Mechanisms and Kinetics of Cadmium and Lead Capture by Calcined Kaolin at High Temperatures

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Abstract—One of the most promising technologies for reducing volatile metal emissions from the waste incineration process is the high-temperature capture of vapor-phase metals before theircondensing intofine particles. Packedbed sorption experiments for the capture of gaseous cadmium and lead using calcined kaolin particles were performed in a temperature range of 973-1,173 K. A calcined kaolin particle is composed of 2-3 µm grains separated by large pores, through which the cadmium and lead vapor easily diffuse. Cadmium and lead react with sorbent to form water-insoluble metal-mineral complexes (PbAl₂Si₂O₈, CdAl₂Si₂O₈, and Cd₂Al₂Si₂O₉). An increase in bed temperature results in an increase of capturing rates, but it has no effect on maximum uptakes for both metals. The diffusional resistance developed in the interior of the porous kaolin particles became limiting only after the conversion of metakaolinite reached a value of 50% or higher. The order of reaction with respect to the gas-phase concentration was determined to be 1.67 and 3.26 for lead and cadmium, respectively. The activation energy, E_a, was estimated to be 10.16 and 5.56 kcal/mol for lead and cadmium, respectively.

Key words: Cadmium, Lead, Kaolin, High Temperature, Sorption

INTRODUCTION

Waste incineration has been viewed as a means to detoxify many hazardous wastes, particularly those containing high levels of hazardous organics. However, it is currently one of the major sources of hazardous metal emissions into the environment. Hazardous metals in waste cannot be destroyed in this process, but they can be transformed both chemically and physically [Barton et al., 1990]. There is, therefore, a potential for these metals to vaporize and easily escape the air pollution control devices. This emission of volatilizable hazardous metals has been identified as one of the greatest health risks associated with waste incineration [Linak et al., 1993].

Cadmium and lead, which are typical hazardous metals emitted into the environment during waste incineration, have a number of industrial applications. Due to the wide range of their uses, cadmium and lead compounds are present in various wastes [Masseron et al., 1999]. Their compounds are all stable solids that do not vaporize at room temperature. However, they easily become unstable in waste incineration conditions and vaporize from the waste combustion chamber at high temperatures [Wang et al., 1999]. Volatilized cadmium and lead species condense into particulate matters in the downstream of a combustion chamber. In most systems, volatilized metals ultimately end up as submicron particles that are difficult to control [Barton et al., 1990]. Due to their highly volatile characteristics, about 10.4% of the cadmium and 2.3% of lead in the waste is emitted into the atmosphere from the municipal waste incinerators [Korzun and Heck, 1990].

The developing technologies of concern, from the point of view of controlling semi-volatile metals like cadmium and lead, are those that prevent the formation of fine particles from their volatilized species [Baochun et al., 1995]. One promising technology is the high-temperature capture of vapor-phase metals before their condensation into fine particles. Many volatile metals can be reactively scavenged by fly ash and earth elements such as calcium, aluminum and silicon, etc [Baochun et al., 1995; Chen et al., 1998; Ho et al., 1991, 1992, 1996; Evans et al., 1999; Mahuli et al., 1997; Masseron et al., 1999; Uberoi et al., 1989, 1990, 1991a, b; Yang et al., 1999]. In most cases, the reactive sorption products consist of water-insoluble metal-mineral complexes. This high-temperature reactive sorption process is thus intriguing, since it suggests that high temperatures can be used for an environmentally friendly purpose to isolate toxic metals rather than emit only environmentally hostile metals by enhancing metal vaporization [Linak et al., 1993].

Kaolinite, which is the characteristic mineral of kaolin (china clay), is among the effective sorbents in removing vapors of cadmium, lead and some alkali metals at high temperatures. In this study, the high-temperature capture of cadmium and lead vapor by using calcined natural kaolin particles is investigated with particular emphasis on the mechanisms and kinetics of the sorption reaction between porous calcined kaolin and gaseous metal vapors. The mechanisms of cadmium and lead capture were observed from the analysis of pre- and post-sorption sorbent samples. The effects of temperature and metal vapor diffusion on the capturing rate were investigated from the analysis of long time experimental sorption data.

EXPERIMENTAL

The principle of this experiment is to pass a simulated flue gas,
which includes lead or cadmium vapor, through the high-temperature bed of an inorganic sorbent. The experimental system, as shown in Fig. 1, mainly consists of a flue gas supplying system, a sorption reactor assembly, and a metal vapor scrubbing train. The flue gas supplying system includes a metal-vaporizing thermo-gravimetric furnace (MAC-500, from LECO Inc.) and a gas mixer. The sorbent bed reactor assembly consists of a 1,373 K ceramic tube furnace and a stainless steel sorbent bed holder assembly. The ceramic tube furnace is a 2-inch ID custom-fabricated single-zone furnace. The sorbent bed holder with a 1-inch ID and a 1.5-inch length is made of a stainless steel tube and 300-mesh stainless steel screens. The capacity of the sorbent bed is about 10 grams for calcined kaolin particles.

Natural kaolinite was calcined at 1,173 K for 2 h in air. Calcined particles with 300-400 µm size range were selected for sorbent particles. The chemical forms of the metal sources, which were volatilized in the thermo gravimetric furnace, were powdered PbCl₂ and CdCl₂ (Aldrich Co. >99.9%). All experiments were performed with a metal vapor-carrier gas of 20 LPM (liter per minute). The major composition of the metal vapor-carrier gas was 8% water, and 16% oxygen by volume, with the remainder consisting of nitrogen. The investigated sorption temperatures (sorbent bed temperatures) were from 973 to 1,173 K. The metal vapor concentrations were controlled from the averaged vaporization rates, which were determined from the weight loss of the sample metal in the vaporizing furnace per experimental duration and gas flow rate. The amount of metal in the reacted sorbent was determined by the weight difference of calcined and metal-sorbed sorbents by dry basis. The structural and morphological difference of raw, calcined and metal-sorbed kaolin was investigated by powder XRD analysis (Philips, X’pert MPD) and SEM (JEOL, JXA 8600).

**KINETIC MODEL OF SORPTION REACTION**

If the kaolinite is used as a sorbent, the reaction scheme for the capture of lead and cadmium chloride can be written as

\[
\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 (s) + \text{MeCl}_2 (g) + \text{H}_2\text{O}(g) \rightarrow \text{MeO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 (s) + 2\text{HCl}(g) \quad (1)
\]

where \(\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2\) is metakaolinite, which is the dehydration product of kaolinite, and \(\text{MeCl}_2\) represents cadmium (CdCl₂) or lead (PbCl₂) [Uberoi et al., 1991]. The overall sorption reaction rate in a packed sorbent bed with flowing gaseous reactant is governed by a combination of mass transfer resistances [Sherwood, 1975]. These resistances include that in the gas-phase, that in the sorbent particles owing to diffusion in pores if the sorbent are porous, and that to the adsorption reaction at the sorbent surface [Moon et al., 1985]. For a packed bed with a high gas flow rate, the resistance in the gas phase can be ignored. Therefore, introducing an effectiveness factor [Chang, 1983], the rate of metal sorption by Eq. (1) can be expressed as

\[
\frac{dx}{dt} = \eta \cdot k \cdot P_{\text{MeCl}_2}^{m} \cdot \frac{S}{S_o} \quad (2)
\]

where \(x\) is the conversion of the sorbent, \(\eta\) is the effectiveness factor, \(k\) is the reaction rate constant based on the partial pressure of metal vapor, \(P_{\text{MeCl}_2}\) is the partial pressure of metal chloride vapor, \(S\) is the available sorbent surface area of the sorbent, and \(m\) is the order of the reaction with respect to the concentration of gaseous reactant [Agnihotri et al., 1984; Kim et al., 1996; Asal et al., 1997; Oh et al., 1999; Kim, 1990; Chun et al., 1996]. The effectiveness factor \(\eta\) in Eq. (2) is the ratio of the average reaction rate within the pore to the maximum reaction rate if pore diffusion is absent [Park et al., 1994]. The available sorbent surface area \(S\) in Eq. (2) can be rewritten as

\[
S = S_o (1-x) \quad (3)
\]

where \(S_o\) is the initial sorbent surface area in the calcined sorbent. Assuming the reaction constant can be represented by the Arrhenius equation, the reaction rate constant \(k\) in Eq. (2) can be rewritten as
where \( k_o \) is the frequency factor and \( E_a \) is the activation energy. Substituting Eqs. (3) and (4) in Eq. (2), and integrating, we get

\[
\text{Eq. (5) shows the linear relationship between conversion versus time } (x/t) \text{ and } \ln P_{MeCl_2} \text{ for a constant temperature as well as that between } x/t \text{ and } 1/T \text{ for a constant partial pressure.}
\]

RESULTS AND DISCUSSION

The results of the long-time experiments are shown in Figs. 2 and 3. An increase in the sorbent bed temperature results in an increase in the metal capturing rate. There were, however, no changes in maximum lead and cadmium uptakes by changing the sorbent bed temperature. The molar reaction rate per unit bed volume, \( M_R \), can be estimated as

\[
M_R = -\frac{1}{V_R} \frac{dn}{dt} = \frac{1}{V_R (1-\varepsilon)} \frac{dn}{dt}
\]

where \(-\frac{dn}{dt}\) is the molar conversion rate of sorbent particles in the bed volume \( V_R \), and \( \varepsilon \) is the void volume fraction in the bed [Sherwood, 1975]. The void volume fraction \( \varepsilon \) was estimated as 0.6, considering that all kaolinite particles were spherical with a mean diameter of 350 \( \mu \)m. The volume of the sorbent bed used for this study, \( V_R \), was 15.2 cm³. The averaged molar reaction rates in each experimental time were calculated by Eq. (6) and the results are plotted in Figs. 4 and 5. For both cadmium and lead, the molar reaction rate at each sorption temperature did not greatly decrease and remained nearly constant until the conversions reached about 50%. The diffusional resistance developed in the interior of the porous kaolinite particles became limiting only after the conversion of metakaolinite reached a value of 50% or higher.

If the molar reaction rate per unit bed volume, \( M_s \), is determined, the ratio of the chemical reaction rate to the molecular diffusion rate, \( \Phi \), is calculated as

\[
\Phi = \psi \frac{r_s}{D_w C_s} M_s
\]

where \( \psi \) is the Thiele modulus (\( \psi = (r_s k_o C_{s,0}^{-1})^{0.5} \)), \( r_s \) is the average radius of the spherical sorbent particles in the bed, \( D_w \) is the effective diffusion coefficient of metal vapor in the porous sorbent bed.

![Fig. 2. Lead sorption in a packed bed of calcined kaolin at 973, 1,073, 1,173 K with a constant PbCl₂-carrying gas passing condition (volumetric flow rate=20 LPM, PbCl₂ concentration=175 ppmv).](image)

![Fig. 3. Cadmium sorption in a packed bed of calcined kaolin at 973, 1,173 and 1,273 K with a constant CdCl₂-carrying gas passing condition (volumetric flow rate=20 LPM, CdCl₂ concentration=106 ppmv).](image)

![Fig. 4. Molar reaction rate of metakaolinite (Al₂O₃·2SiO₂) into lead aluminum silicate (PbO·Al₂O₃·2SiO₂) in unit bed volume, as a function a conversion.](image)
and $C_s$ is the metal vapor concentration at the sorbent surface [Sherwood, 1975]. Using the published correlation between the Thiele modulus, $\psi$, and effectiveness, $\eta$, for spherical particle, $\eta = 3\psi (\tanh \psi - \psi)$, the effectiveness factor, $\eta$, was estimated from Eq. (7).

The applied $D_p$ values in calculating $\psi$ were obtained from the definition $D_p = D_\theta \tau$, where $D$ is the ordinary diffusion coefficient and $\theta$ is the void volume fraction of the spherical particle. The values of $D$, $\theta$ and $\tau$ were obtained from the available data books and previously applied data from other investigators [Satterfield, 1993; Lee et al., 1995; Perry and Green, 1984]. The calculated $\Phi$ values of the sorbent used for lead and cadmium captures for all tested conditions were in the range from 0.009 to 0.03 and from 0.01 to 0.02, respectively. In this range of $\Phi$ values ($\Phi < 1$), the effectiveness factors are known as essentially unity for various geometries and reaction orders [Sherwood, 1975]. This suggests that the overall sorption rate is governed by chemical reaction between metal vapor and sorbent material.

The results of the short-time experiments with varying gaseous reactant concentrations at 1,173 K are shown in Fig. 6. The extent of conversion increased linearly with time at a low conversion up to about 50%. The difference of slopes of the linearly fitted lines in Fig. 6 shows the effects of gaseous reactant concentrations on the extent of conversion. In Fig. 7, the rates of reaction for metal sorption are plotted logarithmically as a function of metal vapor concentration. The slopes of the line fitted to the data show the order of the reaction with respect to metal vapor concentration, $m$ in Eq. (5). The determined order of the reaction with respect to metal vapor concentration, $m$, is 1.67 for lead and 3.26 for cadmium, respectively. These high reaction orders with respect to metal vapor concentration suggest that the application of porous kaolin sorbent for cadmium and lead capture is more effective for the hazardous waste incinerator which burns waste including a significant amount of lead and cadmium.

The results of the short-time experiments with a fixed gaseous reactant concentration at various reaction temperatures are shown in Fig. 8. The effects of reaction temperature on the reaction rates are clearly seen in Fig. 8 by the difference of the slopes of the linearly fitted lines. The extent of temperature dependency of the reaction rate was determined by plotting the slopes of the lines against the reciprocal of temperature, according to the Arrhenius relationship shown in Eq. (5). The observed correlation in Fig. 9 is linear for both metals investigated. The observed activation energies corresponding to the least square linear fit are 5.56 and 10.16 kcal/g-mole for cadmium and lead capture, respectively. The observed activation energies are within the normal range of activation energies for slow reactions, which show a low temperature dependency.

The scanning electron microphotographs of the calcined kaolin particles are shown in Figs. 10a-b. Fig. 10a indicates that the sor-
bent particle is composed of fine metakaolinite (dehydrated product of kaolinite and halloysite), and relatively coarse feldspar and muscovite. Figs. 10a-b also shows that the internal pores of calcined kaolin particle are well developed by numerous fine metakaolinite grains. Fig. 10b illustrates that the calcined kaolin particles are an agglomerate of numerous fine metakaolinite grains and thus have a highly porous structure. The results of BET analysis of calcined kaolin agreed with those of SEM analysis. The measured BET surface area of calcined kaolin was 15.5 m²/g. No micro pores in the calcined sorbent particle were found by BET analysis. The averaged pore diameter is 200.5 Å. These results show that surface area are an agglomerate of numerous fine metakaolinite grains and thus have a highly porous structure. The results of BET analysis of calcined kaolin agreed with those of SEM analysis. The measured BET surface area of calcined kaolin was 15.5 m²/g. No micro pores in the calcined sorbent particle were found by BET analysis. The averaged pore diameter is 200.5 Å. These results show that surface.
of calcined kaolin particles is composed of fine metakaolinite grains, but the fine metakaolinite grains themselves have no porous structures. The scanning electron microphotographs of the lead- and cadmium-sorbed sorbents are shown in Fig. 10c-d, respectively. Lead and cadmium were evenly distributed with the surface and inside the metakaolinite grains in the calcined kaolin particle. However, none of these metals were observed inside the feldspar or muscovite grains. The distribution of cadmium and lead in the fully saturated sorbent particle was similar to the initial distribution of metakaolinite grains in the particles.

The changes in the mineral compositions of the sorbent samples by calcination and by metal sorption are illustrated in Fig. 11a-d. As shown in Fig. 11a, the raw sorbent material supplied from Daemyung Mining Co. is composed of several aluminum silicate minerals. The approximate compositions of raw kaolinite, determined by quantitative XRD software (SIROQUANT), were 58.5% kaolinite (kaolinite and halloysite), 27.9% alkali feldspar, 13.0% muscovite, 0.6% montmorillonite, and a traceable amount of quartz. The calcinations of this raw kaolin cause the dehydration reaction and a lattice rearrangement, converting kaolinite minerals (Al₂O₃·2SiO₂·xH₂O) into metakaolinite (Al₂O₃ ·2SiO₂), which is a suggested chemical sorbent for cadmium and lead capture by Eq. (1) [US DOE, 1979; Yang, 1999]. Some other alkali metals were included as feldspar or illite in the raw kaolin particles as analyzed by XRD pattern analysis (see Fig. 11a): anorthite ((Ca,Na)(Si,Al)O₄ or (Ca,Na) (SiAl)₄O₁₀); muscovite (KAl₂Si₃AlO₁₀(OH)₂). The structures of these alkali metal-containing minerals were not changed by long time sorption experiments as well as by calcination. Both feldspar and muscovite were found in fully saturated sorbent. However, neither kaolinite nor halloysite were found in the fully saturated lead-sorbed sorbent and cadmium-sorbed samples, as shown in Fig. 11c-d. The XRD patterns of metal-sorbed sorbents in Fig. 11c-d show that metakaolinite (Al₂O₃·2SiO₂) in the heated kaolin minerals acted as a chemical sorbent for metal capture. The high temperature sorption reactions generated water-insoluble metal mineral complexes (PbAl₅Si₇O₂₉, CdAl₅Si₇O₂₉ and Cd₂Al₅Si₇O₂₉).

CONCLUSION

The following conclusions were derived from the results of high-temperature cadmium and lead capturing experiments using a packed bed of calcined kaolin.

1. Calcined kaolin particles having small grains separated by large pores are effective sorbents for the capture of lead and cadmium, and the high-temperature reaction between metal vapor (lead and cadmium) and metakaolinite generated water-insoluble metal-mineral complexes (PbAl₅Si₇O₂₉, CdAl₅Si₇O₂₉ and Cd₂Al₅Si₇O₂₉).

2. For both cadmium and lead sorption, an increase in bed temperature results in an increase in capturing rate, but it has no effect on maximum metal uptake. The diffusional resistance developed in the interior of the porous kaolin particles became limiting only after the conversion of metakaolinite reached the value of 50% or higher.

3. The order of the reaction with respect to the gas-phase concentration was determined as 1.67 and 3.26 for PbCl₂ and CdCl₂, respectively. The activation energy, E_a, was estimated as 10.16 and 5.56 kcal/mol for PbCl₂ and CdCl₂, respectively, according to the Arrhenius relationship.

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NOMENCLATURE

c_s : concentration of metal vapor at reaction interface at surface of bead [mol/cm³]
D : molecular diffusion coefficient [cm²/s]
D_p : effective diffusion coefficient of reactants in the pores of the bead [cm²/s]
E_a : activation energy [kcal/mol]
k : reaction rate constant [cm³/mol·s]
k_o : frequency factor [cm³/mol·s]
k_s : intrinsic rate constant based on the pore surface area [cm³/mol·s]
M_t : total reaction rate [mol/s]
m : order of reaction with respect to bulk gas-phase concentration [-]
P accomp : partial pressure of gaseous reactants [kPa]
r_o : radius of a porous spherical bead [cm]
r : distance from the center of sphere [cm]
S : available surface area of sorbent [cm²/g]
$S_0$: initial sorbent surface area [cm$^2$/g]
$t$: reaction time [s]
$T_{sb}$: temperature of sorption bed [°C]
$V_b$: bed volume [cm$^3$]

Greek Letters

\(\eta\): effectiveness factor [-]
\(\Psi\): Thiele modulus
\(\varepsilon\): void volume fraction in the bed [-]
\(\tau\): tortuosity factor [-]
\(\theta\): void fraction of spherical bead [-]
\(\Phi\): reaction factor

REFERENCES


