**Sorption Characteristics of Volatile Heavy Metal in the High Temperature Inorganic Sorbent Bed**

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**ABSTRACT**

The packed bed sorption experiments for the capture of toxic metal (gaseous cadmium and lead chloride) were carried out over a temperature range of 700-900°C. The effects of bed temperature and the metal vapor concentration on the sorption reaction rate were determined with a developed kinetic model. Detailed information on the metal-sorbent interaction was obtained by the XRD (X-ray diffraction) pattern analysis and microscopic analysis of metal-sorbed sorbents. The high-temperature reaction between metal vapor and metakaolinite in calcined kaolin generated the stable complex aluminosilicates (PbAl$_2$Si$_2$O$_8$, CdAl$_2$Si$_2$O$_8$ and Cd$_2$Al$_2$Si$_2$O$_9$). No significant resistance of pore diffusion was found and the chemical reaction at the sorbent surface controlled the overall sorption reaction rates. 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, according to the Arrhenius relationship.

**INTRODUCTION**

The thermal treatment of waste offers a reduction in volume as well as a conversion of toxic organic constituents to harmless or less harmful forms (Barton et al., 1990). However, hazardous metals can neither be generated nor destroyed in the waste thermal process, but they can be transformed both chemically and physically. There is therefore a potential for these metals to vaporize and easily escape the air pollution control devices. The emission of volatile hazardous metals has been identified as one of the greatest health risks associated with hazardous waste incineration (Linak et al., 1993). One of the promising technologies to reduce metal emissions is the in-situ capture of vapor-phase metals using inorganic sorbent. It has been suggested that many volatile hazardous metals such as arsenic, cadmium, lead and selenium can be reactively scavenged by inorganic sorbents (Agnihotri et al., 1998; Ho et al., 1991; Mahuli et al., 1997; Uberoi et al., 1991)

This study tried to apply the above ideas for an entrained flow system using the high-temperature packed bed of sorbent. Accordingly, this study focused on the diffusion of metal vapor into the packed bed of a porous sorbent and the interaction between the metal vapor and sorbent material. The effects of bed temperature and metal vapor concentration on the sorption reaction rate were determined with a developed kinetic model. In order to get a further understanding of the interaction between the gas and solid reactants, the structural and morphological change of the sorbent at the stage of metal sorption was observed by XRD pattern analysis and microscopic analysis of the pre- and post-sorption sorbent sample.
EXPERIMENTAL

The principle of this experiment is to pass a simulated flue gas, which includes lead or cadmium vapor respectively, through the high-temperature bed of an inorganic sorbent. The experimental system mainly consists of a flue gas supplying system, a sorption reactor assembly and a metal vapor scrubbing train (Yang et al., 1999). The flue gas supplying system included a metal-vaporizing thermo-gravimetric furnace (MAC-500, from LECO Inc.) and a gas mixer. The sorbent bed reactor assembly consists of a 1,100 °C 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 of a 1-inch ID and a 1.5-inch length is made of a stainless steel tube and 100-mesh stainless steel screens.

The chemical forms of the metal sources, which were volatilized in the thermo gravimetric furnace, were powdered PbCl₂ and CdCl₂ (Aldrich Co.). All experiments were performed with a metal vapor-carrier gas of 20 LPM (liter per minute). The composition of the flue gas entering the sorption bed, which includes metal vapor, was 8% water, and 16% oxygen by volume, with the remainder consisting of nitrogen. The sorption temperatures investigated were from 700 to 900 °C. The metal vapor concentrations were controlled from the knowledge of the averaged vaporization rates determined by the metal vaporizing furnace and the flue gas flow rate. The amount of adsorbed metal was determined by the weight difference of the pre- and post-sorption sorbent by dry basis. The structural and morphological difference of raw, calcined and metal-sorbed kaolin (Dae-Myung Mining Co.) was investigated by the powder XRD analysis (Philips, X’pert MPD) and SEM (JEOL, JXA 8600).

KINETIC MODEL OF SORPTION REACTION

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

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

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

\[
\frac{dx}{dt} = \eta \cdot k \cdot P_{\text{MeCl}_2}^m \cdot S
\]

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 surface area of the sorbent, and \( m \) is the order of the reaction with respect to the concentration of gaseous reactant (Sherwood et al., 1975; Satterfield et al., 1993). 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. The available sorbent surface area \( S \) in Eq. 2 can be rewritten as

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

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

$$k = k_0 \cdot \exp\left(\frac{-E_a}{RT}\right)$$  \hspace{1cm} (4)

where $k_0$ is the frequency factor and $E_a$ is the activation energy. Substituting Eqs. 3 and 4 in Eq. 2, and integrating, we get

$$\ln\left(\frac{dx}{dt}\right) = \ln(\eta k_0 S_0) + m \cdot \ln(P_{MeCl_2}) - \left(\frac{E_a}{R} \left(\frac{1}{T}\right)\right)$$  \hspace{1cm} (5)

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

**RESULTS AND DISCUSSION**

The results of the long-time cyclic sorption tests using calcined kaolin for cadmium and lead capture are shown in Fig. 1 and 2. As expected, 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 increasing effect of temperature on the capturing rates, which is shown in Fig. 1 and 2, suggests that high-temperature cadmium and lead capture by calcined kaolin is an endothermic chemical reaction.

The changes in the mineral compositions of the sorbent samples by calcination and by metal sorption are illustrated in Fig. 3a-d. As shown in Fig. 3a, the raw kaolin is composed of several aluminum silicate minerals before calcination. The approximate compositions of raw kaolin, 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 converting kaolinite minerals ($Al_2O_3 \cdot 2SiO_2 \cdot xH_2O$) into metakaolinite ($Al_2O_3 \cdot 2SiO_2$), which is amorphous structure as shown in Fig. 2b and suggested chemical sorbent for cadmium and lead capture (Yang et al., 1999). The structures of anorthite ((Ca,Na)(Si,Al) _2 O_8 or (Ca,Na)(Si,Al) _2 Si_2 O_8) and muscovite (KAl _2 Si_3 AlO _10 (OH) _2 ) were not changed by long time sorption experiments as well as by calcination. The XRD patterns of metal-sorbed sorbents in Fig. 3c-d prove that metakaolinite acts as a chemical sorbent for lead and cadmium capture. The XRD pattern of the lead-sorbed kaolin is identical to that which Uberoi et al. investigated (Uberoi et al., 1991). The XRD pattern of the fully saturated cadmium-sorbed kaolin in Fig. 3d is quite different from that which Uberoi et al. investigated (Uberoi et al., 1991). Two kinds of cadmium aluminum silicate were assigned to the XRD patterns. For cadmium capture, the following reaction scheme can be suggested in this study, in addition to the reaction scheme by Eq. 1 (Yang et al., 1999).

\[
CdO\text{Al}_2\text{O}_3\text{2SiO}_2 + CdCl_2(g) + H_2O(g) \rightarrow 2CdO\text{Al}_2\text{O}_3\text{2SiO}_2 + 2HCl(g)
\]  \hspace{1cm} (6)

The scanning electron microphotographs of the lead- and cadmium-sorbed sorbents are shown in Fig. 4a-b, 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 was 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 results of the short-time experiments with varying gaseous reaction concentrations at 900 °C are shown in Fig. 5. The difference of slopes of the linearly fitted lines in Fig. 5 shows the effects of gaseous reactant concentrations on the extent of conversion. In Fig. 6, the rate of reaction for metal sorption is plotted logarithmically as a function of metal vapor concentration, in order to clearly determine the effect of vapor concentration on the sorption reaction rate. 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. This suggests that the application of porous kaolin sorbent for cadmium and lead capture is more effective and promising 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. 7. The effects of reaction temperature on the reaction rates are clearly seen in Fig. 7 by the difference of the slopes of the linearly fitted lines. The reaction rate increases with the increasing reaction temperature. So it can be said that this gas-solid reaction is endothermic chemical reaction. 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 activation energies corresponding to the least squares linear fit are 5.56 Kcal/g-mole for cadmium capture and 10.16 Kcal/g-mole for lead capture. The observed activation energy is within the normal range of activation energies for slow reactions, which show a low temperature dependency.

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REFERENCES

Fig. 1. Lead sorption in a packed bed of kaolinite at 700, 800 and 900 °C with a constant PbCl₂-carrying gas passing condition (volumetric flow rate = 20 LPM, PbCl₂ concentration = 175 ppmv).

Fig. 2. Cadmium sorption in a packed bed of kaolinite at 700, 800 and 900 °C with a constant CdCl₂-carrying gas passing condition (volumetric flow rate = 20 LPM, CdCl₂ concentration = 106 ppmv).

Fig. 3. Powder XRD patterns of raw (a), calcined (b), lead-sorbed (c) and cadmium-sorbed (d) kaolin sorbents.

Fig. 4. SEM of calcined kaolin : (a) fully saturated lead-sorbed kaolin and (b) fully saturated cadmium-sorbed kaolin. MK(meta kaolinite), F(feldspar), M (muscovite), LAS (lead aluminum silicate), CAS (cadmium aluminum silicate).
Fig. 5. Effect of metal vapor partial pressure on kaolinite conversion ($S_o = 15.5$ m$^2$/g, $T = 1173$ K).

Fig. 6. Estimation of reaction order $m$, with respect to metal vapor partial pressure ($S_o = 15.5$ m$^2$/g, $T = 1173$ K).

Fig. 7. Effect of temperature on the conversion of Al$_2$O$_3$.2SiO$_2$ into PbO · Al$_2$O$_3$ · 2SiO$_2$ and CdO · Al$_2$O$_3$ · 2SiO$_2$ ($S_o = 15.5$ m$^2$/g, $P_{PbCl_2} = 16.9$ Pa, $P_{CdCl_2} = 10.2$ Pa).

Fig. 8. Estimation of activation energy of the reaction of cadmium (Cd) and lead (Pb) captures by metakaolinite.