atomic chlorine at low temperatures to effect high levels of mercury conversion. These results may point to the importance of heterogeneous chlorination pathways, possibly involving other reactive species (such as Cl<sub>2</sub>), as key elements in the conversion process at low temperatures.

This paper examines one possible heterogeneous mechanism for low-temperature mercury speciation based on the occurrence of the well-known Deacon process.<sup>4-6</sup> The Deacon process involves the oxidation of HCl in the presence of a metal catalyst to produce Cl<sub>2</sub> and H<sub>2</sub>O. The process can be represented by the global gas-phase reaction



but is actually composed of a sequence of heterogeneous reactions representing the steps of HCl sorption, chlorination, and oxidation<sup>5,6</sup>. The chlorination steps result in the formation of intermediate metallic compounds on the sorbent surface, while the oxidation step releases Cl<sub>2</sub> into the gas phase and results in the regeneration of the catalyst. Hisham and Benson<sup>5</sup> note that the most active catalyst (of the many that they studied) is CuO and that the chlorination steps in general are exothermic.

Ghorishi<sup>7</sup> conducted several experiments that measured steady-state mercury conversion for simulated flue gas passing through a fixed bed of model fly ash particles. Ghorishi observed that the baseline fly ash (composed of 22 wt% Al<sub>2</sub>O<sub>3</sub> and 78 wt% SiO<sub>2</sub>) did not promote mercury conversion, but when trace metal oxides, such as Fe<sub>2</sub>O<sub>3</sub> and CuO, were added to the fly ash, a significant amount of mercury was converted over time. As these metal oxides promote the Deacon process, it was conjectured that this process played a role in mercury conversion. In this work, we develop further this conjecture, which hinges on the hypothesis that the mercury conversion observed is primarily a result of gas-phase reactions with Cl<sub>2</sub> formed through the Deacon process. To this end, new experimental results on the homogeneous reaction of elemental mercury with molecular chlorine are reported, as are mass balance data indicating the degree of surface capture of mercury by model fly ash particles. A new rate coefficient for the gas-phase reaction



is derived, and the results used to determine new rate coefficients for a two-step global mechanism for the Deacon process as catalyzed by CuO.<sup>8</sup> The ability of the proposed three-step mechanism to predict the speciation trends observed by Ghorishi<sup>7</sup> is assessed, and some conclusions and directions for future work are drawn.

## **GAS-PHASE MERCURY-CHLORINE REACTIONS**

A key requirement in the above hypothesis is the ability of elemental mercury (Hg<sup>0</sup>) to react directly with Cl<sub>2</sub> vapor at low (< 500 °C) temperatures. The most comprehensive study, by Hall et al.<sup>9</sup>, indicates that the two gases can react at any temperature and that the relatively slow reaction rate is independent of temperature. Skare and Johansson<sup>10</sup> monitored the mercury vapor concentration in mixtures of mercury vapor, air, and

chlorine gas, enclosed in a gas bag at room temperature. They reported a 40 % drop in the initial mercury vapor concentration over 24 hours. Their results may have been influenced by the decay of chlorine gas concentration due to other factors, which precluded obtaining data at higher temperatures.

To attempt to characterize the degree of reactivity of mercury and chlorine vapor more precisely, experiments were performed in an empty reactor (described in Ref. 7) at temperatures of 150 and 250 °C with a gas mixture consisting of 40 ppbv Hg<sup>0</sup> and 2 ppm Cl<sub>2</sub> in N<sub>2</sub>. The effluent of the reactor was sampled for 90 minutes using a modified Ontario Hydro (OH) mini-impinger train in which each KCl impinger was spiked with 10 mg sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>).<sup>11</sup> The samples were analyzed according to the OH method instruction<sup>11</sup> to obtain mercury speciation. Each test was duplicated. At the reactor temperature of 150 °C, Hg<sup>0</sup> oxidation was 85±5 %, while at the reactor temperature of 250 °C, Hg<sup>0</sup> oxidation was 88±4.5 %. These results were reproducible and indicate that significant gas-phase oxidation of Hg<sup>0</sup> does occur in the presence of Cl<sub>2</sub>. This oxidation is relatively independent of temperature in the range considered. Total mercury recoveries were within an acceptable range of 80 – 120%.

Given these data and the quenching pattern characteristic of this reactor<sup>2</sup>, an Arrhenius rate coefficient for the reaction  $\text{Hg} + \text{Cl}_2 \rightleftharpoons \text{HgCl}_2$  was determined as follows. The evolution of the molar concentration of Hg<sup>0</sup> is given by

$$\frac{d\tilde{\rho}_{\text{Hg}}}{dt} = k_f \tilde{\rho}_{\text{Hg}} \tilde{\rho}_{\text{Cl}_2} \quad (5)$$

$$k_f = A \exp(-B/T) \quad (6)$$

$$\tilde{\rho}_{\text{Cl}_2} = \frac{p_\infty X_{\text{Cl}_2}}{RT} \quad (7)$$

where:

$\tilde{\rho}_{\text{Hg}}$  = molar concentration of Hg<sup>0</sup> (kmol/m<sup>3</sup>)

$\tilde{\rho}_{\text{Cl}_2}$  = molar concentration of Cl<sub>2</sub> (kmol/m<sup>3</sup>)

A = pre-exponential factor

B = characteristic temperature (K)

T = temperature (K)

p<sub>∞</sub> = pressure (101325 Pa)

R = universal gas constant (J/kmol-K)

X<sub>Cl<sub>2</sub></sub> = mole fraction of Cl<sub>2</sub>

In the above, it is assumed that the mercury chlorination reaction being elementary follows the law of mass action. Equation (5) is integrated over the residence time of the fluid within the reactor, with each stage of the quench treated as a plug-flow reactor

characterized by its own average temperature and residence time. The mole fraction of  $\text{Cl}_2$  is assumed to be constant over the reactor, as it is well in excess of the initial mercury mole fraction. With these assumptions, Eq. (5) integrates to

$$\ln(1 - Z) = A \frac{p_{\infty} X_{\text{Cl}_2}}{R} \sum_{k=1}^4 \frac{\exp(-B/T_k)}{T_k} \Delta t_k \quad (8)$$

where

$Z$  = conversion of  $\text{Hg}^0$

$T_k$  = average temperature of the  $k_{\text{th}}$  reactor stage

$\Delta t_k$  = residence time for the  $k_{\text{th}}$  reactor stage

Table 1 gives the parameters for each of the reactor temperatures considered.

**Table 1.** Temperatures and residence times for different reactor stages.

Reactor temperature (K)	$T_1$ (K)	$T_2$ (K)	$T_3$ (K)	$T_4$ (K)	$\Delta t_1$ (s)	$\Delta t_2$ (s)	$\Delta t_3$ (s)	$\Delta t_4$ (s)
423.15 (150 °C)	423.15	378.87	322.21	302.49	2.350	0.225	0.154	1.260
523.15 (250 °C)	523.15	446.31	345.27	308.11	1.890	0.174	0.144	1.200

Equation (8) is evaluated at both reactor temperatures, and the resulting nonlinear system is solved to yield the pre-exponential factor  $A$  and the characteristic temperature  $B$ . The result is the following Arrhenius rate coefficient:

$$k_f = 2 \times 10^8 \exp(-1248/T) \text{ (units of meters, kilomoles, seconds, K)} \quad (9)$$

This may be contrasted with Hall's temperature-independent rate of  $k_f = 3.4 \times 10^6$  (same units) as given in Ref. 1. At room temperature (25 °C), the new rate coefficient yields a value of  $3.04 \times 10^6 \text{ m}^3/\text{kmol}\cdot\text{s}$ , in qualitative agreement with that of Hall. Regression of the data of Skare and Johansson<sup>10</sup> gives a much smaller rate coefficient of  $72 \text{ m}^3/\text{kmol}\cdot\text{s}$ , but this result must be considered suspect in view of their described difficulties in maintaining the stability of  $\text{Cl}_2$  in  $\text{N}_2$  without mercury. Table 2 presents predicted levels of mercury conversion for Ghorishi's test conditions.

**Table 2.** Predicted mercury conversion versus experimental data.

Temperature (K)	Z (% , new rate)	Z (% , Hall)	Z (% , experiment)
423.15	84.74	58.87	85 (+/- 5)
523.15	87.74	49.62	88 (+/- 1)

The Hall rate coefficient results in an underprediction of mercury conversion levels. The best-fit rate as determined from the analysis above performs well and is used in subsequent calculations.

## MERCURY MASS BALANCE DATA

A second consideration in validating the hypothesis of a primarily gas-phase mercury conversion process is the amount of mercury captured by the fly ash versus that released back into the flue gas stream. To close this mass balance and obtain the extent of surface mercury adsorption, the fixed bed reactor described in Ref. 7 was loaded with model fly ash consisting of 22 wt%  $\text{Al}_2\text{O}_3$ , 77 wt%  $\text{SiO}_2$ , and 1 wt%  $\text{CuO}$  at temperatures of 150 and 250 °C. Flue gas consisting of 40 ppbv  $\text{Hg}^0$ , 50 ppmv  $\text{HCl}$ , 2%  $\text{O}_2$ , and 5%  $\text{CO}_2$  in  $\text{N}_2$  was passed through the reactor and the effluent sampled using the spiked OH method.<sup>11</sup> The exposed model fly ash was recovered and analyzed according to the OH method to obtain the amount of mercury captured by the surface. Each test was duplicated. At a reactor temperature of 150°C,  $86\pm 5\%$  of the inlet  $\text{Hg}^0$  was present in an oxidized state (probably  $\text{HgCl}_2$ ) in the gas phase, while  $6.3\pm 1.5\%$  of the inlet  $\text{Hg}^0$  was captured by the fly ash. The remainder was unreacted  $\text{Hg}^0$ . The total mercury mass balance across the reactor was  $98\pm 1\%$ . At a reactor temperature of 250 °C,  $98\pm 0\%$  of the inlet  $\text{Hg}^0$  was present in oxidized form in the gas-phase, while  $1.1\pm 0.5\%$  of the inlet  $\text{Hg}^0$  was adsorbed by the model fly ash. The remainder was unreacted  $\text{Hg}^0$ . The total mercury mass balance across the reactor was  $99\pm 0.3\%$ . As expected from the earlier work<sup>7</sup>, significant oxidation of mercury vapor was observed in the presence of  $\text{CuO}$ .

These results show that the fly ash surface is not inert to mercury and that some consideration of the details of adsorption/desorption processes, as well as possible surface reactions of mercury and chlorine, may be necessary. Without more experimental data, it is difficult to conjecture whether the majority of the mercury conversion takes place within the fly-ash bed itself or in the gas stream. However, given the degree of mercury reactivity with chlorine in the gas phase as evidenced above, it seems logical to maintain the initial premise that the gas-phase reactions are the more important, and that the fly ash simply catalyzes the production of the gas-phase reactant  $\text{Cl}_2$  from  $\text{HCl}$ .

## DEACON PROCESS MODELING

Though much recent progress has been made in developing thermodynamically feasible elementary reactions for the Deacon process<sup>5,6</sup>, there exists no comprehensive set of rate data for these reactions. A two-step global reaction scheme for the Deacon process as driven by a  $\text{CuO}$  catalyst has been proposed by Nieken and Watzenberger<sup>8</sup> and is used as the basis for the present work. The Nieken-Watzenberger mechanism subdivides the process into a chlorination step (which results in the formation of the intermediate surface species  $\text{CuCl}_2$  and the release of gas-phase  $\text{H}_2\text{O}$ ), and a dechlorination step (which results in the formation of  $\text{Cl}_2$  and the regeneration of the catalyst  $\text{CuO}$ ):

### Chlorination



$$k_f = 4.16 \times 10^9 T \exp(-12000/T) \text{ (units of meters, kilomoles, seconds, K)}$$

### Dechlorination



$$k_f = 1.44T^{1/2} \exp(-2000/T) \text{ (units of meters, kilomoles, seconds, K)}$$

The chlorination reaction is first order with respect to CuO and HCl concentration, while the dechlorination reaction follows the law of mass action. The Nieken-Watzenberger mechanism is written on a per-volume basis, though surface species CuO and CuCl<sub>2</sub> are involved. The reaction mechanism thus depends on the initial concentration of CuO in the sorbent and on the voidage of the fixed bed.

This mechanism is solved simultaneously with the mercury chlorination reaction (4) with rate coefficient from Eq. (9) using a plug-flow reactor code. The voidage is a function of spatial distance within the reactor and is set to 0.93 within the fly ash bed and 1.0 outside the bed. The Nieken-Watzenberger mechanism is assumed to apply only within the extent of the bed, while the mercury chlorination reaction is assumed to apply everywhere within the reactor. Test conditions are from Ghorishi<sup>7</sup> and involve CuO concentrations of 0.1 and 1 % by weight of sorbent and temperatures of 150, 200, and 250 °C. The superficial gas velocity and quenching pattern are functions of the temperature, as indicated in Ref. 2. The initial flue gas composition is 40 ppbv Hg<sup>0</sup>, 50 ppmv HCl, 2% O<sub>2</sub>, and 5% CO<sub>2</sub> in N<sub>2</sub>.

Table 3 shows the results of applying Nieken and Watzenberger's mechanism for chlorine formation (with original rate coefficients) with the mercury chlorination reaction (4).

**Table 3.** Mercury conversion for Ghorishi<sup>7</sup> experiments (original Nieken-Watzenberger rates).

Case	% Hg conversion at 150 °C	% Hg conversion at 200 °C	% Hg conversion at 250 °C
Original Nieken-Watzenberger rates, 0.1 wt% CuO	1.07	20.2	91.0
Experiment, 0.1 wt% CuO	66.5	86.8	91.8
Original Nieken-Watzenberger rates, 1 wt% CuO	10.2	87.9	100
Experiment, 1 wt% CuO	95.1	91.6	94.2

As indicated in Table 3, the Nieken-Watzenberger mechanism results in a significant underprediction of mercury conversion levels at the lower temperatures of 150 and 200 °C and at the lower CuO concentration of 0.1 % by weight of sorbent. Agreement improves for the highest temperature of 250 °C and for the higher CuO concentration of 1 % by weight of sorbent. No explanation is given in Ref. 8 as to how the reaction rates were determined, but it is likely that they are representative of a more industrial-scale Deacon-type process, involving much larger HCl concentrations and probably higher temperatures.

This uncertainty as to the validity of the mechanism for the present situation led initially to a sequence of experiments designed to measure actual Cl<sub>2</sub> production in the reactor in the absence of mercury and with a CuO catalyst. The intent was to provide data suitable for refitting the rate coefficients of the Nieken-Watzenberger scheme for the present range of conditions. However, substantial difficulties were encountered in trying to measure sub-ppm Cl<sub>2</sub> concentrations accurately. The experiments did indicate the presence of chlorine vapor at relatively low reactor temperatures, indicating that a Deacon-type process was in effect, but results could not be quantified. As such, an alternative procedure was devised, based on the heterogeneous chlorination results presented earlier.<sup>7</sup>

The procedure starts by determining the amounts of molecular chlorine necessary to effect the levels of mercury conversion observed in Ref. 7, given the gas-phase pathway  $\text{Hg} + \text{Cl}_2 \Rightarrow \text{HgCl}_2$  (with the new rate coefficient) as the only reaction involved. As the data for 1 wt% CuO display more scatter and do not exhibit the anticipated increase in conversion with increasing temperature, attention is focused on the 0.1 wt% data. The second step is to determine the rate coefficient(s) for the Nieken-Watzenberger mechanism that best (in a least-squares sense) produce the desired chlorine concentrations in the steady-state limit, given the bed length and voidage (0.93). This step

is facilitated by realizing that, at steady-state, the net production of the surface species CuO and CuCl<sub>2</sub> is zero, meaning that the forward rate of the chlorination step must equal the forward rate of the dechlorination step. This simplification enables the analytic integration of the plug-flow advection/reaction equations across the extent of the bed: Mass fractions of the reactive species at the end of the bed are thus determined by

$$Y_{HCl}^F = Y_{HCl}^I \exp(-2k_f \tilde{\rho}_{CuO} L / U_g) \quad (12)$$

$$Y_{O_2}^F = Y_{O_2}^I - 1/2 \frac{M_{O_2}}{M_{HCl}} Y_{HCl}^I [1 - \exp(-2k_f \tilde{\rho}_{CuO} L / U_g)] \quad (13)$$

$$Y_{Cl_2}^F = 1/2 \frac{M_{Cl_2}}{M_{HCl}} Y_{HCl}^I [1 - \exp(-2k_f \tilde{\rho}_{CuO} L / U_g)] \quad (14)$$

$$Y_{H_2O}^F = 1/2 \frac{M_{H_2O}}{M_{HCl}} Y_{HCl}^I [1 - \exp(-2k_f \tilde{\rho}_{CuO} L / U_g)] \quad (15)$$

where :

$Y_k$  = mass fraction of species  $k$

F = conditions at the end of the fixed bed

I = conditions at the beginning of the fixed bed

$\tilde{\rho}_{CuO}$  = molar concentration of CuO, referenced to unit total volume (kmol/m<sup>3</sup>)

L = length of the bed (2 cm)

$U_g$  = superficial gas velocity (m/s)

$M_k$  = molecular weight of species  $k$  (kg/kmol)

$k_f$  = rate coefficient of the chlorination step, expressed in general Arrhenius form as  $AT^C \exp(-B/T)$ .

It is of note that the steady-state mass fractions at the end of the bed are dependent only on the rate coefficient of the chlorination step. Mole fractions of the reactive species are determined by  $X_k = \frac{Y_k / M_k}{\sum_l Y_l / M_l}$ , given initial concentrations of the inert species CO<sub>2</sub> and

N<sub>2</sub>. The predicted mole fraction of Cl<sub>2</sub> at the end of the fixed bed is then compared to the target value for each of the three temperatures (150, 200, and 250 °C), with the unknowns being the pre-exponential constant A, the characteristic temperature B, and the exponent C. This closed nonlinear system could not be solved, indicating that the assumed functional form for the rate coefficient is not precise enough. This is of little concern, as the data are not that precise either, and a least-squares solution was found by setting C to 0 and performing the required analysis. The result is a rate coefficient of the form:

$$k_f = 11716 \exp(-2040/T) \text{ (units of meters, kilomoles, seconds, K)} \quad (16)$$

Table 4 compares results obtained from the Niiken-Watzenberger mechanism with refitted chlorination rate coefficient with the data of Ghorishi.<sup>7</sup> Reasonable agreement is evidenced across the range of temperatures for the 0.1 wt % CuO concentration. The model predicts complete conversion for the 1 wt% CuO concentration, while the data indicate that some mercury remains unreacted.

**Table 4.** Mercury conversion for Ghorishi<sup>7</sup> experiments (refitted Niiken-Watzenberger chlorination step).

Case	% Hg conversion at 150 °C	% Hg conversion at 200 °C	% Hg conversion at 250 °C
Refitted rates, 0.1 wt% CuO	67.7	82.5	90.9
Experiment, 0.1 wt% CuO	66.5	86.8	91.8
Refitted rates, 1 wt% CuO	100	100	100
Experiment, 1 wt% CuO	95.1	91.6	94.2

Figures 1 and 2 present steady-state chlorine and mercury mole fractions versus distance along the reactor for the three-step mechanism described above (with refitted rate coefficients). Chlorine is formed within the fly ash bed, while chlorine due to reaction with elemental mercury is depleted downstream of the bed. Mercury is depleted within and downstream of the bed; concentrations at the exit of the straight-section reactor are higher than those in Table 4, indicating that further reaction takes place during the quench of the flue gas stream and in the sampling train.

Figure 1. Chlorine mole fractions versus distance along the reactor.

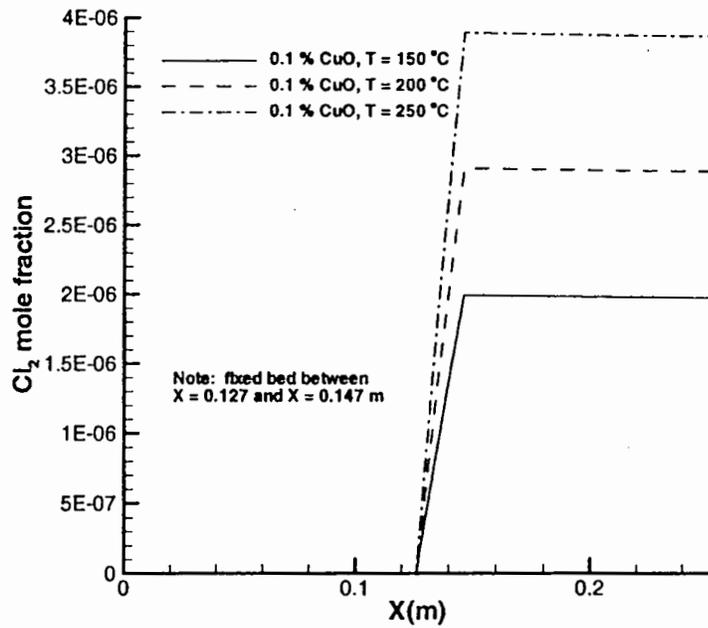
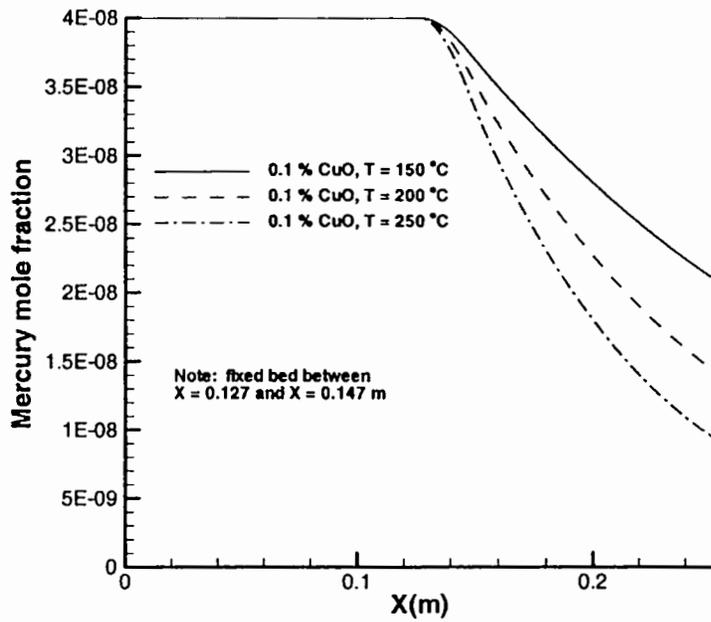


Figure 2. Mercury mole fraction versus distance along reactor.



## CONCLUSIONS

This paper examines one possibility of low-temperature mercury speciation as facilitated by a Deacon-type process for producing  $\text{Cl}_2$ . The viewpoint taken is that elemental mercury and chlorine vapor react primarily in the gas phase, with the production of chlorine vapor from  $\text{HCl}$  catalyzed by metal oxides ( $\text{CuO}$  in this work) present in fly ash. New experimental data for the gas-phase reaction of mercury and chlorine vapor have been obtained and used to determine a new temperature-dependent rate coefficient for the reaction  $\text{Hg} + \text{Cl}_2 \rightleftharpoons \text{HgCl}_2$ . Mass balance analyses have established that, under the present experimental conditions, mercury capture by the surface is a secondary effect. These experimental results give some credence to the premise raised above. An existing chemical kinetics model for chlorination/dechlorination stages of the Deacon process has been refitted to describe existing heterogeneous chlorination data better and, when combined with the mercury-chlorine reaction, has been shown to predict observed speciation trends reasonably well. Future work is planned to conduct an independent validation of the chemical kinetics model through direct measurements of  $\text{Cl}_2$ . Work is also planned to extend the model to account for more realistic situations, which may include the presence of inhibitory agents (such as  $\text{H}_2\text{O}$  and  $\text{SO}_2$ ) in the flue gas and other trace metal oxides (such as  $\text{Fe}_2\text{O}_3$ ).

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