I, Vishnu Sriram, hereby submit this original work as part of the requirements for the degree of Master of Science in Chemical Engineering.

It is entitled:
Study of Reaction Kinetics for Elemental Mercury Vapor Oxidation for Mercury Emission Control

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Study of Reaction Kinetics for Elemental Mercury Vapor
Oxidation for Mercury Emission Control

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Abstract

Elemental mercury (Hg(0)) is a persistent, toxic metal that is released during the combustion of coal in power plants. Its toxicity, and bioaccumulation is of concern for public health and the environment. The need to control and capture mercury is of importance and relevant in today’s world since coal still plays a significant role as it is one of the major energy sources in the United States. While elemental mercury is difficult to capture, oxidized mercury (Hg(2+)) is captured easily due to its high solubility in water and its ability to easily adsorb onto sorbents such as powdered activated carbon (PAC). Previously in our lab, CuCl₂-based substrates have been tested and has shown good potential to play a role in oxidizing Hg(0). Mechanistic studies have been performed on CuCl₂-based substrates and a fundamental understanding of the adsorption of Hg(2+) onto activated carbon (AC) has been investigated in the past.

In order to understand the oxidation kinetics of CuCl₂ and the role it plays in oxidizing Hg(0) oxidation using CuCl₂-based substrate, experiments and kinetic simulations were performed to obtain the activation energy for this reaction. It was found that CuCl₂ played an important role in lowering the activation energy for this reaction compared to other reported values of Hg(0) oxidation catalysts under HCl and O₂ conditions. This work is discussed in Chapter 2.

In addition, we wanted to study the various factors that can impact the adsorption of Hg(2+) in the ductwork and fabric filter by raw AC injection in coal combustion flue gas. Factors such as internal, external mass transfer, inlet HgCl₂ concentration, sorbent loading, and particle size were studied and its impact on the performance was investigated. In-flight Hg(2+) removal was found to be negligible while comparatively, the removal of Hg(2+) in the fabric filter was better but it was negligible nevertheless. For the removal of Hg(2+) in fabric filter, the effect of particle size was significant. A novel discontinuous injection mode was used and resulted in higher sorbent
utilization. However at the end of the cleaning cycle, most of the sorbent capacity was < 0.2%.

This work is discussed in Chapter 3.
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1 Introduction

Mercury is listed as a hazardous air pollutant (HAP) according to the United States Environmental Protection Agency (U.S. EPA). This persistent pollutant is of concern due to its bioaccumulation, high toxicity, high vapor pressure and its ability to stick on to things. It is estimated that the average time of mercury in the atmosphere is around a year while that of the oxidized species is estimated to be few days. Coal combustion is one of the major anthropogenic source of mercury emissions. With coal power accounting for 30% of the country’s electricity production in 2016 and a foreseeable dependency on coal for its utility needs, it is important to make sure that mercury is controlled during the process of combustion of coal.[1]

1.1 Mercury Emissions from Coal-fired Power Plants

Coal contains mercury to the tune of ~ 0.1 ppm.[2] When coal is combusted in a power plant, mercury along with many other toxic metals are released along with combustion products. These metals can have an adverse effect on health and environment. Amongst other metals, mercury is of concern and the U.S. EPA had issued standards known as the Mercury and Air Toxic Standards (MATS) rule, to regulate the mercury among other gases from power plants. The rule in its final form was released and corrected in March 2016.[3] It requires existing and new electric utility steam generating units (EGU) to limit the release of mercury and other toxic metals by > 90%. When combusted, mercury is present in three forms predominantly. It is present as elemental mercury (Hg(0)) , oxidized mercury (Hg(2+)) and particulate-bound mercury (Hg(p)). Depending on the type of coal combusted, the amount of mercury released can vary. Of the three forms, Hg(2+) is easily captured in the flue gas desulphurization unit.
(FGD) due to its high solubility in water while Hg(p) is easily captured using air pollution control devices (APCD). Capture of Hg(0) is most difficult and requires attention to make sure it is captured thoroughly.

### 1.2 Mercury Emission Control in Coal-fired Power Plant

After combustion, elemental mercury (Hg(0)) is released along with other acid gases and other product gases into the exhaust stream. Depending on the type or rank of coal, the concentrations of sulfur and chlorine vary. These different amounts of sulfur and chlorine plays an important role along with other gases such as SO₂, HCl, NOₓ, fly ash in oxidizing mercury.[4] It is predicted that Hg(0) reacts with atomic chlorine which is present in the gas phase, to homogeneously convert Hg(0) to Hg(2+).[5] With chlorine available in varying amounts between 50 and 2000 ppm (wt. basis), mercury chlorination is considered to be one of the major transformations taking place post-combustion in the flue gas. There are many other paths for mercury oxidation involving O₂, NOₓ, etc. that helps in oxidizing mercury. Homogeneous and heterogeneous transformations take place in oxidizing mercury with the latter playing a bigger role compared to the former.[6]

Particulate-bound mercury (Hg(p)) is easily captured in air pollution control devices (APCD). It can be removed by electrostatic precipitators (ESP) and fabric filters (FF).[7] Powdered activated carbon (PAC) injection is considered to be one of the most effective methods to capture mercury.[8] Brominated and halogen impregnated carbon such as DARCO-HG-LH, etc. have been used in the past to oxidize Hg(0) and capture the consequent Hg(2+).[9-11] Hg(2+) has also been captured in the wet flue gas desulphurization units, that have been
used to remove sulfur but can also be used to capture Hg(2+) since it is highly soluble in water.[12]

Heterogeneous reactions involving adsorption of Hg(2+) and oxidation of Hg(0) have also been studied in the past. Na₂S impregnated sorbents or halogen impregnated sorbents have been studied to evaluate the sorption capacity of mercury.[13, 14] Even though it has been studied in the past that fly ash does not adsorb mercury very well, studies have been conducted in the past to evaluate its properties.

Of all the potential mercury capture technologies, selective catalytic reduction (SCR) have been considered as a potential option to oxidize and capture mercury.[15, 16] SCR are traditionally used for the removal of NOₓ. It is considered that heterogeneous fittings can be added to SCR to help oxidize Hg(0) in the post-combustion window before the APCD at around 350-400 °C.

In our lab in the past, studies have been conducted using CuCl₂-impregnated AC and other substrates to study the oxidative and adsorptive capacities of these materials.[11, 17, 18] Adsorption kinetics of CuCl₂-impreganted AC has been studied in detail.[19] In order to study and predict the mercury capture efficiency, it is necessary to study the oxidative performance of CuCl₂ and Hg(0). For this purpose, it was determined that for the oxidation reaction of Hg(0), it was necessary to use a substrate that is chemically inert and one that retains the properties of CuCl₂. For this purpose, α-Al₂O₃ was used since it was studied in the past that the speciation of CuCl₂ is unchanged and the substrate acts chemically inert.[20]
1.3 Objective of this Research

The research objective of this study is to study the kinetics of Hg(0) vapor oxidation and determine the kinetic expression for this reaction. This will help in understanding the intrinsic oxidation mechanism between CuCl$_2$ and Hg(0) and also possibly understand if copper is a suitable candidate for this type of heterogeneous reaction by evaluating the activation energy of the reaction. Gas-solid models would be used appropriately describe the reaction between CuCl$_2$ and Hg(0). In addition to the experimental data, thermodynamic calculations would be performed in order to understand the incomplete conversion of CuCl$_2$ solids. Since the reaction temperature is closer to or greater than the Tamman temperature of the CuCl$_2$ grains, separate experiments would be conducted to quantify the agglomeration or sintering phenomenon, witnessed with the help of scanning electron microscopy (SEM). These resistances due to agglomeration would be taken into account while modeling and the kinetic expression would be determined. Chapter 2 would also describe the results obtained and the activation energy for this reaction would be compared with other reported values and discussed.

Chapter 3 will discuss the various factors influencing the capture of mercury using powdered activated carbon sorbent injection in the ductwork and fabric filter. Simulation results would be presented and discussed. The effect of the different factors would be explained.

The outcome of this independent research would further help to understand the fundamental mass transfer resistances involved in mercury capture and would provide systematic results and information on kinetic reaction of Hg(0) oxidation.
1.4 References


2 Reaction kinetic study of elemental mercury vapor oxidation with CuCl$_2$

2.1 Introduction

Mercury, a hazardous air pollutant (HAP), is regulated under the United States Environmental Protection Agency (U.S. EPA)’s Mercury and Air Toxics Standards (MATS) rule for coal- and oil-fired electric utility generating units (EGUs).[1] It is important to design mercury separation technologies using homogeneous and heterogeneous Hg(0) oxidation reactions for subsequent capture of the resultant and existing oxidized gaseous mercury species (Hg(2+)) in order to comply with the MATS rule. Presently, Powdered Activated Carbon (PAC) sorbent injection and Selective Catalytic Reduction (SCR) catalysts followed by wet Flue Gas Desulfurization (FGD) system are used to reduce mercury emissions in the post-combustion window of the U.S. coal-fired power plants.[2-4] Raw activated carbon (AC) in the presence of halogen gases or halogen-impregnated AC has shown good Hg(0) capture performances.[2, 5, 6] In our previous studies, cupric chloride (CuCl$_2$)-impregnated AC and Al$_2$O$_3$ demonstrated excellent Hg(0) chemisorption or oxidation capabilities, respectively, and its reaction mechanism was studied.[7-9] It was found that CuCl$_2$ reacts with Hg(0) to form CuCl and HgCl$_2$, respectively, as a result of the reaction.[8] However, a kinetic study of the Hg(0) oxidation reaction with CuCl$_2$ has not been reported in the literature.

Several models have been proposed to describe various heterogeneous gas-solid reactions with different reaction mechanisms including the general model, unreacted shrinking core model, and grain model.[10-13] The general model developed by Wen consists of a simple model that takes into account external and internal mass-transfer resistances and chemical reaction.[11, 14] The unreacted shrinking core model is extensively used for the reactions with
solids of low porosity, thereby forming ash layer or product layer around the unreacted core of solid reactant. As the reaction proceeds at a sharp interface between the reactant gas diffused through the product layer and the unreacted solid core, the unreacted core shrinks and the product layer thickness increases. External mass-transfer resistance around the solid, internal mass-transfer resistance inside the solid and the chemical reaction are considered in this model. On the other hand, grain model, developed by Sohn and Szekely, is used for porous solid.[13, 15] The solid is considered to contain small non-porous grains at a microscopic level. The shrinking core mechanism is applied to the grain phase forming the solid. Another predominant phenomenon taking place in gas-solid reactions is thermal sintering leading to deactivation of solids.[16] A loss in activation due to a decrease in active surface sites is common for reactions at high temperatures.[17] In this study, the Hg(0) oxidation kinetics over CuCl₂/α-Al₂O₃ was studied using gas-solid reaction models. A temperature window between 100 and 180 °C was used for potential applications after an air preheater at a typical coal-fired power plant. Both the general model and grain model were used to describe the reaction between Hg(0) vapor and CuCl₂ for the determination of a reaction kinetic expression.

2.2 Experiment

2.2.1 Preparation of CuCl₂/α-Al₂O₃

In this study, α-Al₂O₃ was used as a support since it neither changes the CuCl₂ speciation nor contains potential impurities that can react with Hg(0) vapor.[8] The use of the α-Al₂O₃ support helped disperse CuCl₂ and thus reduce its amount required to study the reaction kinetics. Low surface area α-Al₂O₃ pellets were purchased from Alfa Aesar (Alfa Aesar aluminum oxide-43862, 1/8” pellets, measured BET surface area = 0.79 m²/g). The
pellets were crushed and passed through a 40-μm sieve. The powdered α-Al₂O₃ was impregnated with CuCl₂·2H₂O (Sigma-Aldrich, >98% purity) using wetness incipient method by adding a known amount of aqueous solution of CuCl₂·2H₂O. The loading used on the support was set to 2%(wt) CuCl₂. After the impregnation, the sample was left to dry at room temperature overnight, and was subsequently used for different characterizations and performance tests.

2.2.2 CuCl₂/α-Al₂O₃ characterizations

Thermal gravimetric analysis-mass spectrometry (TGA, TA Instruments TGA Q5000IR and MS, Pfeiffer-Vacuum Thermostar) was used to check the thermal stability of the sample. The 2%(wt) CuCl₂/α-Al₂O₃ sample was heated from room temperature to 180 °C at a ramp rate of 1 °C/min in 25 mL/min of N₂ flow (99.999% UHP, Wright Brothers, Inc.). After the temperature reached 180 °C, the sample was kept isothermally for 4 hours. The amount of sample used was ~60 mg.

In order to examine the sample morphology, scanning electron microscopy (SEM, FEI, XL30) was used. The samples were pretreated by heating them at the respective reaction temperatures and removing them from the furnace at different times in order to view the morphological changes with respect to temperature and time. Before viewing these samples under the SEM, the samples were sputter coated with a thin layer of gold. The samples were viewed in back-scattering mode in order to obtain atomic number contrast for the differentiation between CuCl₂ grains and α-Al₂O₃ particles.

Separate chemisorption tests were carried out in order to determine the dispersion kinetics for CuCl₂ over the α-Al₂O₃ support with respect to temperature.[18] The samples were
kept at different reaction temperatures (i.e. 100, 140, and 180 °C) in N₂ flow. Then ~ 200 mg of a sample were taken out for chemisorption tests. The chemisorption tests were performed by static-volumetric carbon monoxide (CO) adsorption measurements using Micromeritics ASAP 2020. CO was found to have excellent affinity to Cu(I) sites. It was reported that Cu(I)-CO bonds are stronger than Cu(II)-CO interactions. Therefore, it was necessary to reduce CuCl₂ to CuCl in order to determine its dispersion over the α-Al₂O₃ support. Ethylene was used to reduce CuCl₂ to CuCl as used for ethylene oxychlorination reactions in the literature. The samples were heated to 110 °C for 15 min to remove any potential moisture before the tests. Then the samples were reduced using ethylene gas at 200 mmHg for 30 min at 75 °C followed by evacuation for 15 min. This reduction step was repeated three times to ensure that CuCl₂ was completely reduced to CuCl. Then an evacuation process was performed to desorb ethylene molecules potentially adsorbed onto the α-Al₂O₃ phase at 35 °C for 15 min followed by CO chemisorption at 35 °C. Volume adsorbed by the sample was measured at a pressure range of 50-500 mmHg. Some physically adsorbed CO gas molecules were removed by evacuating the sample after the first analysis. This was followed by repeating the CO adsorption. Thus, the first analysis gave the volume adsorbed derived from both chemical and physical adsorption while the repeated analysis gave the volume adsorbed as a result of physical adsorption only. The dispersion values were determined by calculating the volume intercept derived from the differences between the first and repeated analysis obtained from the isotherms.

2.2.3 Hg(0) breakthrough curves in fixed-bed system

For the Hg(0) oxidation kinetic study, Hg(0) breakthrough curves were obtained using a fixed-bed system shown in Fig. 2.1. Different inlet Hg(0) concentrations (5, 10, and 20 ppbv)
were used to test the sample at different reaction temperatures of 20, 100, 140, and 180 °C. Elemental mercury vapor was generated by flowing 1 L/min of N\textsubscript{2} (99.999% UHP, Wright Brothers, Inc.) gas through an Hg(0) permeation tube (Dynacal, VICI Metronics) immersed in an oil bath. A temperature controller (Fisher Scientific Isotemp 2100) was used to control the temperature of the oil bath within ±0.1 °C of a set point temperature. For each run, 25 mg of the sample mixed with 4 g of silica, sand was added to the fixed-bed reactor made of quartz. The reaction zone was measured to be ~20 mm. At the outlet of the reactor, the concentrations of Hg(0) and Hg(2+) were measured using the Ontario Hydro method.[20] A combination of 1 M KCl followed by 4%(w/v) KMnO\textsubscript{4}/10%(v/v) H\textsubscript{2}SO\textsubscript{4} impinger solutions were used to capture the Hg(2+) and Hg(0), respectively. Then, both of the mercury species were quantified using a cold vapor atomic absorption spectrophotometer (Model 400A, Buck Scientific, Inc.).
2.2.4 CuCl$_2$ utilization and equilibrium calculations

The unreacted CuCl$_2$ percentage was determined based on the stoichiometry for the reaction chemistry shown in equation (2.1).[8]

$$\text{Hg}(0) + 2\text{CuCl}_2 \rightarrow \text{HgCl}_2 + 2\text{CuCl}$$ \hspace{1cm} (2.1)

Since the amount of Hg(0) reacted can be determined from the breakthrough curves, the amount of CuCl$_2$ reacted can also be calculated based on stoichiometry, at a given temperature and an inlet Hg(0) concentration. This way the CuCl$_2$ unreacted can be calculated out since the amount of CuCl$_2$ placed in the reactor is known. Then the conversion of CuCl$_2$ during the reaction was determined as shown in equation (2.2).
The stoichiometric ratios on the other hand, were calculated differently. The moles of Hg(0) reacted was calculated using the breakthrough curves. Since the amount of CuCl\(_2\) placed in the reactor was known assuming that 100% of CuCl\(_2\) is reacted, the stoichiometric ratios were calculated by dividing the moles of CuCl\(_2\) reacted to the moles of Hg(0) reacted.

Equilibrium calculations were performed for the reaction between Hg(0) vapor and CuCl\(_2\) by using standard enthalpies and free energies of formation values obtained from the NIST-JANAF tables summarized in Table 2.3.[21] Equilibrium conversion was calculated based on equilibrium constant using the van’t Hoff equation.

\[
\frac{d \ln(K_{eq})}{dT} = \frac{\Delta H}{RT^2}
\]

where \(K_{eq}\) is the equilibrium constant; \(\Delta H\) is the enthalpy of reaction; and R is the universal gas constant.

### 2.3 Model for Hg(0) Oxidation Reaction Kinetics

#### 2.3.1 Model theory and assumptions

In this study, two models were used to describe the reaction kinetics for the reaction between Hg(0) and CuCl\(_2\) at low and high temperatures. It is based on our experimental observations that the agglomeration of CuCl\(_2\) grains is not noticeable at 20 °C but becomes significant between 100-180 °C. More detailed explanations are given in the Results and Discussion section. Two schematics for the different models are shown in Fig. 2.2. For the Hg(0) oxidation reaction at 20 °C, the general model assuming no sintering of CuCl\(_2\) grains was used to describe the reaction.[11, 14] External and internal mass-transfer resistances were
taken into consideration in this model. On the other hand, the Hg(0) oxidation reaction at higher temperatures (i.e. 100, 140 and 180 °C) illustrates the combined effects of simultaneous Hg(0) oxidation reaction with CuCl\textsubscript{2} and sintering of CuCl\textsubscript{2} grains. The mass-transfer resistance related to the product layer diffusion (i.e. Hg(0) diffusion through reacted CuCl/α-Al\textsubscript{2}O\textsubscript{3} layer) and the chemical reaction at the reaction interface was taken into account. It is assumed that each grain follows a shrinking core mechanism.[15, 22, 23] In this study, the Hg(0) oxidation reaction with CuCl\textsubscript{2} in the fixed-bed reactor was modeled using the following assumptions:

1. The gas flow in the fixed-bed system is considered to be plug flow.
2. Axial diffusion along the fixed-bed reactor is negligible.
3. The α-Al\textsubscript{2}O\textsubscript{3} particles and CuCl\textsubscript{2} grains are considered to be spherical and uniform in size.
4. The CuCl\textsubscript{2}/α-Al\textsubscript{2}O\textsubscript{3} particles are uniformly dispersed in the fixed-bed reactor.
5. The pressure drop across the fixed-bed system is negligible.
6. The reaction is considered to be isothermal.

2.3.2 Model equations

2.3.2.1 General model

As shown in Fig. 2.2(a), CuCl\textsubscript{2} was assumed to be uniformly coated over the α-Al\textsubscript{2}O\textsubscript{3} substrate in the general model. Inter-particle diffusion between the particles was taken into account. Based on the reaction chemistry shown in equation (2.1), the reaction kinetics was further assumed to be first order with respect to Hg(0) and CuCl\textsubscript{2} as shown in equation (2.4). Therefore, the intrinsic reaction rate expression for Hg(0) oxidation is given as

$$
\left( -r_{Hg}^m \right) = -\frac{dC_{Hg,p}}{dt} = k_m C_{Hg,p} C_{CuCl_2} = \frac{1}{2} \left( -r_{CuCl_2}^m \right)
$$

2.4
where $-r_{Hg}^{m}$ is the intrinsic Hg(0) oxidation rate based on particle volume (gmol Hg(0) reacted/(m$^3$ particle·s)); $-r_{CuCl_2}^{m}$ is the intrinsic reaction rate based on particle volume (gmol CuCl$_2$ reacted/(m$^3$ particle·s)); $k^{m}$ is the oxidation rate constant based on particle volume (m$^3$/(g·s)); $C_{Hg,p}$ is the Hg(0) concentration inside the particle phase (gmol Hg(0)/m$^3$); and $C_{CuCl_2}$ is the CuCl$_2$ concentration inside the particle phase (gmol CuCl$_2$/m$^3$).

To describe the inter-particle diffusion of Hg(0) between the pores of the CuCl$_2$/α-Al$_2$O$_3$ particles and the reaction of Hg(0) with CuCl$_2$ over the support, a shell mole balance for Hg(0) was formulated over the entire CuCl$_2$/α-Al$_2$O$_3$ particle phase as shown in eq. (2.5).

\[
\varepsilon_p \frac{\partial C_{Hg,p}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 D_r \frac{\partial C_{Hg,p}}{\partial r} \right) - \left( -r_{Hg}^{m} \right)
\]

where $D_r$ is the effective pore diffusion coefficient for Hg(0) vapor inside the pore (m$^2$/s); and $\varepsilon_p$ is the particle porosity.
Figure 2.2: Schematic of (a) general model and (b) grain model
Another shell mole balance for Hg(0) was used to describe the change in Hg(0) concentrations as a result of the reaction along the length of the reactor, and is given in eq. (2.6).

\[
\varepsilon_b \frac{\partial C_{Hg,b}}{\partial t} = -u_z \frac{\partial C_{Hg,b}}{\partial z} (1 - \varepsilon_b) (-r_{Hg,obs}^m)
\]

where \(-r_{Hg,obs}^m\) is the observed Hg(0) oxidation rate based on particle volume (gmol Hg(0) reacted/(m$^3$ particle⋅s)); \(C_{Hg,b}\) is the Hg(0) concentration in the bulk gas phase (gmol Hg(0)/m$^3$); \(u_z\) is the superficial gas velocity (m/s); and \(\varepsilon_b\) is the bed porosity. The observed reaction rate was taken by considering a volume integral of Hg(0) oxidation rate over the entire CuCl$_2$/α-Al$_2$O$_3$ particle phase and is given as

\[
\left( -r_{Hg,obs}^m \right) = \int \left( -r_{Hg,int}^m \right) dV = \frac{3}{V} \frac{4}{3} \pi R_p^3 D_v \frac{\partial C_{Hg,p}}{\partial r} \bigg|_{z,r=R_p,r}
\]

By coupling the observed reaction rate \(\left( -r_{Hg,obs}^m \right)\) derived from the local Hg(0) concentration inside the pores \(C_{Hg,p}\) with eq. (2.6), the concentration of Hg(0) in the bulk phase \(C_{Hg,b}\) can be determined.

A set of initial conditions (ICs) and boundary conditions (BCs) for eqs. (2.4), (2.5) and (2.6) are given as

ICs:

\[
C_{Hg,b} (z,t = 0) = 0; \quad C_{Hg,p} (z,r,t = 0) = 0; \quad C_{CuCl_2} (t = 0) = C_{CuCl_2,b}
\]

BCs:
It is worth mentioning that the external mass transfer between the particle and bulk gas phases was taken into account in one of the BCs.

2.3.2.2 Grain model

The grain model was formulated so that the effects of CuCl$_2$ sintering and Hg(0) oxidation reaction were taken into consideration. As shown in Fig. 2.2(b), each CuCl$_2$ grain forms a product layer around itself as Hg(0) vapor diffuses and reacts with CuCl$_2$, thereby forming CuCl between 100-180 °C. Then diffusing Hg(0) reacts with CuCl$_2$ at the interface between the product layer comprising CuCl and the unreacted CuCl$_2$ core (at r=r$_c$). At the beginning of the Hg(0) reaction with pure CuCl$_2$, the reaction interface (r$_c$) is the same as the grain radius (R$_g$). As the reaction proceeds, the reaction interface retreats toward the center of the grain (i.e. r$_c$ < R$_g$) throughout the reaction. Therefore, this model constitutes a moving boundary problem. Thus, as the reaction proceeds, the mass-transfer resistance to Hg(0) diffusion through the product layer increases with an increase in the thickness of the product layer.

An intrinsic Hg(0) oxidation kinetic expression is written in first order with respect to Hg(0) as shown in eq. (2.10). In the grain model, CuCl$_2$ is assumed to be available only at the reaction interface, and thus the reaction kinetics is also dependent on CuCl$_2$ available only at the reaction interface. This dependence can be shown by taking a shell mole balance for CuCl$_2$ around the unreacted CuCl$_2$ shrinking core as shown in eq. (2.10). These two rate expressions

\[
C_{Hg,b}(z=0,t) = C_{Hg,b}^{in}; \quad D_e \frac{\partial C_{Hg,p}(z=0,t)}{\partial r} = 0;
\]  

\[
D_e \frac{\partial C_{Hg,p}(z,r,R_p,t)}{\partial r} = k_g \left( C_{Hg,b}(z,t) - C_{Hg,p}(z,R_p,t) \right)
\]  

![Equation Image](image-url)
are stoichiometrically related, and thus the reaction kinetics for Hg(0) shows the dependence of CuCl$_2$ in terms of the radius of the unreacted CuCl$_2$ shrinking core. It is also worthwhile to mention here that this kinetic expression should be included as one of the boundary conditions (BCs).

$$\left(-r_{Hg}^n\right) = k^n C_{Hg,pdt} \bigg|_{r=r_c} = \frac{1}{2} \left(-r_{CuCl_2}^n\right) = -\frac{1}{2} \rho_{CuCl_2} \frac{dr_c}{dt} \quad 2.10$$

where $C_{Hg,pdt}$ is the concentration of Hg(0) inside the product layer (gmol Hg(0)/m$^3$); $\rho_{CuCl_2}$ is the density of CuCl$_2$ (gmol/m$^3$); $k''$ is the reaction rate constant (m/s); and $r_c$ is the reaction interface between the unreacted CuCl$_2$ core and the CuCl product layer (m).

The sintering kinetics for grain sintering and agglomeration (details are given in the Results and Discussion section) is expressed by CuCl$_2$ dispersion, and is given by a general power law expression in eq. (2.11).[16, 17]

$$\frac{dD}{dt} = -k_s \left(D - D_{eq}\right)^m \quad 2.11$$

where $D$ is dispersion (%); $k_s$ is the sintering rate constant (1/s); $m$ is the sintering order; and $D_{eq}$ is the limiting dispersion at equilibrium (%).

A shell mole balance for Hg(0) is taken to describe the diffusion of Hg(0) through the product layer of the grain phase for the Hg(0) reaction with CuCl$_2$ taking place at the interface between the CuCl$_2$ shrinking core and the CuCl product layer as shown in eq. (2.12).

$$\frac{\partial C_{Hg,pdt}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D_5 \left(\frac{D - D_{eq}}{D_0 - D_{eq}}\right) \frac{\partial C_{Hg,pdt}}{\partial r}\right) \quad 2.12$$

where $D_5$ is the product layer diffusion coefficient (m$^2$/s); and $D_0$ is the initial dispersion (%).

The sintering kinetics for CuCl$_2$ grains in eq. (2.11) is incorporated into eq. (2.12) to describe
the increasing diffusional resistance generated by the product layer in the grain phase as the reaction proceeds.

Another shell mole balance is formulated to describe the Hg(0) concentration profile along the length of the reactor as shown in eq. (2.13).

$$\varepsilon_b \frac{\partial C_{Hg,b}}{\partial t} = -u_z \frac{\partial C_{Hg,b}}{\partial z} - \left(1 - \varepsilon_b\right) \left(-r_{Hg,obs}^{m}\right) \frac{A}{V} \tag{2.13}$$

where $-r_{Hg,obs}^{m}$ is the observed Hg(0) oxidation rate based on particle surface (gmol Hg(0) reacted/(m² particle-s)); $u_z$ is the superficial gas velocity (m/s); $A$ is the surface area of grain; $V$ is the volume of grain; and $\varepsilon_b$ is the bed porosity. Taking a volume average over the local Hg(0) oxidation rate $\left(-r_{Hg}^{m}\right)$ over the entire grain volume gives the observed oxidation rate $\left(-r_{Hg,obs}^{m}\right)$ at the external surface of the grain.

$$\left(-r_{Hg,obs}^{m}\right) \frac{A}{V} = \left(-r_{Hg,obs}^{m}\right) \frac{\int \left(-r_{Hg}^{m}\right) dV}{V} = \frac{3}{R_g} \frac{D}{D_0 - D_{eq}} \frac{\varepsilon}{4} \frac{R^3}{\pi} \frac{\partial C_{Hg,ptd}}{\partial r} \bigg|_{r=R_g} \tag{2.14}$$

where $R_g$ is the radius of each grain; $-r_{Hg,obs}^{m}$ is the observed Hg(0) oxidation rate based on particle volume (gmol Hg(0) reacted/(m³ particle-s)). The observed oxidation rate given in eq. (2.14) is coupled with the mole balance given in eq. (2.13) to obtain the bulk-phase Hg(0) concentration profile along the reactor ($C_{Hg,b}$).

The eqs. (2.10), (2.11), (2.12) and (2.13) have the following set of initial (ICs) and boundary conditions (BCs).

ICs:
\[ r_c(t = 0) = R_g; \quad D(t = 0) = D_0; \quad C_{Hg,pdt}(z, r, t = 0) = 0; \quad C_{Hg,b}(z, t = 0) = 0 \quad 2.15 \]

BCs:
\[ C_{Hg,pdt}|_{z,r=R_g,t} = C_{Hg,b}(z, t); \]
\[ D_s \frac{\partial C_{Hg,pdt}}{\partial r} \bigg|_{z,r=r_c,t} = \left(-r''_{Hg}\right) \bigg|_{z,r=r_c,t} = k'' C_{Hg,pdt}|_{z,r=r_c,t}; \quad C_{Hg,b}(z = 0, t) = C_{Hg,b}^{in} \quad 2.16 \]

In the grain model, most mass-transfer resistance would exist in the product layer where sintering takes place throughout the reaction. Thus the external mass-transfer resistance between the grain and bulk gas phases was neglected as shown in the BCs. The profiles for \( r_c(t), D(t), C_{Hg,pdt}(z, r, t) \) and \( C_{Hg,b}(z, t) \) are obtained by solving eqs. (2.10), (2.11), (2.12) and (2.13) with ICs and BCs in eqs. (2.15) and (2.16) and the two unknown parameters of \( k'' \) and \( D_s \). Therefore, this model constitutes a two parameter optimization problem solving for \( k'' \) and \( D_s \) by comparing the model predictions with the experimental breakthrough data. Upon the completion of an iterative solution process for \( k'' \) and \( D_s \), a temporal profile for the reaction interface \( (r_c(t)) \) is also determined.

The conversion of the solid-phase \( CuCl_2 \) \( (X_{CuCl_2}) \) is calculated by taking the volume integral of the local conversion inside the grain over the entire reactor length \( (L) \) as shown in eq. (2.17).
\[ X_{CuCl_2} = \frac{1}{L} \int_0^L 1 - \left(\frac{r_c}{R_g}\right)^3 \, dz \quad 2.17 \]
2.3.3 Normalization

The set of the governing equations, initial and boundary conditions given in eqs. (2.10), (2.11), (2.12), (2.13), (2.15) and (2.16) have been normalized using the following set of dimensionless variables.

\[
\xi_c = \frac{r_c}{R_g}, \delta = \frac{D}{D_0}, \delta_{eq} = \frac{D_{eq}}{D_0}, \xi = \frac{r}{R_g}, \gamma = \frac{C_{Hg, pht}}{C_{Hg, b}}, \zeta = \frac{z}{L}, \gamma_B = \frac{C_{Hg, b}}{C_{Hg, b}}
\]

A set of the normalized governing eqs. is given as:

\[
\left(-r_{Hg}^n\right) = 2 \times \left(-r_{CuCl_2}^n\right) = \rho_B \times R_g \times \frac{\partial \xi_c}{\partial t} = -2 \times k \times \gamma_{\xi=\xi_c} \times C_{Hg, b}^{in}
\]

\[
\frac{\partial \delta}{\partial t} = -k_s (\delta - \delta_{eq})^{\nu}
\]

\[
R_t^2 \times \xi^2 \times \frac{\partial \gamma}{\partial t} = \frac{\partial}{\partial \xi} \left( \xi^2 D_s \left( \frac{\delta - \delta_{eq}}{(1 - \delta_{eq})} \right) \frac{\partial \gamma}{\partial \xi} \right)
\]

\[
\varepsilon_g \frac{\partial \gamma_{\xi}^n}{\partial t} = - \frac{u_g}{L} \frac{\partial \gamma_{\xi}^n}{\partial \xi} - (1 - \varepsilon_g) \frac{3 \times D_s \left( \frac{\delta - \delta_{eq}}{(1 - \delta_{eq})} \right) \frac{\partial \gamma}{\partial \xi}}{R_g^2 \left( \frac{\delta - \delta_{eq}}{(1 - \delta_{eq})} \right) \frac{\partial \gamma}{\partial \xi}}
\]

ICs:

\[
\xi_c (t = 0) = 1, \delta(t = 0) = 1, \gamma(\xi, \xi, t = 0) = 0, \gamma_B (\xi, t = 0) = 0
\]

BCs:

\[
\gamma(\xi, \xi = 1, t) = \gamma_B (\xi, t) \frac{D_s}{R_g} \frac{\partial \gamma}{\partial \xi}_{\xi=\xi_c, \xi=\xi_c} = -k_n \times \gamma_{\xi=\xi_c}^n \gamma_B (\xi = 0, t) = 1
\]

The normalized conversion of CuCl\(_2\) is given in eq. (2.25).

\[
X_B = \int_0^1 \left(1 - \xi_c^3\right) d\xi
\]
2.3.4 Parameters used in this model

COMSOL Multiphysics (version 4.4) was used to simulate the set of the coupled equations in the above section 2.3.3.[24] The bulk-phase concentration of Hg(0) at the outlet of the reactor \( C_{Hg,b}(z = L) \) and the conversion of the solid-phase CuCl\(_2\) \( (X_{CuCl2}) \) were used to assess the performance of the catalyst at different reaction temperatures and inlet Hg(0) concentrations. A summary of the parameters used in this model is given in Table 2.1. The mass-transfer coefficient, used in the general model, was calculated by using the Ranz-Marshall correlation given in eq. (2.26).[25, 26]

\[
Sh = \frac{2R_g k_g}{D_m} = 2 + 0.6\left(R_e\right)^{1/2} \left(Sc\right)^{1/3}
\]  

2.26

Table 2.1. Test conditions for fixed-bed runs.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow mode</td>
<td>Down-flow</td>
</tr>
<tr>
<td>Flow rate</td>
<td>1 L/min at 20 °C and 1 atm</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>20, 100, 140, 180 °C</td>
</tr>
<tr>
<td>Gas</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Superficial gas velocity</td>
<td>0.15 m/s</td>
</tr>
<tr>
<td>Reactor diameter</td>
<td>12 mm</td>
</tr>
<tr>
<td>Fixed-bed height</td>
<td>20 mm</td>
</tr>
<tr>
<td>Sorbent amount</td>
<td>25 mg with 4 g silica</td>
</tr>
<tr>
<td>Inlet Hg(0) concentration</td>
<td>5, 10, 20 ppbv</td>
</tr>
<tr>
<td>Gas hourly space velocity</td>
<td>26,515 h(^{-1})</td>
</tr>
<tr>
<td>Dopant loading</td>
<td>2% (wt.) CuCl(_2)/α-Al(_2)O(_3)</td>
</tr>
<tr>
<td>Bed porosity</td>
<td>0.98</td>
</tr>
<tr>
<td>Particle porosity</td>
<td>0.90</td>
</tr>
<tr>
<td>Effective diffusivity</td>
<td>(2.71 \times 10^{-7}) m(^2)/s</td>
</tr>
</tbody>
</table>

In this model, the two unknown parameters of product layer diffusion coefficient \( (D_s) \) and kinetic constant \( (k'') \) were determined through parameter estimation. Two least-square objective functions defined in eq. (2.27) were used to determine the two parameters by
comparing the model predictions with the experimental breakthrough and solid conversion results.

\[
\text{Min} \sum_{i=0}^{t_f} \left( C_{Hg,b}^{cal} (z = L, t) - C_{Hg,b}^{exp} (z = L, t) \right)^2 \\
\text{Min} \sum_{i=0}^{t_f} \left( X_{CuCl_2}^{cal} (t) - X_{CuCl_2}^{exp} (t) \right)^2
\]

2.4 Results and Discussion

2.4.1 CuCl\(_2\) utilization and equilibrium calculations

Table 2.2. Stoichiometric ratio of CuCl\(_2\) to Hg(0) reacted as a function of different reaction temperature and inlet Hg(0) concentration.

<table>
<thead>
<tr>
<th>Reaction temperature (°C)</th>
<th>Inlet Hg(0) concentration (ppbv)</th>
<th>Average stoichiometric ratio of CuCl(_2) to Hg(0) reacted</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100</td>
<td>3.1</td>
<td>3.0</td>
</tr>
<tr>
<td>140</td>
<td>5.4</td>
<td>5.6</td>
</tr>
<tr>
<td>180</td>
<td>13.0</td>
<td>13.2</td>
</tr>
</tbody>
</table>

Fig. 2.3. shows the unreacted CuCl\(_2\) percentage calculated from each experimental run at the end of the reaction, as a function of reaction temperature and inlet Hg(0) concentration. It can be seen that the CuCl\(_2\) utilization increases with a decrease in reaction temperature while it is not influenced by inlet Hg(0) concentration. At 180 °C, the unreacted CuCl\(_2\) percentage is ~80% while at 20 °C, all of the CuCl\(_2\) is reacted. Table 2.2 shows the stoichiometric ratio of CuCl\(_2\) to Hg(0) reacted. The stoichiometric ratio of CuCl\(_2\) to Hg(0) for a complete conversion of CuCl\(_2\) should be 2:1 as shown in the reaction chemistry of eq. (2.1). However, the ratio values were found to deviate from the ratio of 2 for a complete conversion as the reaction temperature increases. When the reaction temperature increases from 100 to 180 °C, the
average stoichiometric ratio of CuCl₂ to Hg(0) increased from 3.0 to 13.1. These results indicate that the reactivity of CuCl₂ decreases at higher reaction temperatures.

**Figure 2.3:** CuCl₂ utilization as a function of inlet Hg(0) concentration (5, 10, and 20 ppbv) and different reaction temperatures (20, 100, 140, and 180 °C).

In order to investigate this non-ideal behavior, equilibrium calculations were performed to check if the exothermicity of the reaction prevents CuCl₂ from complete conversion. Table 2.3 shows the calculated thermodynamic values for the reaction of Hg(0) and CuCl₂.[21] The Gibbs free energy change for Hg(0) oxidation with CuCl₂ is calculated to be negative while the enthalpy of reaction at different reaction temperatures are almost similar. For a temperature range between 100 and 180 °C, the equilibrium constant values are on the order of ~ 10^{12}-10^{14}. 

25
Based on these equilibrium constant values, the equilibrium conversion was calculated to be 100%. Therefore, it is concluded that this reaction should reach complete CuCl\textsubscript{2} conversion at equilibrium in the temperature range. Therefore, an increase in the unreacted CuCl\textsubscript{2} values with temperature shown in Fig. 2.3. cannot be explained by thermodynamics.

Table 2.3. Calculated thermodynamic values for reaction between CuCl\textsubscript{2} and Hg(0) at different reaction temperatures.

<table>
<thead>
<tr>
<th>Reaction temperature (°C)</th>
<th>ΔH\textsubscript{r} (kJ/gmol)</th>
<th>ΔG (kJ/gmol)</th>
<th>Equilibrium constant (K)</th>
<th>Equilibrium conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>-72.26</td>
<td>-101.05</td>
<td>1.40×10\textsuperscript{14}</td>
<td>100</td>
</tr>
<tr>
<td>140</td>
<td>-72.25</td>
<td>-104.14</td>
<td>1.47×10\textsuperscript{13}</td>
<td>100</td>
</tr>
<tr>
<td>180</td>
<td>-72.09</td>
<td>-107.24</td>
<td>2.30×10\textsuperscript{12}</td>
<td>100</td>
</tr>
</tbody>
</table>

2.4.2 TGA-MS analysis

TGA-MS experiments were performed in order to check the thermal stability of the 2%(wt) CuCl\textsubscript{2}/α-Al\textsubscript{2}O\textsubscript{3} sample. The results are shown in Fig. 2.4. The early weight loss up to 100 °C in the sample was close to ~0.7%. An expected weight loss derived from the dihydrate (2H\textsubscript{2}O) loss in the 2%(wt) CuCl\textsubscript{2}·2H\textsubscript{2}O/α-Al\textsubscript{2}O\textsubscript{3} was 0.4%.[8] When the sample was heated to 180 °C, ~0.8% of total weight loss was observed. This weight loss was attributed to the moisture from dihydrate (2H\textsubscript{2}O) and α-Al\textsubscript{2}O\textsubscript{3} substrate as confirmed by MS. As expected, the sample did not exhibit any chloride ion signals from CuCl\textsubscript{2} at a mass to charge ratio (m/e) of 35 when it was heated up to 180 °C. This result suggests that the stoichiometric ratios for the incomplete conversions cannot be attributed to the loss of activity in CuCl\textsubscript{2} due to the evolution of chlorine from the samples.
2.4.3 SEM analysis of CuCl$_2$/α-Al$_2$O$_3$

Fig. 2.5. shows the temporal SEM analysis of 2%(wt) CuCl$_2$/α-Al$_2$O$_3$ samples, used in this study. The images were taken at different temperatures and sampling times in back scattering mode to distinguish between CuCl$_2$ grains and α-Al$_2$O$_3$ particles, based on their different atomic numbers. As shown in Fig. 2.5(a) and 5(b), CuCl$_2$ grains are not visible at 20 °C. It seems that the CuCl$_2$ grains are uniform over the α-Al$_2$O$_3$ substrate and do not agglomerate or form clusters. Therefore, the general model was used for the reaction at 20 °C. However, at higher temperatures such as 100 and 180 °C as shown in Fig. 2.5(c)-(f), CuCl$_2$
grains are clearly visible. These grains seem to start to be formed less than an hour from the start of the reaction. Although it is difficult to validate from the images whether the grain agglomerates continue to grow with time, it is reasonable to speculate that the incomplete CuCl$_2$ utilization in this temperature range is attributed to the agglomeration phenomenon. It is considered that it is difficult for Hg(0) vapor to diffuse into the sintered CuCl$_2$ agglomerates and react with the unreacted CuCl$_2$ grains. This sintering effect is more pronounced at higher temperatures, and the diffusion of Hg(0) vapor is limited due to the sintering. The effect of sintering or agglomeration of CuCl$_2$ grains is reported to take place when the reaction temperature is higher than the Tamman temperature.[27] Tamman temperature is generally considered to be approximately one half of the absolute melting point in Kelvin of the CuCl$_2$ grains, which is necessary for them to be mobilized on the $\alpha$-Al$_2$O$_3$ substrate. The calculated Tamman temperature was found to be 771 K (112 °C) for CuCl$_2$. This is why CuCl$_2$ grains are not clearly visible in the 20 °C samples in Fig. 2.5(a) and 5(b) while CuCl$_2$ grain agglomerates are clearly visible from the 100 and 180 °C samples.
2.4.4 Dispersion kinetics for CuCl₂ over α-Al₂O₃

Table 2.4. Optimum dispersion kinetic parameters used in eq. (2.11) as a function of different reaction temperature.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>D_{eq}</th>
<th>k_s (1/s)</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.68</td>
<td>0.04</td>
<td>0.85</td>
</tr>
<tr>
<td>140</td>
<td>0.56</td>
<td>0.36</td>
<td>1.43</td>
</tr>
<tr>
<td>180</td>
<td>0.37</td>
<td>0.91</td>
<td>1.30</td>
</tr>
</tbody>
</table>

The effect of sintering was quantified by separately performing chemisorption tests on the samples to determine the dispersion of CuCl₂ over α-Al₂O₃ support at different reaction temperatures as shown in Fig. 2.6. Then the dispersion kinetics was determined with an empirical equation given in eq. (2.11).[16, 17] The optimum sintering rate constant (k_s) and sintering order (m) for different reaction temperatures are summarized in Table 2.4. The value of limiting dispersion (D_{eq}) decreases as the reaction temperature increases. It shows that the
dispersion of CuCl2 grains quantified by CO chemisorption decreases to a larger extent at higher temperatures. The optimum sintering kinetic constant (k_s) increased from 0.04 (1/s) at 100 °C to 0.91 (1/s) at 180 °C. The early loss of the dispersion of CuCl2 at high temperature accounts for the low CuCl2 utilization at high temperature shown in Fig. 2.3.

Figure 2.6: Relative CuCl2 dispersion on α-Al2O3 as a function of time at different reaction temperatures (100, 140, and 180 °C).
2.4.5 Model predictions for Hg(0) reaction, diffusion, and CuCl$_2$ conversion
Figure 2.7: Hg(0) breakthrough data and simulated results for 2% (wt) CuCl$_2$/α-Al$_2$O$_3$ as a function of different inlet Hg(0) concentration and reaction temperature.

Note: Lines are model predictions.
Figure 2.8: CuCl$_2$ conversion data and simulated results for 2% (wt) CuCl$_2$/α-Al$_2$O$_3$ as a function of different inlet Hg(0) concentration and reaction temperature.

Note: Lines are model predictions.
Fig. 2.7 and Fig. 2.8 show the experimental breakthrough curves at the outlet of the reactor and the calculated CuCl$_2$ conversion obtained using eq. (2.17) under different reaction temperatures (20, 100, 140 and 180 °C) and three different inlet Hg(0) concentrations (5, 10, and 20 ppbv), respectively. Overall, model predictions for all the temperatures and inlet Hg(0) concentrations are in good agreement with the experimental breakthrough curve and conversion results. Among all the breakthrough data, the breakthrough time at 20 °C for 20 ppbv inlet Hg(0) concentration was longest, and its CuCl$_2$ conversion was almost complete. On the other hand, as the temperature between 100 and 180 °C went higher, the breakthrough times became shorter and the final conversion was lower. These results are attributed to the sintering and agglomeration phenomenon of the CuCl$_2$ grain phase at the high temperatures. At all the reaction temperatures, the breakthrough time was longer as inlet Hg(0) concentration was lower as seen in Fig. 2.7. It is also interesting to note that the final CuCl$_2$ conversion reached almost the same value at a given temperature regardless of inlet Hg(0) concentration as shown in Fig. 2.8. This is most likely because the conversion is limited by sintering, which is a function of temperature. The time required to reach a final conversion increased with a decrease in inlet Hg(0) concentration.
Figure 2.9: (a) Change in diffusional flux as a function of inlet Hg(0) concentration along the reactor length, (b) Bulk-phase Hg(0) concentration profile along the length of the reactor at different reaction temperatures, (c) The observed and intrinsic Hg(0) oxidation rate along the
length of the reactor at different reaction temperatures \( C_{\text{Hg, b}}^{\text{in}} = 10 \text{ ppbv, } t = 1 \text{ hr} \), (d) The observed and intrinsic Hg(0) oxidation rate along the length of the reactor at different reaction temperatures \( C_{\text{Hg, b}}^{\text{in}} = 10 \text{ ppbv, } t = 8 \text{ hrs} \), (e) Hg(0) concentration profiles inside the product layer at the inlet and outlet of the reactor \( z / L = 0 \& 1 \) and at different reaction temperatures \( C_{\text{Hg, b}}^{\text{in}} = 10 \text{ ppbv, } t = 8 \text{ hrs} \), (f) The rate of change in the radius of the unreacted CuCl\(_2\) core at the inlet and outlet of the reactor \( z / L = 0 \& 1 \) and at different reaction temperatures \( C_{\text{Hg, b}}^{\text{in}} = 10 \text{ ppbv} \).

A higher inlet Hg(0) concentration results in a higher diffusional flux in the product layer inside the grain. As shown in Fig. 2.9(a), this leads to a higher Hg(0) oxidation rate at the reaction interface between the unreacted CuCl\(_2\) grains and the product layer, leading to a shorter breakthrough time. Fig. 2.9(b) shows the bulk-phase Hg(0) concentration profiles along the length of the reactor for an inlet Hg(0) concentration of 10 ppbv and a reaction time of 8 hours. As the reaction temperature increases, the outlet Hg(0) concentration increases, indicating low reactivity. This is more pronounced at 180 °C, suggesting that the reaction rate greatly slows down from 140 to 180 °C. This can also be clearly seen from the reaction rates plotted as a function of the reactor length in Fig. 2.9(c) and (d). The observed and intrinsic Hg(0) oxidation rates calculated by eq. 2.14 and eq. 2.10, respectively, along the reactor length at different temperatures for an inlet Hg(0) concentration of 10 ppbv and a reaction time of 1 hour are shown in Fig. 2.9(c). Both the observed and intrinsic reaction rates are close and decrease along the reactor length at a short reaction time of 1 hour since most Hg(0) vapor reacts with freshly available CuCl\(_2\) close to the reactor inlet. As a result, both of the reaction rates significantly decrease with a significant decrease in Hg(0) concentrations towards the reactor outlet. At higher reaction temperatures, both of the reaction rates are relatively higher due to higher
reaction kinetics. However, after 8 hours of the reaction shown in Fig. 2.9(d), a difference in the observed and intrinsic Hg(0) reaction rates becomes larger but decreases along the reactor length. The reaction rates at 140 °C are higher than those at 100 °C. However, at 180 °C, both of the Hg(0) oxidation rates near the reactor inlet are even lower than those at 100 and 140 °C although both rates at 180 °C gradually decrease along the reactor length. This is because the product of $D_s$ and $\left(\frac{D - D_{eq}}{D_0 - D_{eq}}\right)$ significantly decreases with an increase in the reaction temperature and time since the loss of dispersion is particularly significant at 180 °C (Table 2.5). A change in the reaction rates significantly slows down along the reactor length since the dispersion of CuCl$_2$ starts to reach a limiting dispersion value (i.e. $D_{eq}$) at 180 °C. This can be corroborated by low CuCl$_2$ conversion values at high temperatures.

The Hg(0) concentration profile along the product layer thickness is shown in Fig. 2.9(e). As the reaction temperature increases, the diffusional resistance derived from the combined effects of sintering and the increased product layer thickness also increases. This can be easily observed from the slope of the Hg(0) concentration in the product layer. At the reactor inlet, the slope becomes steeper with an increase in the reaction temperature, indicating that the diffusional resistance becomes larger. At the reactor outlet, this effect becomes particularly pronounced at 180 °C. The Hg(0) concentration profile inside the product layer at 180 °C is even higher than those at 100 and 140 °C. The Hg(0) concentrations are kept relatively high inside the product layer at 180 °C due to the low reactivity derived from the combined effects of sintering and product layer resulting in increased diffusional resistance. Fig. 2.9(f) shows the temporal evolution of the reaction interface between the unreacted core and the product layer at different temperatures. As shown in Figs. 2.3 and 2.8, the final conversion of CuCl$_2$ at a temperature is almost constant while the conversion decreases with an increase in the reaction
temperature. This decrease in conversion is indicated in Fig. 2.9(f) with the location of the reaction interface ($r_c$). At the final reaction time, the $r_c$ value at 100 °C is much smaller than that at 180 °C, indicating that the reaction interface moves much closer to the center of the grain at 100 °C. This shows that the conversion at a given inlet Hg(0) concentration increases with a decrease in the reaction temperature.

The incomplete conversion of the CuCl$_2$ grains are attributed to the sintering and agglomeration of CuCl$_2$ grains. As discussed in the previous section, sintering is predominant at the reaction temperature between 100 and 180 °C since this temperature range is higher than the Tamman temperature, above which CuCl$_2$ grains become mobile and form clusters and agglomerates.[27] Since the sintering kinetics for CuCl$_2$ grains is faster at higher temperatures, the diffusion kinetics for Hg(0) vapor through the sintered CuCl product layer significantly decreases at higher temperatures. This leads to lower CuCl$_2$ utilization at the high temperatures as shown in Fig. 2.3.

2.4.6 Hg(0) reaction and diffusion kinetics

Table 2.5 shows the optimum values determined for the product layer diffusion coefficient ($D_s$) and reaction rate constant ($k''$) using the double optimization method used in eq. (2.27) that minimizes the sum of the least square values between the experimental and simulation data for both the breakthrough and conversion curves. It can be seen that both $D_s$ and $k''$ increase with an increase in reaction temperature. Using the general model, the reaction rate constant was estimated to be 0.13 m/s at 20 °C while the rate constant obtained using the grain model increased to 0.28 m/s at 180 °C. As expected, the rate constant increased as the
reaction temperature increased from 20 to 180 °C. The temperature dependence of the rate constant was plotted in Fig. 2.10(a).

Table 2.5. Optimum reaction rate constant (k") and product layer diffusivity (D_s) as a function of different reaction temperatures and inlet Hg(0) concentrations.

<table>
<thead>
<tr>
<th>Reaction Temperature (°C)</th>
<th>Inlet Hg(0) concentration (ppbv)</th>
<th>k&quot; (m/s)</th>
<th>Average k&quot; (m/s)</th>
<th>D_s (10^{-8} m^2/s)</th>
<th>D_s' = D_s (D - D_{eq})/(1 - D_{eq}) (10^{-8} m^2/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>20</td>
<td>0.13</td>
<td>0.13</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100</td>
<td>5</td>
<td>0.17</td>
<td>0.18±0.03</td>
<td>22.5</td>
<td>22.5</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.16</td>
<td></td>
<td>5.9</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.21</td>
<td></td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>140</td>
<td>5</td>
<td>0.21</td>
<td>0.26±0.07</td>
<td>24.8</td>
<td>24.8</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.24</td>
<td></td>
<td>7.78</td>
<td>7.78</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.34</td>
<td></td>
<td>2.63</td>
<td>2.63</td>
</tr>
<tr>
<td>180</td>
<td>5</td>
<td>0.21</td>
<td>0.28±0.07</td>
<td>37.8</td>
<td>37.8</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.28</td>
<td></td>
<td>7.98</td>
<td>7.98</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.34</td>
<td></td>
<td>2.7</td>
<td>2.7</td>
</tr>
</tbody>
</table>

Assuming Arrhenius-type temperature dependence in eq. (2.28), the activation energy (E_a) and the pre-exponential factor (k_0) were determined.

\[
k" = k_0 \exp \left( \frac{-E_a}{RT} \right)
\] 2.28
Figure 2.10: Temperature dependence of (a) reaction rate constant ($k''$), and (b) product layer diffusion ($D_s$) for reaction between CuCl$_2$/α-Al$_2$O$_3$ and Hg(0).
The activation energy was calculated to be 5.58 kJ/gmol and the Arrhenius pre-exponential factor \(k_0\) was calculated to be 1.21 m/s. The activation energy for Hg(0) oxidation with CuCl\(_2\) was compared with other activation energy values reported in the literature for homogeneous and heterogeneous Hg(0) reaction systems using halogen gases and different catalysts. These reported values are summarized in Table 2.6. It is seen that the activation energy for Hg(0) oxidation using CuCl\(_2\) is significantly lower than the other reported values between 20 and 120 kJ/gmol.[28-34] Presto et al. reported an activation energy value of 20 kJ/gmol for Hg(0) oxidation using Ir catalyst soaked in aqueous HCl while Gao et al. reported an activation energy value of 37.73 kJ/gmol using a commercial SCR-based catalyst in a post combustion temperature window of 26-400 °C. Niksa et al. reported an activation energy value of 142 kJ/gmol for a homogenous Hg(0) oxidation reaction involving Cl\(_2\) gas while the homogeneous gas-phase reaction between Hg(0) and HCl, was predicted to have an activation energy of 332 kJ/gmol.[35] These reported values are much higher than that for the heterogeneous Hg(0) reaction with CuCl\(_2\) found in this study, suggesting that CuCl\(_2\) works as an excellent redox catalyst for Hg(0) oxidation. In conjunction with our previous mechanistic study of the reaction of Hg(0) vapor with CuCl\(_2\), this study result also validates that CuCl\(_2\) greatly enhances the Hg(0) oxidation reaction by not only providing Cl for Hg(0) oxidation but also lowering the activation energy barrier for the reaction by reducing Cu(2+) to Cu(1+).[8]

The product layer diffusion coefficient (D\(_S\)) values in Table 2.5 show that D\(_S\) increases with an increase in reaction temperature following Arrhenius temperature dependence shown in eq. (2.29). As shown in Fig. 2.10(b), the activation energy for the diffusion was calculated to be 7.74 kJ/gmol.
\[ D_s = D_{s0} \exp \left( -\frac{E_a}{RT} \right) \]

2.29

**Table 2.6.** Comparison of activation energy with other reported values for heterogeneous Hg(0) oxidation reactions.

<table>
<thead>
<tr>
<th>Activation Energy Ea (kJ/gmol)</th>
<th>Temperature range (°C)</th>
<th>Catalyst used</th>
<th>Gas conditions used</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.58</td>
<td>20-180</td>
<td>2% (wt) CuCl2/α-Al2O3</td>
<td>5, 10 and 20 ppbv Hg(0) in 1 L/min N2 flow</td>
<td>This study</td>
</tr>
<tr>
<td>20</td>
<td>137</td>
<td>Ir/HCl</td>
<td>~1 ppbv Hg(0), ~9% O2, ~250 ppm SO2, ~400 ppm NOx, ~10% CO2, and 6.5 ppm HCl</td>
<td>31</td>
</tr>
<tr>
<td>30</td>
<td>175-225</td>
<td>Gold-coated on quartz filter</td>
<td>~6 ppbv Hg(0), SO2, NO, Cl2, H2O, O2, and CO2</td>
<td>34</td>
</tr>
<tr>
<td>34</td>
<td>150-350</td>
<td>SCR catalyst (1% (wt) V2O5-10% (wt) WO3-TiO2)</td>
<td>5 ppbv Hg(0), 12% CO2, 5% O2, 5% H2O, 10 ppm HCl in air, and N2</td>
<td>32</td>
</tr>
<tr>
<td>37</td>
<td>26-400</td>
<td>WO3-V2O5/TiO2</td>
<td>~7.3 ppbv Hg(0), N2: 8% O2, and HCl</td>
<td>29</td>
</tr>
<tr>
<td>40</td>
<td>138-160</td>
<td>1% (wt) Gold/Alumina beads</td>
<td>1.2 ppbv Hg(0), 5.25% O2, 500 ppm SO2, 12.5% CO2, 50 ppm HCl and N2</td>
<td>30</td>
</tr>
<tr>
<td>58</td>
<td>170-400</td>
<td>V2O5/MoO3/TiO2</td>
<td>~1 ppbv Hg(0), pure N2, pure O2, 10% NO in N2, 10% NH3 in N2, and 5% HCl in N2</td>
<td>33</td>
</tr>
<tr>
<td>75</td>
<td>357-371</td>
<td>Honeycomb SCR</td>
<td>~1.2-2.4 ppbv Hg(0), 6% O2, 74% N2, 12% CO2, 8% H2O, 10 ppm H2SO4, 1000 ppm SO2, 400 ppm NO, NH3 and 15 ppm HCl</td>
<td>28</td>
</tr>
<tr>
<td>120</td>
<td>140-157</td>
<td>1% (wt) Platinum/Alumina beads</td>
<td>1.2 ppbv Hg(0), 5.25% O2, 500 ppm SO2, 12.5% CO2, 50 ppm HCl and N2</td>
<td>30</td>
</tr>
<tr>
<td>142</td>
<td>327-727</td>
<td>No catalyst – Homogeneous reaction</td>
<td>370 ppbv Hg(0), 10% CO2, 10% O2, 8% H2O, Cl2</td>
<td>35</td>
</tr>
</tbody>
</table>
It is interesting to note that the value of $D_S$ is a function of inlet Hg(0) concentration. This trend has been reported for the sulfation of calcium oxide.[36, 37] It was reported that the crystal growth associated with the product formation leads to a high porous product layer at low inlet gas concentration. This leads to a high product-layer diffusion coefficient inside the product layer. These reported observations are consistent with the results obtained in this study where the value of $D_S$ is high at low inlet Hg(0) concentration. It is also noteworthy from Table 2.5 that a product of $D_S$ and $\left(D - D_{eq}\right)/\left(D_0 - D_{eq}\right)$ significantly decreases with reaction time, which adds significant mass-transfer resistance to Hg(0) diffusion through the product layer.

### 2.5 Conclusions

The reaction kinetics for the heterogeneous Hg(0) oxidation reaction with CuCl$_2$ was studied using CuCl$_2$/α-Al$_2$O$_3$ under N$_2$ atmosphere. The general and grain models were used to determine the reaction rate constant and product layer diffusion coefficient using a fixed-bed system at 20 °C and 100-180 °C, respectively. Both model predictions were generally in good agreement with the experimental data. It was found that the sintering of CuCl$_2$ over α-Al$_2$O$_3$ support at 100-180 °C significantly increased the mass-transfer resistance to Hg(0) diffusion inside the reacted CuCl product layer leading to an incomplete conversion of the CuCl$_2$ grain phase. Nevertheless, the reaction rate constant for the intrinsic Hg(0) oxidation reaction was successfully determined by taking into account the mass-transfer resistance. The activation
energy value determined from the Arrhenius temperature dependence of the rate constants was much lower than other activation energy values reported for other catalysts evaluated for heterogeneous Hg(0) oxidation reactions with halogen gases in the literature. In conjunction with our previous study of the reaction mechanism of Hg(0) vapor with CuCl₂, this study result strongly supports that the activation energy barrier for Hg(0) oxidation reaction can greatly be lowered with CuCl₂ following a Mar-Maessen mechanism by the simultaneous reduction of Cu(2+) to Cu(1+) and readily available surface Cl sites.

2.6 Nomenclature

\[ C_{Hg,b} \] Hg(0) concentration in the bulk gas phase, g mol Hg(0)/m³

\[ C_{Hg,b}^{in} \] inlet Hg(0) concentration in the bulk gas phase, g mol Hg(0)/m³

\[ C_{Hg,p} \] Hg(0) concentration in the particle phase used in general model, g mol Hg(0)/m³

\[ C_{Hg,pdt} \] Hg(0) concentration inside the product layer, g mol Hg(0)/m³

\[ C_{CuCl_2} \] CuCl₂ concentration inside particle used in general model, g mol CuCl₂/m³

\[ C_{CuCl_2,0} \] initial CuCl₂ concentration inside particle, g mol CuCl₂/m³

\[ D \] dispersion of CuCl₂ over α-Al₂O₃, %

\[ D_e \] effective pore diffusion coefficient for Hg(0) vapor inside the pore, m²/s

\[ D_{eq} \] limiting dispersion at equilibrium, %

\[ D_m \] molecular diffusion coefficient for Hg(0) vapor, m²/s

\[ D_0 \] initial dispersion, %
\( D_s \)  
product layer diffusion coefficient for Hg(0) vapor used in grain model, m\(^2\)/s

\( k'' \)  
oxidation rate constant based on particle volume used in general model, m\(^3\)/(g\cdot s)

\( k' \)  
oxidation rate constant based on particle surface used in grain model, m/s

\( k_g \)  
gas-phase mass-transfer coefficient, m/s

\( k_s \)  
sintering rate constant, 1/s

\( L \)  
height of fixed-bed reactor, m

\( m \)  
sintering order

\( \text{Re}_p \)  
Reynolds number

\( R_g \)  
radius of CuCl\(_2\) grains, m

\( R_p \)  
radius of sorbent particle, m

\( \text{Sc} \)  
Schmidt number

\( \text{Sh} \)  
Sherwood number

\( r \)  
radial distance inside particle, m

\( r_C \)  
reaction interface between unreacted CuCl\(_2\) core and CuCl product layer, m

\( -r_{\text{Hg}}^m \)  
intrinsic Hg(0) oxidation rate based on particle volume used in general model, gmol Hg(0) reacted/(m\(^3\) particle\cdot s)

\( H_{\text{Hg}}(0) \) reacted/(m\(^3\) particle\cdot s)

\( -r_{\text{Hg}}'^m \)  
intrinsic Hg(0) oxidation rate based on particle surface used in grain model, gmol Hg(0) reacted/(m\(^2\) particle\cdot s)

\( H_{\text{Hg}}(0) \) reacted/(m\(^2\) particle\cdot s)

\( -r_{\text{Hg,obs}}^m \)  
observed Hg(0) oxidation rate based on particle volume used in general model, gmol Hg(0) reacted/(m\(^3\) particle\cdot s)
\(-r_{\text{Hg,obs}}^o\) observed Hg(0) oxidation rate based on particle surface used in grain model, g mol Hg(0) reacted/(m^2 particle\cdot s)

\(-r_{\text{CuCl}_2}^o\) intrinsic CuCl\(_2\) reaction rate based on particle surface used in grain model, g mol CuCl\(_2\) reacted/(m^2 particle\cdot s)

\(-r_{\text{CuCl}_2}''\) intrinsic CuCl\(_2\) reaction rate based on particle volume used in general model, g mol CuCl\(_2\) reacted/(m^3 particle\cdot s)

\(t\) time, s

\(u_z\) superficial gas velocity, m/s

\(X_{\text{CuCl}_2}\) conversion of CuCl\(_2\)

\(Z\) axial distance inside fixed-bed reactor, m

**Greek letters**

\(\varepsilon_b\) bed porosity, -

\(\varepsilon_p\) particle porosity, -

\(\rho_{\text{CuCl}_2}\) CuCl\(_2\) solid density, g mol/m\(^3\)

\(\delta\) dimensionless dispersion, see eq. (2.18)

\(\delta_{eq}\) dimensionless dispersion at infinite time, see eq. (2.18)

\(\xi\) dimensionless radial distance inside particle, see eq. (2.18)

\(\xi_C\) dimensionless radial distance inside product layer, see eq. (2.18)

\(\gamma\) dimensionless Hg(0) concentration in product layer, see eq. (2.18)
\( \gamma_B \)  
\text{dimensionless Hg(0) bulk concentration, see eq. (2.18)}

\( \zeta \)  
\text{dimensionless axial distance inside fixed-bed reactor, see eq. (2.18)}

### 2.7 References


3  Modeling of mercuric chloride removal in ductwork and fabric filter by raw activated carbon injection

The contents of this chapter has been published in whole or in part in the following journal article:


3.1 Introduction

The recent Mercury and Air Toxic Standard (MATS) rule limits the emissions of mercury (Hg) from power plants across the United States.[1] Under the MATS rule, the U.S. Environmental Protection Agency (U.S. EPA) started to reduce the mercury emissions from coal-fired power plants in 2015. Existing electric utility generating units (EGU) would limit their emissions below 0.18-18.14 g/GWh while newer EGUs would have stricter standards of limiting their emissions below 0.04-18.14 g/GWh depending on the type of fuel the EGU utilizes.[2] Activated carbon injection has shown promise in controlling gaseous mercury emissions in the particulate matter control devices (PMCDs).[3, 4] Previous model results suggest that the removal of oxidized mercury (Hg(2+)) in an entrained flow, using powdered activated carbon (PAC) sorbent is insignificant due to the mass-transfer resistance associated with the sorbent and its short residence time.[5, 6] It was also demonstrated through the U.S. Department of Energy’s (U.S. DOE) Field Test Program that the in-flight removal of mercury vapor with short residence times was insignificant.[7] In contrast, the removal of mercury in the PMCDs such as fabric filter (FF) and electrostatic precipitator (ESP) was reported to be significant.[6, 8]
It has been reported that raw activated carbon (AC) does not physically adsorb elemental mercury (Hg(0)) vapor in a typical post-combustion temperature window (e.g. 60-170 °C).[5, 9] Halogenated AC has shown good potential to increase the removal of both Hg(0) and Hg(2+) species.[10, 11] However, little has been reported about the capture performance of each mercury species by AC sorbent in terms of the physical and chemical properties of AC such as surface area, porosity, reactions kinetics, and adsorption kinetics and equilibrium. Since a typical mercury concentration in coal combustion flue gas is on the order of ppb, a minimum AC sorbent to mercury mass ratio must be much higher than its stoichiometric ratio (e.g., ~>10,000:1) to achieve >90% removal with a typical AC sorbent of a ~20-µm diameter.[12, 13] However, it is also difficult to find previous systematic studies about the effects of sorbent particle size, surface area, pore diameter and adsorption equilibrium and kinetics that can greatly impact on mercury capture performances in the ductwork and PMCDs.

Depending on a level of coal combustion, some unburned carbon remains in fly ash often as a consequence of low-NOx combustion systems. It has been reported that the mercury removal performances by fly ash carbons greatly vary with respect to various parameters such as surface area, carbon content, chlorine content in coal, coal types, surface functionalities on carbon.[14-16] One of the previous studies predicted that < 5% of mercury could be adsorbed by unburned carbon fly ash.[15] Despite the wide performance variations, there is a consensus that the adsorption capacity of fly ash carbons are generally limited. A previous study reported that the capacity for HgCl₂ is ~10 times smaller than that of raw AC.[14, 17]

In this study, the removal of mercuric chloride (HgCl₂) as a model oxidized mercury species in the ductwork and fabric filter using a raw AC sorbent (i.e. Norit America’s DARCO-HG) has been systematically studied by taking into account the physical parameters of the raw
AC sorbent, the physical adsorption equilibrium and kinetics for HgCl₂, inlet HgCl₂ concentrations, sorbent injection loadings, and external/internal mass transfer. The impacts of these considerations on capture performances in the ductwork and filter cake are demonstrated. A consideration of the pressure drop across the filter cake is also presented for the sorbent injection in a typical range of fly ash loadings. Previous studies have shown the effects of flue gas constituents on the adsorption capacity of HgCl₂ onto activated carbon.[18, 19] SO₂ was reported to have a negative effect on the sorption as it reacts with basic sites on AC. HCl helped in increasing the sorption capacity while NO₂ helped in promoting the negative effect of SO₂ on the sorption capacity of HgCl₂ onto carbon. However, these effects have not been quantified for the adsorption of HgCl₂ and thus have not considered in this study.

3.2 Kinetic Model for HgCl₂ Adsorption onto Raw AC

3.2.1 Model assumptions

Physical adsorption is considered a main mechanism for HgCl₂ adsorption onto raw AC for sorbent injection after air preheater at ~120-160 °C.[19] The adsorption kinetics was based on the Langmuir theory for this study as the experimental adsorption kinetic data best fit this theory.[20, 21] In a post-combustion entrained flow after sorbent injection, the adsorption of HgCl₂ onto sorbents comprises of mainly three steps: (1) the external mass transfer of bulk phase HgCl₂ to the outer surface of the sorbent; (2) the internal mass transfer due to pore diffusion inside the sorbent particle; and (3) the surface adsorption of HgCl₂ onto the inner pore surface of the sorbent. In this study, the adsorption of HgCl₂ onto AC sorbent has been modeled using the following assumptions:

1) The flue gas in the ductwork and filter cake follows plug flow;
2) The axial diffusion is negligible;

3) The sorbent particles are spherical in shape and have a uniform particle size;

4) The adsorption process is isothermal since HgCl$_2$ is present in trace amounts;

5) The properties of the sorbent used are constant; and

6) The adsorption of HgCl$_2$ on the inner walls of the ductwork is negligible.

### 3.2.2 Model equations

#### 3.2.2.1 In-flight model

The intrinsic HgCl$_2$ adsorption kinetic expression is given by the Langmuir theory in eq. 3.1. All of the symbols used in the equations are summarized in the nomenclature section.

$$
r_A = \rho_p \frac{dq}{dt} = \rho_p \left( k_1 (q_{\text{max}} - q) C - k_2 \left( = \frac{4}{k} \right) q \right)
$$

At equilibrium ($r_A = 0$), the kinetic rate expression leads to the following Langmuir isotherm.

$$
q^* = q_{\text{max}} \frac{KC^*}{1 + KC^*}
$$

The two parameters of ($q_{\text{max}}$) and K obtained from the Langmuir isotherm given in eq. 3.2 are used in the Langmuir kinetic expression shown in eq. 3.1.

A shell mole balance is formulated to describe the adsorption of HgCl$_2$ inside the sorbent particle. The expression is given as

$$
\varepsilon \frac{\partial C}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 D \frac{\partial C}{\partial r} \right) - r
$$

The local adsorption rate given in eq. 3.1 is coupled with the adsorption kinetic expression in eq. 3.3 in order to calculate the concentration of HgCl$_2$ inside the pore.
Then a mole balance inside the ductwork is taken to describe the in-flight adsorption of HgCl$_2$ in an entrained flow as shown in eq. 3.4.

\[
\frac{\partial C_b}{\partial t} = -r_{ads} \frac{m_{sc}}{D_p}
\]  

The observed adsorption rate expression at the external surface of the sorbent ($r = R_p$) is calculated by taking a volume average of the local HgCl$_2$ adsorption rate inside the pores over the entire sorbent particle. This expression is denoted as

\[
r_{ads} = \frac{3}{R_p} D_e \left( \frac{\partial C}{\partial r} \right)_{(r = R_p)}
\]  

Then the observed adsorption rate is coupled with the mole balance in eq. 3.4 to predict the bulk-phase HgCl$_2$ concentration.

The set of eqns. (3.1), (3.3), and (3.4) has the following initial conditions (ICs) and boundary conditions (BCs).

Initial conditions (ICs):

\[
q(r, t = 0) = 0; C(r, t = 0) = 0; C_B(t = 0) = C_B^{in}
\]  

Boundary conditions (BCs):

\[
\left. \frac{\partial q}{\partial r} \right|_{(r=0,t)} = 0; \left. \frac{\partial C}{\partial r} \right|_{(r=0,t)} = 0; \left. \frac{\partial C}{\partial r} \right|_{(r=R_p,t)} = \frac{k_g}{D_e} \left( C_B(t) - C(r = R_p, t) \right)
\]  

By solving the coupled governing equations comprised of eqns. (3.1), (3.3), (3.4) with ICs and BCs in eqns. (3.6) and (3.7), the profiles of $q(r, t)$, $C(r, t)$ and $C_B(t)$ can be obtained.

The governing equations (eqns. (3.1), (3.3), (3.4)), and the ICs and BCs given in eqns. (3.6) and (3.7) are normalized with the following dimensionless variables.

\[
\gamma \equiv \frac{C}{C_B^{in}}; \gamma_B \equiv \frac{C_B}{C_B^{in}}; \psi \equiv \frac{q}{q_{max}}; \xi \equiv r \frac{R_p}{D_e}; \tau \equiv \frac{t}{\frac{R_p}{D_e}}
\]
The normalized governing equations with the ICs and BCs are given in eqns. (3.9)-(3.13).

\[
\frac{\partial \phi}{\partial \tau} = \frac{\varepsilon_p R_p^2}{D_e} \left[ k_1 (1 - \phi) \gamma C^m_B - k_2 \left( \frac{k_p}{k_e} \right) \phi \right]
\]

\[
\xi^2 \frac{\partial \gamma}{\partial \tau} = \frac{\partial}{\partial \xi} \left( \xi^2 \frac{\partial \gamma}{\partial \xi} \right) - \frac{\rho \xi^2 q_{max} R_p^2}{D_e C^m_B} \left[ k_1 (1 - \phi) \gamma C^m_B - k_2 \left( \frac{k_p}{k_e} \right) \phi \right]
\]

\[
\frac{\partial \gamma_B}{\partial \tau} \bigg|_{(\xi=0, \tau)} = 0; \gamma(\xi, \tau = 0) = 0; \gamma_B (\tau = 0) = 1
\]

\[
\frac{\partial \phi}{\partial \xi} \bigg|_{(\xi=0, \tau)} = 0; \frac{\partial \gamma}{\partial \xi} \bigg|_{(\xi=0, \tau)} = 0; \frac{\partial \gamma}{\partial \xi} \bigg|_{(\xi=1, \tau)} = \frac{k_p R_p}{D_e} \left( \gamma_B (\tau) - \gamma (\xi = 1, \tau) \right)
\]

3.2.2.2 Filter cake model

A detailed description about our filter cake model is given in our previous study.[22]

The dimensionless normalized variables, governing equations, and ICs and BCs used in the filter cake model are given in eqns. (3.14)-(3.19).

\[
\gamma \equiv \frac{C}{C^m_B}; \gamma_B \equiv \frac{C_B}{C^m_B}; \phi \equiv \frac{q}{q_{max}}; \xi \equiv \frac{r}{R_p}; \tau \equiv \frac{u}{L_F}; \lambda \equiv \frac{z}{L_F}
\]

\[
\frac{\partial \phi}{\partial \tau} = \frac{L_F}{u} \left[ k_1 (1 - \phi) \gamma C^m_B - k_2 \left( \frac{k_p}{k_e} \right) \phi \right]
\]

\[
\varepsilon_p u \xi^2 \frac{R_p^2}{L_D} \frac{\partial \gamma}{\partial \tau} = \frac{\partial}{\partial \xi} \left( \xi^2 \frac{\partial \gamma}{\partial \xi} \right) - \frac{\rho \xi^2 q_{max} R_p^2}{D_e C^m_B} \left[ k_1 (1 - \phi) \gamma C^m_B - k_2 \left( \frac{k_p}{k_e} \right) \phi \right]
\]

\[
\varepsilon_p \frac{\partial \gamma_B}{\partial \tau} + \frac{\partial \gamma_B}{\partial \lambda} = - \frac{3(1 - \varepsilon_p)}{\varepsilon_p} \frac{D_e L_F}{R_p^2 u} \frac{m_{AC}}{m_{AC} + m_{AC}} \frac{\partial \gamma}{\partial \xi} \bigg|_{(\tau=1, \xi)}
\]

59
ICs:

\[ \varphi(\lambda, \xi, \tau = 0) = 0; \gamma(\lambda, \xi, \tau = 0) = 0; \gamma_B(\lambda, \tau = 0) = 0 \]  \hspace{1cm} 3.18

BCs:

\[ \left. \frac{\partial \varphi}{\partial \xi} \right|_{(\lambda, \xi = 0, \tau)} = 0; \left. \frac{\partial \gamma}{\partial \xi} \right|_{(\lambda, \xi = 0, \tau)} = 0; \left. \frac{\partial \gamma}{\partial \xi} \right|_{(\lambda, \xi = 1, \tau)} = \frac{k_e R_p}{D_e} \left( \gamma_B(\lambda, \tau) - \gamma(\lambda, \xi = 1, \tau) \right); \gamma_B \left( \lambda = \frac{L_c}{L}, \tau \right) = 1 \]  \hspace{1cm} 3.19

Darcy’s law is used to express the pressure drop across the filter cake. The pressure drop is given as the sum of two terms, one of which is related to the clean filter medium, \( \Delta P_f \), while the other one is related to the dust cake itself, \( \Delta P_c \).[23]

\[ \Delta P = \Delta P_f + \Delta P_c \]  \hspace{1cm} 3.20

The pressure drop across the clean fabric is given by

\[ \Delta P_f = S_E \times V \]  \hspace{1cm} 3.21

where \( S_E \) is the resistance due to the fabric and \( V \) is gas velocity. The pressure drop due to the dust is given by

\[ \Delta P_c = K_2 \times C_i \times V^2 \times t \]  \hspace{1cm} 3.22

where \( K_2 \) is the specific cake coefficient; \( C_i \) is the inlet dust concentration; and \( t \) is filtration time. The \( \Delta P_c \) term is especially important as it is generally larger in magnitude than the first term, \( \Delta P_f \). \( K_2 \) depends on the type of a dust, mean particle diameter of dust and is a measure of how fast the dust accumulates in the filter cake. It is found experimentally.[24]
3.2.3 Parameters used in the model

The HgCl₂ adsorption model was applied to DARCO-HG AC sorbent. Table 3.1 lists the physical properties of the sorbent and diffusion coefficient values. The Langmuir adsorption equilibrium and intrinsic kinetic parameters were obtained from our previous study.[21] Another dataset for the DARCO-G60 AC sorbent reported in a previous study is also shown in Tables 3.1 and 3.2 for a comparison of modeling results.[20] The effective diffusivity inside the pores of the sorbent \( (D_e) \) and the gas-phase mass transfer coefficients \( (k_g) \) were calculated to be \( 9.05 \times 10^{-8} \) m²/s and 2.12 m/s, respectively.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Particle density, ( \rho_p ) (g/cm³)</th>
<th>BET surface area (m²/g)</th>
<th>Pore volume ( v_p ) (cm³/g)</th>
<th>Particle porosity, ( \varepsilon_p )</th>
<th>( d_{pore} ) (nm)</th>
<th>Knudsen diffusivity (m²/s)</th>
<th>Effective diffusivity (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DARCO-HG</td>
<td>0.950</td>
<td>476</td>
<td>0.53</td>
<td>0.50</td>
<td>6.2</td>
<td>3.71 ( \times ) 10⁻⁷</td>
<td>9.05 ( \times ) 10⁻⁸</td>
</tr>
<tr>
<td>DARCO-G60[20]</td>
<td>0.450</td>
<td>230</td>
<td>Not available</td>
<td>0.60</td>
<td>3.7</td>
<td>2.21 ( \times ) 10⁻⁷</td>
<td>7.86 ( \times ) 10⁻⁸</td>
</tr>
</tbody>
</table>

Molecular diffusivity = \( 1.53 \times 10^{-5} \) m²/s

To calculate the pressure drop across the filter cake, a dust velocity of 0.02 m/s was taken.[23] Typically, activated carbon sorbent loading is \( \sim \)1-5% of the fly ash loading.[25] This way, the fly ash loading was calculated to be 10 g/m³. The value of the specific cake resistance, \( K_2 \), was calculated to be \( 1 \times 10^5 \) s⁻¹ (=10 inches of H₂O/fpm/(lb/ft²)) and \( 0.63 \times 10^5 \) s⁻¹ (=6.25 inches of H₂O/fpm/(lb/ft²)) based on the dust velocity and the mass mean diameter of fly ash dust of 10 μm and 20 μm, respectively.

61
Table 3.2. Langmuir adsorption equilibrium and kinetic constants used in this study.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>( q_{\text{max}} ) (g HgCl(_2)/g sorbent)</th>
<th>( K ) (m(^3)/g HgCl(_2))</th>
<th>( k_1 ) (m(^3)/(g-s))</th>
<th>( k_2 ) (1/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DARCO-HG</td>
<td>0.055</td>
<td>2.1 \times 10^4</td>
<td>0.2</td>
<td>9.5 \times 10^{-6}</td>
</tr>
<tr>
<td>DARCO-G60[20]</td>
<td>0.0387</td>
<td>4.77 \times 10^2</td>
<td>0.2</td>
<td>4.19 \times 10^{-4}</td>
</tr>
</tbody>
</table>

3.3 Results and Discussion

The model was solved by using COMSOL Multiphysics (version 4.4). The in-flight HgCl\(_2\) removal performance of the sorbent was assessed by using two parameters. The first one was normalized average HgCl\(_2\) uptake \( \left( q_{\text{avg}} / q_{\text{max}} \right) \) as an indicator for the sorbent utilization. It was calculated by

\[
q_{\text{avg}} (t) = \frac{[C_B^{\text{in}} - C_B (t)]}{m_{AC}}
\]

3.23

The other performance parameter was HgCl\(_2\) removal represented by normalized bulk-phase HgCl\(_2\) concentration \( \gamma_B (t') = C_B (t) / C_B^{\text{in}} \). In a typical power plant, the in-flight residence time of a sorbent after air preheater is estimated to be \( \sim 1.5-2 \) s until the sorbent particles are collected at PMCDs.[26] Therefore, in this study, all simulations have been run for \( \leq 5 \) s.

On the other hand, for the study of HgCl\(_2\) capture in a fabric filter, the average HgCl\(_2\) uptake was modified for the capture in the filter cake by

\[
q_{\text{avg}} (t) = \int_0^t \left( C_B^{\text{in}} - C_B^{\text{out}} (t) \right) dt
\]

3.24

The normalized HgCl\(_2\) concentration at the outlet of the filter cake was determined by

\[
\gamma_B (\lambda = 0, \tau) = \frac{C_B^{\text{out}} (z = 0, t)}{C_B^{\text{in}}}
\]

3.25
Table 3.3. Base case simulation parameters used for in-flight and fabric filter capture.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet HgCl\textsubscript{2} concentration</td>
<td>1 ppbv (=11 µg/dscm)</td>
</tr>
<tr>
<td>Sorbent injection loading</td>
<td>0.1 g/m\textsuperscript{3} (=6.2 lb/MMcf)</td>
</tr>
<tr>
<td>Temperature</td>
<td>140 °C</td>
</tr>
<tr>
<td>Residence time in ductwork for in-flight capture</td>
<td>5 s</td>
</tr>
<tr>
<td>Filtration time for fabric filter capture</td>
<td>90 mins</td>
</tr>
</tbody>
</table>

The operating conditions listed in Table 3.3 were selected as a base case and were used to study the effects of different factors. In the base case, a sorbent injection loading of 0.1 g/m\textsuperscript{3} was chosen since most power plants cannot allow for the loading greater than 0.16 g/m\textsuperscript{3} (=10 lb/MMacf).[7] A schematic of mercury capture by PAC injection is shown in Figure 3.1.

![Schematic of post-combustion capture of mercury in a typical coal-fired power plant.](image)

Figure 3.1: Schematic of post-combustion capture of mercury in a typical coal-fired power plant.

3.3.1 In-flight HgCl\textsubscript{2} removal study

3.3.1.1 Effects of sorbent particle size and inlet HgCl\textsubscript{2} concentration

The HgCl\textsubscript{2} removal efficiency and sorbent utilization as a function of in-flight residence time for different particle sizes ranging from 10 to 30 µm and varying inlet HgCl\textsubscript{2} concentrations ranging from 1 ppbv (=11 µg/dscm) to 5 ppbv (=55 µg/dscm) for raw AC
sorbent are shown in Figure 3.2(a) and 2(b), respectively. It is evident that HgCl$_2$ removed in the ductwork is $< \sim 0.5\%$ up to 5-s residence time for all the particle sizes and inlet HgCl$_2$ concentrations at the baseline sorbent injection loading of 0.1 g/m$^3$. Although it is difficult to find experimental data obtained for the in-flight removal of HgCl$_2$ under well-controlled settings in the literature, a previous paper taking into account the adsorption kinetics and equilibrium for another PAC sorbent also reported that the removal under similar conditions was negligible.[5] As the sorbent particle size increases from 10 to 30 μm, the internal mass-transfer resistance increases and thus HgCl$_2$ removal efficiency decreases from $\sim 0.5$ to 0.25%. It is seen that a variation in the inlet HgCl$_2$ concentrations does not affect the HgCl$_2$ removal efficiency. This suggests that the external mass-transfer resistance derived from the HgCl$_2$ concentration difference in the bulk gas phase is not critical to HgCl$_2$ removal in the ductwork. Since the sorbent has a very short residence time in the duct, the in-flight capture of HgCl$_2$ is negligible.

From Figure 3.2(b), it can be seen that the sorbent utilization of DARCO-HG is very small as $\sim<0.005\%$ of the maximum sorbent capacity was utilized. Although a variation in sorbent particle sizes and inlet HgCl$_2$ concentrations does play a role in the sorbent utilization, these effects are noted insignificant. The sorbent utilization decreases from $\sim 0.0048$ to 0.0026% with an increase in sorbent particle size from 10 to 30 μm. The sorbent utilization increases with an increase in the inlet HgCl$_2$ concentration as the sorbent can adsorb more HgCl$_2$. 
Figure 3.2: Effects of sorbent particle size and inlet HgCl$_2$ concentration on (a) HgCl$_2$ removal efficiency, (b) sorbent utilization as a function of in-flight residence time, where external and internal mass transfer resistances were considered for all cases (DARCO-HG,
m_{AC} = 0.1 \text{ g/m}^3, T = 140 ^\circ \text{C}). Effects of sorbent loading, internal mass transfer (int MT) and external mass transfer (ext MT) on (c) HgCl$_2$ removal efficiency and (d) sorbent utilization as a function of in-flight residence time (DARCO-HG, C_{B}^{in} = 1 \text{ ppbv} (=11 \mu \text{g/dscm}), D_p = 20 \mu \text{m}, T = 140 ^\circ \text{C}).

3.3.1.2 Effects of sorbent loading and external/internal mass transfer

The in-flight HgCl$_2$ removal efficiency and sorbent utilization with respect to sorbent loading and external/internal mass transfer are shown in Figure 3.2(c) and (d), respectively. Although the removal is insignificant, the effect of sorbent loading is pronounced. When the sorbent loading increases from 0.1 g/m$^3$ (=6.2 lb/MMcf) and 1 g/m$^3$ (=62 lb/MMcf), the HgCl$_2$ removal efficiency almost proportionally increases from ~0.4% to ~3.4%.

On the other hand, external mass transfer is found to play an insignificant role as the HgCl$_2$ removal efficiency is almost identical in the presence and absence of an external mass-transfer consideration. When external mass-transfer is taken into account, the Ranz and Marshall equation in eq. (3.26) is used for the mass-transfer coefficient (k_g) in eqns. (3.7) and (3.13).

\[
Sh = 2 + 0.6 \left( \frac{Re}{d_p} \right)^{\frac{1}{5}} \left( \frac{Sc}{d_p} \right)^{\frac{1}{5}}
\]

3.26

When it is not considered for the case of excluding external mass transfer, the surface concentration was set to the bulk-phase concentration (i.e. C(R_p, t) = C_B(t)). The external mass-transfer resistance is found to be insignificant and can thus be ignored.

The role of internal mass transfer comprising pore diffusion and surface adsorption is more pronounced for the in-flight capture. The internal pores provide the surface area and pore volume required for the adsorption and transport of HgCl$_2$ inside AC. When the internal surface area is reduced, the maximum adsorption capacity in the Langmuir adsorption kinetics in eq. (3.1) is also reduced. The pore size governs the pore diffusion of HgCl$_2$ and determines the
effective diffusivity via the Knudsen diffusivity in the model. The pore diffusion of HgCl₂ inside DARCO-HG is primarily governed by the Knudsen diffusion. In order to examine the effect of pore diameter and maximum adsorption capacity, the model predictions using DARCO-HG were compared with those using DARCO-G60. The parameters obtained for DARCO-G60 in Tables 3.1 and 3.2 were used to predict the HgCl₂ removal and sorbent utilization. When the reduced effectiveness diffusivity (D_{eff}), maximum adsorption capacity (q_{max}), and adsorption equilibrium constant (K) were used for DARCO-G60, HgCl₂ removal decreased from ~0.35% (DARCO-HG) to ~0.30% (DARCO-G60) for a short residence time of 5 s given in Fig. 3.2(c). The corresponding sorbent utilization in Fig. 3.2(d) shows that DARCO-G60 is better utilized for the in-flight removal since the maximum adsorption capacity (0.0387 g HgCl₂/g sorbent for DARCO-G60) is less than that of higher surface area sorbent (0.055 g HgCl₂/g sorbent for DARCO-HG). It is also seen that better sorbent utilization can be achieved at low sorbent loading, high porosity, and no external mass transfer. However, it should be noted that these effects on the in-flight removal is negligible.

3.3.1.3 Effects of particle size, sorbent loading and residence time

The local HgCl₂ concentration profile inside the sorbent as a function of the radius of the particle with different sorbent particle sizes varying from 10 to 30 μm and in-flight residence times varying from 2 to 5 s is shown in Figure 3.3(a). It is clearly shown that a variation in the residence times from 2 to 5 s makes almost no difference in the HgCl₂ concentrations inside the sorbent with the different particle sizes. This indicates that the residence times are too short to result in different local HgCl₂ concentrations inside the sorbent.
Figure 3.3: (a) Effects of sorbent particle size and in-flight residence time on the HgCl$_2$ concentration inside the sorbent as a function of radius of the particle (DARCO-HG; C$_{Hg}^{in}$, 1 ppbv (= 11 µg/dscm), $m_{AC} = 0.1$ g/m$^3$, $T = 140$ ºC). (b) Effects of sorbent loading and in-
flight residence time on the HgCl$_2$ concentration inside the sorbent as a function of radius of the particle (DARCO-HG, C$_{in}^{Hg}$ = 1 ppbv (= 11 µg/dscm), D$_p$ = 20 µm, T = 140 ºC).

Figure 3.3(b) shows the local HgCl$_2$ concentration profiles with respect to sorbent loading ranging from 0.1 to 1 g/m$^3$ and residence time varying from 2 to 5 s. The result suggests that even the 10-time difference in the sorbent loadings has an insignificant impact on the local HgCl$_2$ concentration profiles.

3.3.2 Fabric filter HgCl$_2$ removal study

3.3.2.1 Effects of sorbent particle size and external/internal mass transfer

Figure 3.4(a) and (b) show the HgCl$_2$ removal efficiency and sorbent utilization as a function of filtration time in terms of sorbent particle size, external, and internal mass transfer. The results show that the sorbent particle size plays a major role in HgCl$_2$ removal efficiency on FF. For example, a smaller sorbent with a 10-µm diameter shows a ~90% HgCl$_2$ removal efficiency at 40 min while a larger sorbent with a 30-µm diameter shows ~70% removal. A smaller particle has less resistance to adsorption when compared to a larger sorbent. The result also estimates that it takes ~60 min to achieve 90% HgCl$_2$ removal when the sorbent with a 20-µm diameter is continuously injected at 0.1 g/m$^3$. 


Figure 3.4: Effects of sorbent particle size and internal (int MT)/external mass transfer (ext MT) on (a) HgCl$_2$ removal efficiency and (b) sorbent utilization for continuous sorbent injection (DARCO-HG, $C_B^{in} = 1$ ppbv ($= 11$ µg/dscm), $m_{AC} = 0.1$ g/m$^3$, $T = 140$ ºC). Effects
of sorbent loading and internal (int MT)/ external mass transfer (ext MT) on (c) HgCl$_2$ removal efficiency and (d) sorbent utilization for continuous (CI) and discontinuous (DI) sorbent injection (DARCO-HG, C$_{B_{in}}$ = 1 ppbv (= 11 µg/dscm), m$_{AC}$ = 0.1 g/m$^3$, T = 140 ºC).

The sorbent utilization for a smaller particle is found to be better compared to a larger one. However, it needs to be noted that the adsorption capacity of a small sorbent is small compared to the capacity of the large one. To study the effect of internal mass transfer, two sorbents with different surface areas were compared. The internal pores required for adsorption was found to be an important factor with the smaller surface area sorbent showing lower HgCl$_2$ removal efficiency.

### 3.3.2.2 Effects of sorbent loading and external/internal mass transfer

The temporal removal of HgCl$_2$ and sorbent utilization with respect to sorbent loading and external/internal mass transfer are shown in Figure 3.4(c) and (d), respectively. Sorbent loading and filtration time are the most important factors affecting the HgCl$_2$ removal efficiency in FF. As a case study, the HgCl$_2$ removal performances are compared for continuous and discontinuous sorbent injection methods introducing the same amount of the raw AC sorbent during a cleaning cycle. By injecting a 10-time higher sorbent loading (i.e. 1 g/m$^3$) in 10% of a cleaning time (i.e. 9 min), a HgCl$_2$ removal efficiency of ~90% can be achieved within the first 10% of the filtration time. If the same amount of sorbent is used at a lower sorbent loading (i.e. 0.1 g/m$^3$), the same ~90% HgCl$_2$ removal can be achieved after ~66% of the entire filtration time. As shown in Figure 3.4(d), while a continuous sorbent loading at 0.1 g/m$^3$ can utilize ~0.15% of the total adsorption capacity, a discontinuous loading at 1 g/m$^3$ can achieve ~0.20%.
The role of external mass transfer is also found to be insignificant in FF. This shows that the external mass-transfer resistance estimated by the Ranz and Marshall equation is diffusion limited and insignificant under FF conditions. However, the effect of internal mass transfer is significant as can be seen in Figure 3.4 (c-d). In the case of discontinuous loading, it is seen that HgCl$_2$ removal efficiency decreases after sorbent injection is cut-off for smaller surface area sorbent. This is because the desorption of HgCl$_2$ from the sorbent is significant. This is not evident in DARCO-HG as the equilibrium constant is relatively higher.

3.3.2.3 Effects of sorbent particle size and continuous/discontinuous injection

An additional case study is conducted for continuous and discontinuous injection in terms of sorbent particle size by taking into account external and internal mass transfer. The effect of the sorbent particle size on the removal is much more pronounced for continuous injection as shown in Figure 3.5(a). When the particle diameter varies from 10 to 30 μm, the HgCl$_2$ removal efficiency for continuous injection varies noticeably. For example, a 90% HgCl$_2$ removal efficiency is achieved at ~40 min for a continuous injection of 10-μm particles while it takes ~78 min to achieve the same 90% removal with 30-μm particles. On the other hand, the removal for discontinuous injection is less sensitive to the particle size. This difference is attributed mainly to the sorbent injection loading ($m_{AC}$) in eq. (3.17). When discontinuous injection is used, the thick sorbent layer accumulated on the filter cake as a result of high loading during an initial filtration period significantly removes HgCl$_2$, thus leading to less dependence on the particle size.
Figure 3.5: Effects of sorbent particle size and loading on (a) HgCl\textsubscript{2} removal efficiency and (b) sorbent utilization when external and internal mass transfers were considered for
continuous (CI) and discontinuous (DI) sorbent injection (DARCO-HG, C_{in} = 1 ppbv (= 11 µg/dscm), T = 140 °C).

Figure 3.5(b) shows better sorbent utilization for continuous injection up to later filtration phase as a result of low continuous loading. However, if longer filtration time is allowable, discontinuous injection shows better utilization. This will be governed by allowable pressure drop across the filter cake, and is discussed in the next section.

### 3.3.2.4 Pressure drop across the filter cake

Figure 3.6 shows the pressure drop across the filter cake in terms of fly ash particle size and cake thickness as a function of filtration time. Typically, fabric filters have an operating pressure drop ranging between 871 Pa (=3.5 inches of H2O) and 2,240 Pa (=9 inches of H2O) with an average operating pressure drop of ~1,593 Pa (=6.4 inches of H2O).[23] In practice, a typical sorbent loading is ~1-5% of fly ash loading and a typical fly ash loading is ~10 g/m$^3$.[25] Using Darcy’s law, the pressure drop can be estimated for the filter cake. The particle size distribution of fly ash is reported to range from 5 µm to as big as 100 µm with an average particle size of ~10-20 µm comparable to the size of raw AC.[27] Therefore, in this study, the pressure drop is estimated using fly ash particles with 10- and 20-µm diameters injected at 10 g/m$^3$. As shown in Figure 3.6, the pressure drop is sensitive to the particle size. For a dust diameter of 10 µm, an average cleaning cycle based on the average pressure drop could be close to ~70 min while for 20-µm dust particles, an average cleaning cycle can last up to 90 min, which is used in this study. The filter cake thickness was estimated to be ~1.5 mm for a filtration time of 90 min.
3.4 Conclusions

A detailed case study on the adsorption of HgCl$_2$ by DARCO-HG sorbent was performed. The modeling results showed that the in-flight capture of HgCl$_2$ was almost negligible with an HgCl$_2$ removal efficiency of $\approx$0.5% at 140 °C. The sorbent utilization was $<0.005\%$ of the maximum adsorption capacity of the raw AC. Among the parameters studied, high sorbent loading, maximum adsorption capacity (as a driving force for adsorption kinetics) and residence time were found to play a role in HgCl$_2$ removal efficiency. However, there seems to be no practical solution to increase mercury removal in the ductwork. Most HgCl$_2$ removal could be achieved in fabric filter. For the removal in FF, particle size significantly
influenced the removal performance for continuous injection whereas it did not show an advantage for discontinuous injection using the same amount of sorbent over the same cleaning cycle. The sizable filter cake thickness promptly piled from discontinuous injection could compensate for the sensitivity of particle size. Most pressure drop across the filter cake was derived from fly ash loading and size, which can determine the cleaning cycle and sorbent loading required to meet the performance goal.

3.5 Nomenclature

\[ C \] HgCl\(_2\) concentration inside the pore, g HgCl\(_2\)/m\(^3\)

\[ C_{b} \] HgCl\(_2\) concentration in the bulk gas phase, g HgCl\(_2\)/m\(^3\)

\[ C_{b}^{in} \] inlet HgCl\(_2\) concentration in the bulk gas phase, g HgCl\(_2\)/m\(^3\)

\[ C_{b}^{out} \] outlet HgCl\(_2\) concentration in the bulk gas phase, g HgCl\(_2\)/m\(^3\)

\[ C_{i} \] inlet dust concentration, lb/ft\(^3\)

\[ D_{e} \] effective pore diffusion coefficient, m\(^2\)/s

\[ D_{p} \] sorbent particle diameter, m

\[ K \] equilibrium constant, K=k\(_1\)/k\(_2\), m\(^3\)/g HgCl\(_2\).

\[ k_{1} \] adsorption rate constant, m\(^3\)/(g·s)

\[ k_{2} \] desorption rate constant, 1/s

\[ K_{2} \] specific cake coefficient, 1/s

\[ k_{g} \] gas-phase mass-transfer coefficient, m/s

\[ m_{AC} \] sorbent injection loading in flue gas, g/m\(^3\)
\( m_{Ash} \) fly ash concentration in flue gas, g/m\(^3\)

\( L \) filter cake thickness, m

\( L_f \) final cake thickness formed at a final filtration time \( (t_f) \)

\( \Delta P \) pressure drop across the filter cake, Pa

\( \Delta P_c \) pressure drop due to filter cake, Pa

\( \Delta P_f \) pressure drop due to filter, Pa

\( S_E \) residual drag due to fabric, Pa/(m/s)

\( q \) HgCl\(_2\) uptake onto sorbent, g HgCl\(_2\)/g sorbent

\( q_{avg} \) average HgCl\(_2\) uptake onto sorbent, g HgCl\(_2\)/g sorbent

\( q_{max} \) maximum HgCl\(_2\) adsorption capacity, g HgCl\(_2\)/g sorbent

\( R_p \) radius of sorbent particle, m

\( r \) radial distance inside sorbent, m

\( r_A \) intrinsic HgCl\(_2\) adsorption rate, g HgCl\(_2\) adsorbed/(m\(^3\) sorbent\( \cdot \)s)

\( r_{A,obs} \) observed HgCl\(_2\) adsorption rate, g HgCl\(_2\) adsorbed/(m\(^3\) sorbent\( \cdot \)s)

\( t \) time, s

\( t_f \) final filtration time, s

\( u \) superficial gas velocity, m/s

\( V \) gas velocity, m/s

\( z \) axial filter cake thickness from fabric filter surface, m

* equilibrium state

**Greek letters**
\( \varepsilon_b \) bed porosity

\( \varepsilon_p \) particle porosity

\( \rho_p \) sorbent particle density, g/m³

\( \phi \) in-flight dimensionless sorbent uptake, see eq. (3.8)

\( \xi \) in-flight dimensionless radial distance, see eq. (3.8)

\( \gamma \) in-flight dimensionless pore concentration, see eq. (3.8)

\( \gamma_B \) in-flight dimensionless bulk concentration, see eq. (3.8)

\( \tau' \) in-flight dimensionless time, see eq. (3.8)

\( \phi \) filter cake dimensionless sorbent uptake, see eq. (3.14)

\( \xi \) filter cake dimensionless radial distance, see eq. (3.14)

\( \lambda \) filter cake dimensionless axial distance, see eq. (3.14)

\( \gamma \) filter cake dimensionless pore concentration, see eq. (3.14)

\( \gamma_B \) filter cake dimensionless bulk concentration, see eq. (3.14)

\( \gamma^\text{out} \) filter cake dimensionless outlet bulk concentration

\( \tau \) filter cake dimensionless time, see eq. (3.14)

### 3.6 References


4 Summary and Recommendations for Future Work

4.1 Summary

A study on the kinetics of mercury oxidation using CuCl₂-based substrate was performed to understand the oxidation mechanism for Hg(0) oxidation reaction. Experiments were performed between 100-180 °C to simulate the reactor temperature in a coal-fired power plant after the air pollution control devices (APCDs). It was found that the stoichiometric ratio between CuCl₂ and Hg(0) were well above the ideal value of two. Furthermore, it was found that CuCl₂ agglomerates and sinters thereby leading to an additional mass transfer resistance that results in the incomplete conversion of the solid phase. In order to quantify this and incorporate it to the oxidation kinetic model, chemisorption tests were performed. Mass balances were formulated for Hg(0) and CuCl₂ phases and a modified grain model was adopted to obtain the kinetic expression for the Hg(0) oxidation reaction. It was found that the activation energy associated with the reaction was significantly lower than that of similar Hg(0) oxidation catalysts evaluated in halogen gases in the literature. This result reinforces our previous studies and idea that CuCl₂ is a good candidate for Hg(0) oxidation.

Mercury removal in the ductwork and fabric filter was simulated using previous experimental data, obtained from our lab. The effect of various factors were evaluated for mercury removal. It was found that the particle size played an important role in mercury removal. The results showed that inflight mercury removal was insignificant and there was no practical solution to increase its removal in the ductwork.
4.2 Future work

There is scope to develop a more robust model by incorporating a multi-component flue gas system and understand the effect of gases such as HCl, SO$_2$, NO$_x$, NH$_3$, etc on the kinetics of Hg(0) oxidation. The model can also be extended to incorporate the oxidation and adsorption kinetics of mercury to fully evaluate the performance of mercury removal in the low-temperature window in a coal-fired power plant. The model can also be enhanced by including mass-transfer resistances associated with mesoporous and microporous materials. Process economics can be performed to understand the feasibility and efficiency of this system for practical applications in different environmental and atmospheric conditions.