Capture of Volatile Hazardous Metals Using a Bed of Kaolinite

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Abstract—One of the promising technologies for reducing metals emission from the waste thermal process is the capture of vapor-phase metals through the use of solid sorbents. This study investigated the use of natural kaolinite for the removal of several volatile metals. The capture of cadmium and lead using a packed bed with porous kaolinite of the size range 300-400 μm was effective. The capturing efficiency increased as the bed temperature increased. The ratio of the sorption reaction rate to the diffusion rate varied on the 10^{-2} order of magnitude. This suggests that the resistance of the diffusion within the pores of kaolinite particles is not significant in the selection of sorbent particle size for practice. The capturing mechanism for cadmium chloride is different from that for lead chloride. Cadmium can be reactively scavenged by $CdO \cdot Al_2O_3 \cdot 2SiO_2$ as well as metakaolinite, suggesting that a unit mole of metakaolinite can ultimately capture two moles of cadmium.

Key words : Capture of Vapor Phase Metal, High Temperature Sorption Bed, Metakaolinite, Effectiveness Factor, Lead and Cadmium Sorption Reaction

INTRODUCTION

Incineration is a proven, commercially available technology for the treatment of most organically contaminated waste. If hazardous metals are also present, there is a potential for these metals to emit. During incineration the hazardous metals in the feed stream are partitioned between the bottom ash stream and an off-gas stream containing entrained fly ash and vapors of volatile elements or compounds. A further partitioning of the off-gas stream takes place in the particulate emission control devices that efficiently remove larger fly ash particles but are less efficient for vapors and finer particles [Vidic et al., 1995]. A significant fraction of volatile compounds of hazardous metals like arsenic, cadmium, lead and mercury is emitted as vapors or fine particles [Palmer et al., 1988; Yang et al., 1996]. These emitted hazardous metals are respirable and therefore present potential health hazard [Davidson et al., 1974]. Nonvolatile hazardous metals are released with the ash, which also has to be appropriately conditioned for safe disposal.

One promising technology for reducing metal emission from the waste thermal process is in-situ capture of vapor-phase metals through the use of solid sorbents. It has been suggested that many volatile hazardous metals such as arsenic, cadmium, lead and selenium can be reactively scavenged by inorganic sorbents [Baochun et al., 1995; Ho et al., 1991, 1992, 1996; Mahuli et al., 1997; Uberoi et al., 1989, 1990, 1991]. Injection of powdered sorbents may be effectively used even if the pertinent condition still remains to be determined [Linak et al., 1991]. Passing through a high-temperature fluidized bed or fixed bed of inorganic sorbents can also capture vapor-phase metal species in the flue gas [Ho et al., 1992]. This high-tempera-

ture reactive scavenging process is 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 metals vaporization.
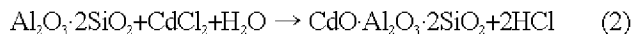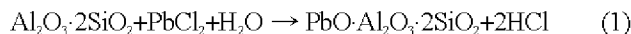
Many studies in this field completed to date have focussed on the investigation of relative effectiveness of various inorganic sorbents. Wouterlood et al. compared the effectiveness of various sorbents for arsenic capture [Wouterlood et al., 1979]. Their study indicated that physical sorption of arsenious oxide (As_4O_6) by carbon offered the most promising basis for removing that arsenic compound from the industrial flue gases at a temperature about 200 °C. At higher temperatures, however, the amount of arsenic capture may decrease since thermodynamic equilibrium aids the dissociation of physically sorbed arsenic compounds. To tackle this problem, Mahuli et al. and Ghosh-Dastidar et al. investigated the effectiveness of mineral sorbent for reactive scavenging of arsenic vapors and selenium vapors at higher temperatures up to 1,000 °C [Ghosh-Dastidar et al., 1996; Mahuli et al., 1997]. Comparisons with three other mineral sorbents (kaolinite, alumina, and silica) showed that Ca $(OH)_2$ is the most effective for arsenic compounds (As_2O_3) and selenium compounds (SeO_2). Baochun et al. investigated a multifunctional sorbent for the simultaneous removal of alkali vapors (NaCl and KCl), hazardous metal vapor $(PbCl_2)$ and sulfur vapor (SO_2) [Baochun et al., 1995]. This multi-functional sorbent used was a mixture of naturally occurring aluminium silicate sorbent with lime. The proposed sorbent was effective in simultaneous removal of the tested contaminants.

Uberoi et al. investigated the relative effectiveness of various inorganic sorbents (silica, alumina, kaolinite, bauxite and emathlite) for cadmium and lead removal using a thermogravimetric reactor [Uberoi et al., 1990, 1991]. Their investigation showed that kaolinite was very effective for lead but less effective for cadmium. After X-ray diffraction analyses of the metal-sorb-

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ed sorbents, they suggested the following overall reactions for lead and cadmium capture on aluminum silicate sorbent:

$$Al_2O_3 \cdot 2SiO_2 + PbCl_2 + H_2O \rightarrow PbO \cdot Al_2O_3 \cdot 2SiO_2 + 2HCl \quad (1)$$

$$Al_2O_3 \cdot 2SiO_2 + CdCl_2 + H_2O \rightarrow CdO \cdot Al_2O_3 \cdot 2SiO_2 + 2HCl \quad (2)$$

This idea is useful for the control of lead and cadmium emission due to the chlorinated waste combustion, since cadmium and lead are the most typical hazardous metals of how chlorides are more volatile than oxides of the same metal [U.S. EPA., 1993; Yang et al., 1994, 1998].

Other approaches to exploiting the above ideas are to inject sorbent into a flow combustor and to use sorbent as a bed material in fluidized combustor. Scotto et al. investigated the capture of vaporized lead by kaolinite injection in a 17 kW downflow combustor [Scotto et al., 1992]. In the absence of chlorine, injection of kaolinite sorbents was extremely effective in scavenging the lead vapor. Ho et al. studied fluidized bed technology for metals emission control [Ho et al., 1991, 1992]. They suggested the following three possible mechanisms for metal capture when using inorganic sorbent as a bed material: vapor-sorbent reaction, similar to that investigated by Uberoi et al.; trapping of the metal by melted ash and subsequent coalescence of the liquid with sorbent particles, and particulate capture through coagulation of condensed metal aerosol with sorbent particles [Ho et al., 1992; Uberoi et al., 1990].

This study tried to apply the above ideas for entrained flow systems. Using the sorbent bed connected with a metal-vaporizing furnace, we investigated the sorption characteristics of calcined natural kaolinite for vapor-phase chlorides of lead, cadmium, copper and sodium vapors. The objectives of this study were to gain information on the interaction between metal vapor and sorbent and to investigate the extent to which diffusion reduces the sorption reaction within the porous sorbent.

THEORETICAL

From the experimental data, the extent to which diffusion reduces the sorption reaction rate within the porous kaolinite particle is determined as follows. Considering that the sorption reaction is a simple irreversible surface reaction involving a single metal vapor and the sorbent particle is in the form of a porous spherical particle of radius r_0, a metal vapor balance on a differential shell at radius r leads to the following differential equation [Sherwood et al., 1975].

$$\frac{d^2c}{dr^2} + \frac{2}{r}\frac{dc}{dr} = \frac{S_v k_s c^m}{D_p} \quad (3)$$

where the reaction rate is expressed as $k_s c^m$ gram moles per second per square centimeter of surface and S_v represents the pore surface per unit volume of the bead. This can be solved to give the reaction rate as gram moles per second for the single particle of radius r_0

$$M_A = 4\psi \pi r_0 c_s D_p \left[\frac{1}{\tanh\psi} - \frac{1}{\psi} \right] \quad (4)$$

where c_s is the concentration of metal vapor at the surface of sorbent particle, and

$$\psi = r_0 \sqrt{\frac{S_v k_s c_s^{m-1}}{D_p}} = r_0 \sqrt{\frac{k_v s_s^{m-1}}{D_p}} \quad (5)$$

Eqs. (4) and (5) express the sorption rate as gram moles per second for the single sorbent particle of radius r_0, where k_s is the intrinsic rate constant based on the pore surface area and k_v is per unit of gross volume of the bead. The quantity ψ is known as Thiele modulus. If the metal vapor concentration were c_s throughout the particle, the rate would be $(4\pi/3)r_0^3 k_v c_s$. The actual rate is known as effectiveness factor, represented by:

$$\eta = \frac{3}{\psi}\left[\frac{1}{\tanh y} - \frac{1}{y} \right] \quad (6)$$

The effectiveness factor η is a measure of the extent to which diffusion reduces the reaction rate within the porous particle [Chang, 1983; Park et al., 1984]. Since molar reaction rate per unit bed volume is $\eta k_v(1-\varepsilon)c_s^m$, effectiveness factor η is given by

$$\Phi \equiv \psi^2 \eta = \frac{r_0^2}{D_p c_s}\left[-\frac{1}{V_R(1-\varepsilon)}M_A \right] \quad (7)$$

where $-M_A$ is the molar conversion rate in the bed volume V_R, and ε is the void volume fraction in the bed.

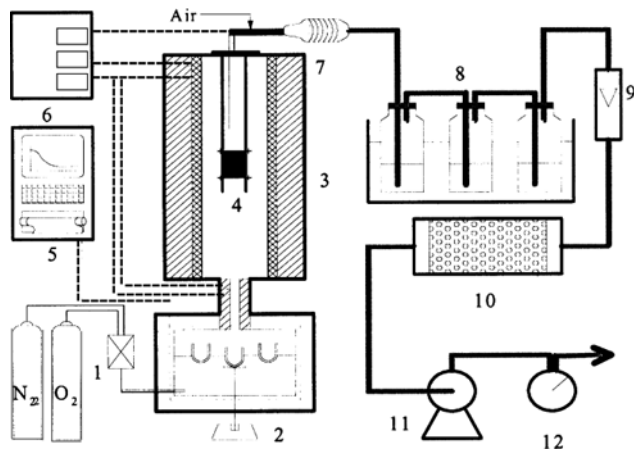## EXPERIMENTAL

1. Experimental Set-Up

The experimental system that is used in this study, which is shown in Fig. 1, mainly consists of a thermogravimetric furnace, sorption reactor assembly and particulate sampling train.

The metal-vaporizing thermogravimetric furnace is a commercial multi-sample thermogravimetric furnace (MAC-500, LE-CO Inc.). The details of the thermogravimetric furnace system are described elsewhere [Yang et al., 1994]. The cover of the furnace is modified to allow feeding of filtered ambient air with controlled volumetric flow rate. The off-gas draft system of the thermogravimetric furnace has been modified to allow connecting with a high-temperature sorption reactor. The connection tube is a 1-m long and 1-in ID stainless steel flexible tube.

The sorption reactor assembly consists of a 1,100 °C ceramic tube furnace and a stainless steel sorbent bed holder. The ceramic tube furnace is a 2-in ID custom-fabricated single-zone furnace. The sorbent bed holder with a 1-in ID and a 1.2-in length is made of stainless steel tube and 300-mesh stainless steel screens. The capacity of the sorbent bed is about 10-g for tested calcined kaolinite particles. The gas passing through the sorbent bed is cooled to low temperatures below the dew point of metal vapors by mixing with filtered ambient air in order to condense residual metal vapors out into particles. EPA's multiple metal sampling train was installed after the sorption bed.

2. Sorbent Preparation

Kaolinite mineral is selected as an investigating inorganic sorbent, based on the most promising results from other researchers. Natural kaolinite was supplied by Dae-Myoung Mining Co. at San-Chung Kun in Kyungnam province in Korea. The supplied natural kaolinite was calcined at 900 °C for 2 h in air.

Fig. 1. Schematic diagram of experimental system.

1. Mass flow controller
2. Thermogravimetric furnace (TGF)
3. High-temperature tube furnace
4. Sorbent bed
5. TGF control and data acquisition system
6. HTF controller
7. Filter
8. Impingers
9. Flow regulator
10. Silicagel bed
11. Vacuum pump
12. Dry gasmeter

Heating of natural kaolinite involves the following series of dehydration reaction and lattice rearrangement [U.S. DOE, 1979]: pore water is lost with lattice changes at 100-150 °C; any organic material is oxidized at 200-300 °C; oxidation of pyrites begins at 400 °C; and hydroxyl water is driven away from the mineral at 500-900 °C, converting kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot xH_2O$) into metakaolinite ($Al_2O_3 \cdot 2SiO_2$) that is suggested chemical sorbent by in Rxns. 1 and 2.

The calcined kaolinite was classified into several particle size

Table 1. Physical and chemical properties of calcined natural kaolinite in the size range 300-400 μm

Physical properties	Apparent density [g/cc]	0.82
	BET surface area [m²/g]	407
Chemical composition, wt% (EPMA)	Al_2O_3	32.83
	SiO_2	50.78
	CaO	14.80
	Fe_2O_3	1.59

groups. Calcined particles with 300-400 μm size range were selected for sorbent bed materials. Specific surface area, particle density, and the chemical composition of this size range of calcined kaolinite are shown in Table 1.

3. Experimental Procedure

The retention of the following three volatile hazardous metals and one alkali metal was evaluated in the experiment: lead, cadmium, copper and sodium. The chemical forms of metal sources used are stable chlorides: $PbCl_2$, $CdCl_2$, $CuCl_2$ and NaCl. All powdered metal chlorides used in this study were high-purity commercial reagents (Aldrich Co., >99.9%).

Experimental conditions that are divided into single metal sorption and multi-component metal sorption are shown in Table 2. Each experiment was initiated by the heating of the sorption bed furnace to the investigating sorption temperature (T_B). Weighed amounts of sample metal powder were then loaded onto alumina crucibles in the metal vaporizing thermogravimetric furnace. The metal vaporizing furnace was heated with a maximum heating rate of 99 °C/min and it was maintained at the vaporizing temperature (T_F). The set gas flow rates (V_G) that are shown in Table 3 were not varied with time during each experiment. No pore plugging was thus expected

Table 2. Conditions for single and multi-component metal sorption experiments

System	Metal-vaporizing condition			Sorbent bed condition			
	T_F (°C)	W_M (g)	R_V (g/min)	T_B (°C)	V_G (L/min)	c_m (ppm)	t (min)
Single vapor	800	$PbCl_2$: 3.0	0040	700	65.3	170	67
	800	$PbCl_2$: 3.0	0.045	800	72.0	194	61
	800	$PbCl_2$: 3.0	0.040	900	78.7	175	62
	700	$CdCl_2$: 3.0	0.016	700	65.3	104	144
	700	$CdCl_2$: 3.0	0.015	800	72.0	100	149
	700	$CdCl_2$: 3.0	0.016	900	78.7	107	144
Multicomponent	700	$PbCl_2$: 0.5	0.034	700	91.4	17.2	80
		$CdCl_2$: 0.6	0.007			33.9	80
		NaCl : 2.0	0.011			46.7	160
		$CuCl_2$: 2.0	0.004			27.5	160
	700	$PbCl_2$: 2.0	0.017	800	100.8	32.7	170
		$CdCl_2$: 2.0	0.013			42.4	180
		NaCl : 2.0	0.006			49.8	240
		$CuCl_2$: 2.0	0.005			32.4	280
	800	$PbCl_2$: 0.5	0.054	900	110.2	27.3	50
		$CdCl_2$: 0.6	0.011			52.6	50
		NaCl : 2.0	0.015			72.3	80
		$CuCl_2$: 1.0	0.010			66.8	80

during each experiment since there was no significant pressure drop increase. The metal vapor concentrations in Table 2 are calculated values based on weight loss of each sample metal. The gas drafted into the sorbent bed from the metal-vaporizing furnace was maintained at a temperature above the furnace temperature by external heating of the connecting stainless steel tube.

After passing the sorbent bed the gas was diluted and cooled by supplying filtered air at the room temperature with a flow rate of about 5 L/min. EPA's multiple metal sampling train collected the residual metal species in the gas after passing the sorbent bed.

In order to gain information on the sorption mechanisms, single metal sorption experiments at 700 °C shown in Table 2 were conducted for a much longer time. After each experiment was finished by the complete volatilization of 5-g sample metal compounds in the metal-vaporizing furnace, the weight of metal-sorbed sorbent was measured. About 1-g sample of the metal-sorbed sorbent was then taken for powder X-ray diffraction (XRD) analysis. The residual sorbent particle was reused for further weight gain. The experiment in this manner continued until the additional weight gain did not appear. Also, part of the metal-sorbed samples were heated to 1,000 °C in an inert atmosphere (99.9% N_2) to observe the fraction physically sorbed.

4. Analysis and Data Collection

After each experiment, the quantity of metal sorbed was first observed by the weight increase of sorbent. Another two analysis techniques were used to support the sorbed quantity determined by the weight measurement. The chemical compositions of metal-sorbed sorbent were analyzed by EPMA (JEOL, JXA 8600). The liquids collected from the vapor collection train were analyzed using ICP-AES (JOVIN, YVON JP 50P). The structures of metal-sorbed sorbents were investigated by powder XRD analysis (Philips, X'pert MPD) using $K\alpha_1$ in the 2θ range 10-50.

The following data were collected: the weight loss of metals in the thermogravimetric furnace (W_A), the quantity of metal sorbed on sorbent particles analyzed by EPMA (W_B), the quantity of metal sorbed determined by weight difference of sorbent before and after each experiment (W_C), the quantity of metals collected on sampling filter (W_D), and the quantity of metal collected in vapor-collecting impingers (W_E). These primary data values can be used to determine the fraction sorbed (F_S). Eqs. (6) and (7) were used to calculate the fraction sorbed (F_S) for single and multi-component sorption experiments, respectively:

$$F_S = W_C/(W_C+W_D+W_E) \quad (8)$$

$$F_S = W_B/W_A \quad (9)$$

RESULTS AND DISCUSSION

The fraction sorbed (F_S) from single metal ($PbCl_2$ or $CdCl_2$) sorption experiments based on the weight gain of sorbent is plotted as a function of temperature in Fig. 2. For both cadmium and lead, more than 80% of the vapor was sorbed at the temperatures of 800 °C and 900 °C. At a temperature of 700 °C, about
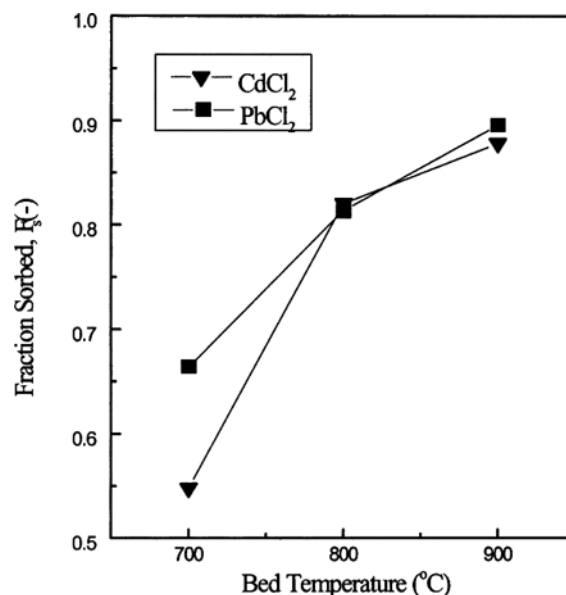

Fig. 2. Fraction sorbed for single vapor at 700, 800 and 900 °C sorption temperatures.

66% of lead vapor and 55% of cadmium vapor were sorbed. The increasing effect of sorbent bed temperature on sorption reaction rate was found for both cadmium and lead vapors. Capturing efficiencies for cadmium and lead vapors were similar at the sorption temperatures of 800 °C and 900 °C.

The sorption of metals on the sorbent is a combination of three processes: (1) physical adsorption or condensation; (2) transport to the reaction site; and (3) reaction with sorbent [Wu et al., 1995]. The rate of process (1) decreases as the temperature increases, while the rates of processes (2) and (3) increase with the temperature. The overall capturing efficiencies shown in Fig. 2 suggest that the temperature effect on process (2) and/ or (3) is greater than that on process (1). However, the temperature effect on the overall capturing efficiency becomes smaller as the temperature increases. The rate of physical adsorption or condensation process becomes greatly reduced as the temperature increases. Also, the resistance of the transport process increases as the sorption reaction progresses, since the reaction product acts as the resistance of the transport of metal to the unreacted sorbent. This explains the reason for the relatively small increase of overall capturing efficiency from 800 °C to 900 °C, compared to the significant increase of overall capturing efficiency from 700 °C and 800 °C.

The fraction sorbed of each metal vapor ($PbCl_2$, $CdCl_2$, NaCl and $CuCl_2$) from multi-component metal sorption experiments is plotted as a function of temperature in Fig. 3. With an exception in the case of copper, the fraction sorbed of other three metal vapors increased as sorption temperature increased. In the presence of other metal vapors, lead capturing efficiency at the sorption temperature of 900 °C was higher than 80% and this was similar to that for single lead vapor sorption. The cadmium capturing efficiency in the presence of other vapors also increased with sorption temperature, but the efficiencies at three tested temperatures were much lower than those of single metal sorption, respectively. Capturing efficiencies of sodium and
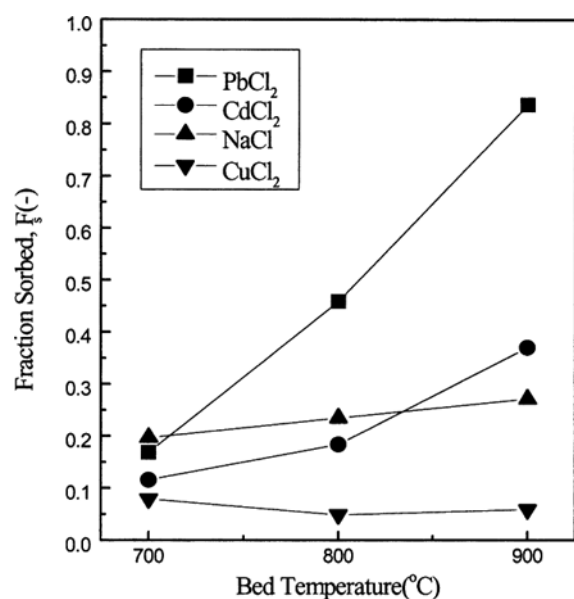
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Fig. 3. Fraction sorbed for multi-component vapor at 700, 800 and 900 °C sorption temperatures.

copper were not much varied with sorbent bed temperature and the efficiencies were relatively lower than those of lead and cadmium.

The capturing efficiency of lead was significantly higher than that of any other metal vapor in multi-component sorption experiments. The concentration of lead in mixed vapor is smaller than that of any other metal vapor as shown in Table 2. Therefore, the rate of physical adsorption or condensation process of lead at given temperatures must be smaller since lead has the lowest vapor pressure. Also, the resistance of the transfort process of lead must be greater than that of any other metal vapor in mixed vapor, since the lead vapor has the largest molecular weight. This suggests that the reaction process of lead with sorbent is much faster than any other metal. The resistance of the transport process of mixed metal vapors increases as relatively fast lead sorption progresses, since the lead-sorbed product (lead aluminum silicate: $PbO \cdot Al_2O_3 \cdot 2SiO_2$) acts as the resistance of the transport of other metals to the unreacted sorbent. This suggestion can partially explain the reason for the difference of cadmium capturing efficiencies between single and multi-component sorption experiments as well as relatively low capturing efficiencies for copper and sodium. The present study is only the first phase of a multi-component metal sorption study that is underway. Further comprehensive investigations of the

interaction of various metals with sorbent is required to completely understand the different capturing efficiencies of metal vapors that is shown in Fig. 3.

Uberoi et al. showed the efficiency of lead capturing by packed bed of calcined kaolinite with a size range 60-80 mesh (177-250 μm) was slightly over 80% [Uberoi et al., 1990]. Our experimental results showed lead capturing efficiency at 700 °C was 66%. Uberoi et al. used a two-zone furnace: one for the vaporization of 100-mg lead chloride and the other for 100-mg sorbent bed [Uberoi et al., 1990]. Their investigation was performed with lead chloride source at 495 °C. This relatively low temperature of vaporizing zone suggests that their experiments were performed at much lower concentrations of lead chloride vapor than those in our experiments. This comparison implies that lowering metal vapor concentration may increase the capturing efficiency. However, the following discussions suggested that reducing the sorbent particle size have no significant effect on increasing capturing efficiency.

Application of a packed sorbent bed for entrained flue gas requires knowledge about the effectiveness factor, η in Eq. (4), which represents the extent to which diffusion reduces the sorption reaction rate within porous sorbent [Moon et al., 1984]. Determined effectiveness factors of porous kaolinite particle bed (300-400 μm) for cadmium chloride and lead chloride are shown in Table 3. Also included in Table 3 are the used parameter values for calculating effectiveness factors. All the quantities of parameters in Table 3 with an exception of D_p were obtained from single vapor sorption experiments. Effective diffusion coefficients D_p in Table 3 were estimated from the definition $D_p = D\theta/\tau$, where D the ordinary diffusion coefficient, τ the tortuosity factor, and θ the void fraction of spherical bead, respectively [Satterfield, 1993]. The values of D, θ and τ were obtained from available data books and previously applied data by other investigators' [Lee et al., 1995; Perry, 1984; Satterfield, 1993].

Calculated values of $\psi^2\eta$ using Eq. (7), which represent the ratio of chemical reaction rate to molecular diffusion rate, are in the 10^{-2} order of magnitude. Determined effectiveness factors of 300-400 μm kaolinite sorbent bed are nearly unity, regardless of sorption temperature tested. It can, therefore, be positively said that the resistance of diffusion of cadmium and lead vapors in the pores of calcined kaolinite is not significant in the design of high-temperature sorbent bed. Little increase of lead and cadmium uptake can be accomplished by reducing the sorbent particle size, but this has the practical disadvantage of increasing the pressure drop for flue gas flow in packed beds of
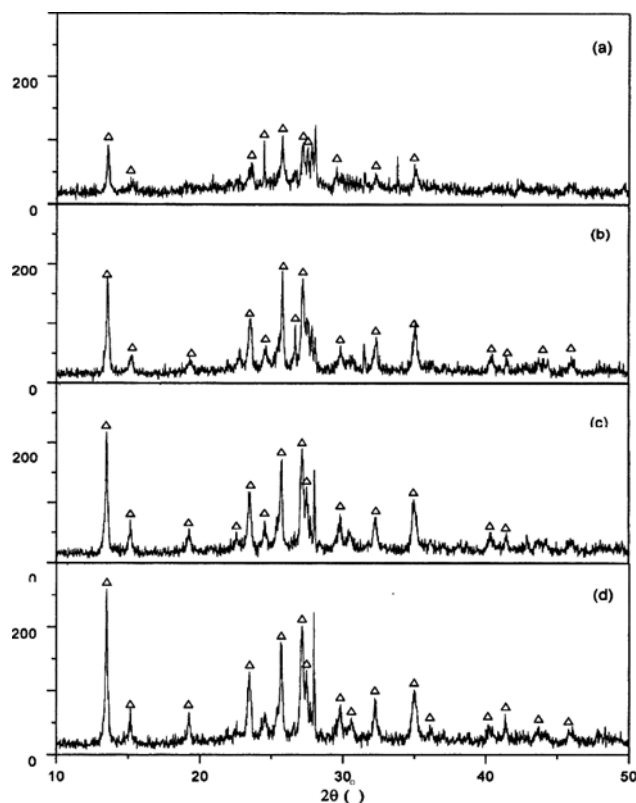
Table 3. Parameters for calculating effectiveness factor (η) and reaction constant (k₂), and calculated results

Metal species	T_b	D	D_p	c_s ($\times 10^{-9}$)	M_A / V_R ($\times 10^{-8}$)	Φ	Ψ	η	k_v ($\times 10^9$)
PbCl₂	700	0.78	0.09	2.22	1.42	0.034	0.186	0.9977	1.58
	800	0.88	0.11	2.21	2.09	0.045	0.207	0.9972	2.05
	900	0.99	0.12	1.82	3.56	0.083	0.288	0.9945	4.69
CdCl₂	700	0.97	0.12	1.32	1.48	0.049	0.222	0.9967	4.54
	800	1.09	0.14	1.15	1.73	0.059	0.242	0.9961	6.29
	900	1.22	0.15	1.12	4.03	0.124	0.354	0.9917	14.0

sorbent particles. The sorbent particles used in this study were in the size range between 300 μm and 400 μm. The pressure drop across sorbent bed with 1-in ID and 1.2-in length slightly exceeded 200 mmH$_2$O during each experiment. The problems associated with this significant pressure drop must be solved for practical application in a real thermal process, considering the presence of other particulate contaminants.

There was no weight loss of each metal-sorbed sorbent obtained from experiments when it was heated at 1,000 °C for 2 h in an inert atmosphere (>99.9% N$_2$). This suggests that no physical sorption occurred, since the chloride, oxide and elemental forms of cadmium and lead are volatile at 1,000 °C in an inert atmosphere. Since the reaction between metakaolinite and cadmium or lead chlorides is known as irreversible and $\psi^2\eta$ <0.3, the second order reaction was considered in calculating the reaction constant k$_v$ using Eq. (5) [Satterfield, 1993]. The determined reaction constants (k$_v$) based on pore surface area varied in the order of 10^{-2} and the values are slightly increasing as the sorption temperature increases.

The typical powder XRD patterns of metal-sorbed sorbent obtained from long time sorption experiments are shown in Figs. 4 and 5. The XRD patterns of lead-sorbed sorbent in this study is identical to that Uberoi et al. suggested [Uberoi et al., 1990]. The lead-sorbed sorbent has a chemical formula of PbO·Al$_2$O$_3$·2SiO$_2$. This is a product of reaction between metakaolinite and lead chloride. Fig. 4 also shows that the peak intensity of the product increases as the lead uptake increases. The XRD
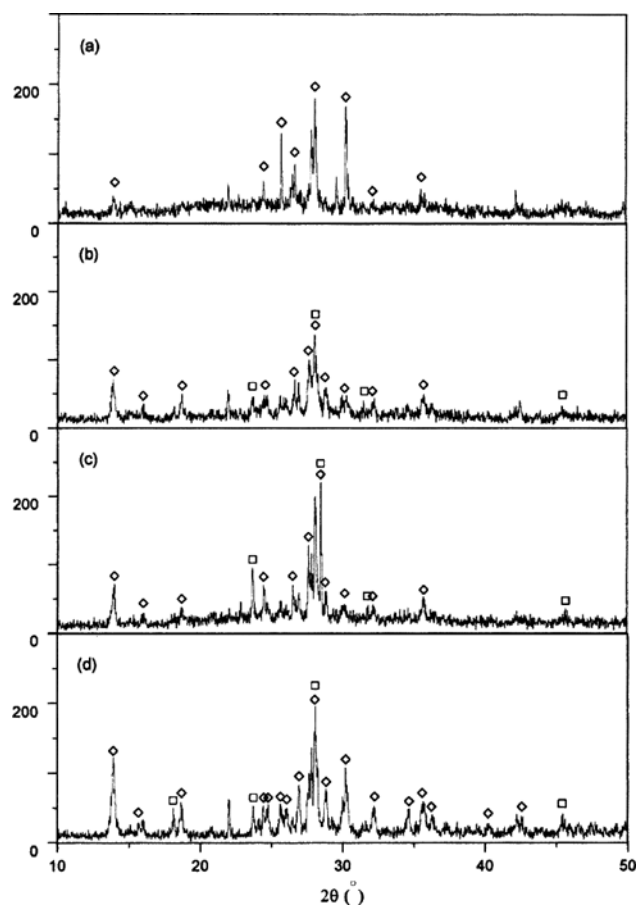
patterns of cadmium-sorbed sorbent in Fig. 5 are quite different from that Uberoi et al. suggested [Uberoi et al., 1991]. The chemical formula is assigned to CdO·Al$_2$O$_3$·2SiO$_2$, when the weight gain becomes 8%. 2CdO·Al$_2$O$_3$·2SiO$_2$ is found in the XRD patterns after the further weight gain. Two kinds of cadmium aluminum silicate are present. Therefore, the following reaction is suggested in this study, in addition to the reaction that Uberoi et al. proposed as Rxn. 2 [Uberoi et al., 1991].

$$CdO·Al_2O_3·2SiO_2+CdCl_2+H_2O \rightarrow$$
$$2CdO·Al_2O_3·2SiO_2+2HCl \qquad (10)$$
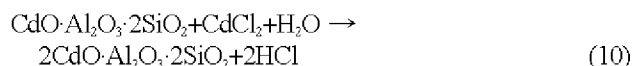
These results are also proven by the weight gain of sorbent. From the chemical composition in Table 1, the maximum quantity of metakaolinite can be estimated as 0.715-g/g sorbent. Based on stoichiometry of Rxn. 1, the sorbent of this study should have an ultimate sorption capacity of 0.718-g PbO/g kaolinite. The maximum uptake obtained is 0.491-g PbO/kaolinite, which corresponds to about 70% of sorption capacity. Above additional reaction (Rxn. 9) for cadmium sorption can be supported by maximum weight gain. If the cadmium sorption reaction follows only Rxn. 2 and no physical sorption occurs, the sorbent used should have maximum sorption capacity of 0.413-g CdO/g kaolinite. However, the maximum weight gain obtained in this study showed an uptake of 0.440-g CdO/kao-

Fig. 4. Powder XRD patterns of lead-sorbed kaolinite.
(weight gain: (a) 20.0%, (b) 32.6%, (c) 42.5%, and (d) 49.3%). △ : PbO·Al$_2$O$_3$·2SiO$_2$

Fig. 5. Powder XRD patterns of cadmium-sorbed kaolinite.
(weight gain: (a) 8.5%, (b) 19.1%, (c) 35.0, and (d) 44.1%). ◇ : CdO·Al$_2$O$_3$·2SiO$_2$ □ : 2CdO·Al$_2$O$_3$·2SiO$_2$

linite, showing that $2CdO \cdot Al_2O_3 \cdot 2SiO_2$ as well as $CdO \cdot Al_2O_3 \cdot 2SiO_2$ must be present in the cadmium-sorbed sorbent.

CONCLUSION

From the results of laboratory high-temperature sorption experiments using the bed of porous kaolinite particles in the size range 300-400 μm, the following conclusions were derived.

1. The capturing efficiency for cadmium and lead by the high-temperature bed with porous kaolinite increases with the bed temperature, regardless of the presence of other metal vapors such as copper chloride and sodium chloride.

2. The resistance of the diffusion of cadmium and lead vapors within the pores of calcined kaolinite may not be significant in the selection of sorbent particle size for practical application. The ratio of the sorption reaction rate to the diffusion rate was found to be in the 10^{-2} order of magnitude for both of cadmium and lead vapors.

3. Powder XRD patterns of metal-sorbed kaolinite revealed that the capturing mechanism for cadmium is quite different from that for lead. Cadmium chloride reacts with $CdO \cdot Al_2O_3 \cdot 2SiO_2$ as well as metakaolinite, suggesting that a unit mole of metakaolinite can ultimately capture two moles of cadmium.

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NOMENCLATURE

c : concentration of metal within the spherical bead [gmol/cm^3]
c_m : concentration of metal vapor at outside spherical bead [ppm]
c_s : concentration of metal vapor at the surface of sorbent particle [gmol/cm^3]
D : molecular diffusion coefficient [cm^2/s]
D_p : effective diffusion coefficient of reactants in the pores of the bead [cm^2/s]
F_S : fraction sorbed [-]
k_s : intrinsic rate constant based on the pore surface area [cm^4/gmol·s]
k_v : volume reaction rate constant [cm^3/gmol·s]
M_A : total reaction rate [gmol/s]
m : order of reaction with respect to bulk gas-phase concentration [-]
n : molar quantity of sorbed metal on sorbent particle [mol]
R_v : metal vaporizing rate [g/min]
r_0 : radius of a porous spherical bead [cm]
r : distance from the center of sphere [cm]
S_v : pore surface area per unit volume of the bead [1/cm]
t : reaction time [s]
T_B : temperature of sorption bed [°C]
T_F : temperature of metal vaporizing furnace [°C]
V_R : bed volume [cm^3]
V_G : volumetric reactant gas flow rate [L/min]

W_A : weight loss of metals in the thermogravimetric furnace [g]
W_B : quantity of metal sorbed on sorbent particles analyzed by EPMA [g]
W_C : quantity of metal sorbed, based on weight gain [g]
W_D : quantity of collected metals on filter [g]
W_E : quantity of metal collected in vapor-scrubbing impingers [g]
W_M : quantity of loaded metal [g]

Greek Letters
η : effectiveness factor [-]
ψ : Thiele modulus defined by Eq. (5)
Φ : factor defined by Eq. (7) [-]
ε : void volume fraction in the bed [-]
τ : tortuosity factor [-]
θ : void fraction of spherical bead [-]

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