



Simultaneous capture of metal, sulfur and chlorine by sorbents during fluidized bed incineration

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Abstract

Metal capture experiments were carried out in an atmospheric fluidized bed incinerator to investigate the effect of sulfur and chlorine on metal capture efficiency and the potential for simultaneous capture of metal, sulfur and chlorine by sorbents. In addition to experimental investigation, the effect of sulfur and chlorine on the metal capture process was also theoretically investigated through performing equilibrium calculations based on the minimization of system free energy. The observed results have indicated that, in general, the existence of sulfur and chlorine enhances the efficiency of metal capture especially at low to medium combustion temperatures. The capture mechanisms appear to include particulate scrubbing and chemisorption depending on the type of sorbents. Among the three sorbents tested, calcined limestone is capable of capturing all the three air pollutants simultaneously. The results also indicate that a mixture of the three sorbents, in general, captures more metals than a single sorbent during the process. In addition, the existence of sulfur and chlorine apparently enhances the metal capture process. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Metal capture; Emission control; Fluidized bed; Sorbent; Adsorption; Chemisorption

1. Introduction

Metal emissions from waste incineration and power generation plants are currently a great environmental and regulatory concern [1]. An effective technology for metal emission control is to use sorbents to capture metals during high temperature combustion, especially under fluidization operation. Our recent publications [2,3] have clearly indicated that metal capture efficiency can be as high as 97% depending on metal species, sorbents involved and operating parameters. The previous studies, however, have not investigated the effects of other pollutants on the efficiency of metal capture by sorbents. The objectives of this work are to further investigate the effect of sulfur and chlorine on metal capture by sorbents during fluidized bed incineration and the potential of simultaneous metal, sulfur and chlorine capture by sorbents during the process.

Metal capture experiments were carried out in a well-instrumented 76-mm inside diameter (ID) fluidized bed

incinerator burning artificially prepared test materials in a fluidized bed of various sorbents. The test materials were prepared from wood pellets spiked with various concentrations of metals, sulfur and chlorine. The metals involved in the test were organic lead, cadmium and chromium, and the sorbents involved were bauxite, zeolite, calcined limestone, and their mixtures. In addition to experimental investigation, the effect of sulfur and chlorine on the metal capture process was also theoretically investigated through performing equilibrium calculations based on the minimization of system free energy.

2. Scientific discussion

This section reviews the past studies on metal–sorbent reactions and the concept of chemical equilibrium relevant to the metal capture process. They are discussed below.

2.1. Chemical absorption reactions

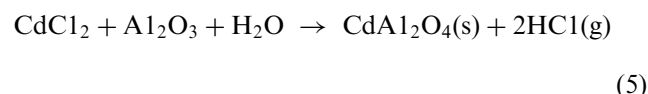
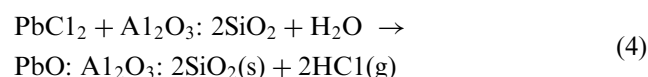
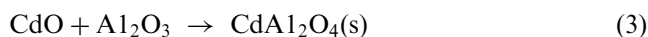
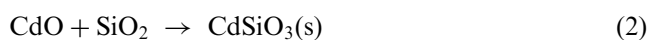
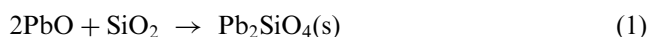
The following chemical absorption reactions between metal vapors and a variety of sorbents at high temperatures have been reported [3,4]

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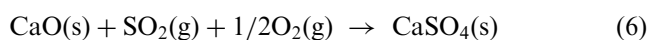
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Nomenclature

d_p	sorbent particle diameter, mm
U	air superficial velocity, cm/s
U_{mf}	minimum fluidization velocity, cm/s
M_b	metal concentration in incinerated sorbent, ppm
M_o	metal concentration in original sorbent, ppm
M_w	metal concentration in wood pellets, ppm
W_b	weight of collected incinerated sorbent, g
W_w	weight of wood pellets, g
ϕ	specific capture capacity, mg/kg
ψ	percent capture, %



In addition to the above metal–sorbent reactions, metal capture by lime has also been reported [3]. The capture of metal by lime, however, has been attributed to “particle scrubbing” instead of chemisorption [5]. For lime to capture SO_2 and HCl , the following two reactions have been well-recognized:



2.2. Chemical equilibrium

Equilibrium composition represents the thermodynamically preferred chemical speciation under a specific state. The composition reveals potential chemical reactions within the system. In this study, equilibrium calculations were performed using a software program [6] based on the minimization of system free energy.

3. Experimental

The experimental aspects of the study are described in this section. These include facilities, test material, procedure, chemical analysis and metal capture analysis.

3.1. Facilities

Metal capture experiments were carried out in a 7.6 cm (3") ID fluidized bed incinerator. A schematic diagram of the experimental apparatus is shown in Fig. 1. It includes a 6.4 cm (2.5") ID fluidized bed preheater, a 7.6 cm (3") ID fluidized bed incinerator assembly, a pressure and temperature monitoring assembly, two cyclones, a water scrubber and a bag house.

The fluidized bed incinerator was fabricated from inconel and consisted of a 15.2 cm (6") high plenum section, a distributor, and a combustion section of 55.9 cm (22") in height. Associated with the combustion section was a 2.54 cm (1") ID tube for waste feeding at the top, a pressure tap 40.6 cm (16") above the distributor, an ash discharge tube at the bottom of the distributor, and a pressure tap below the distributor. The distributor was a perforated plate with 2% open area ratio. A split-type tubular furnace equipped with an automatic temperature controller was applied to the outside wall of the incinerator. The exposed parts of the apparatus were heavily insulated with refractory fibers and covered with heavy duty aluminum foil on the surface. The exiting flue gas from the combustor went through two cyclones and a water scrubber before it entered a baghouse containing filter papers. The clean flue gas was then discharged into the ambient air.

3.2. Test materials

The combustible test materials used in this study were prepared from cylindrical wood pellets about 0.48 cm (3/16") in diameter and 0.64 cm (1/4") in length. To prepare a necessary metal concentration (normally 1000 ppm) in wood, the exact amount of a metal species was dissolved in 15 ml of water. This metal solution was then completely absorbed into the wood pellets uniformly. The metals involved in this study were lead acetate [$\text{Pb}(\text{CH}_3\text{CO}_2)_2$], cadmium acetate [$\text{Cd}(\text{CH}_3\text{CO}_2)_2$], and chromium acetylacetonate [$\text{Cr}(\text{C}_{15}\text{H}_{21}\text{O}_6)$]. In addition to metals, sulfur and chlorine were also artificially introduced into the wood. They were prepared similarly to that of metals in wood with the solutions being elemental sulfur in carbon disulfide (CS_2) solution and chloroacetone ($\text{CH}_3\text{COCH}_2\text{Cl}$) in water, respectively. The sorbents used in this study were calcined limestone, bauxite and zeolite. Table 1 summarizes the chemical composition of the sorbents. The physical properties of the sorbents are summarized in Table 2.

3.3. Procedure

The experiments were carried out batchwise. In an experimental run, an amount of 20–60 g of wood pellets containing various metals and concentrations was prepared and burned in a bed of 300–600 g of either a single

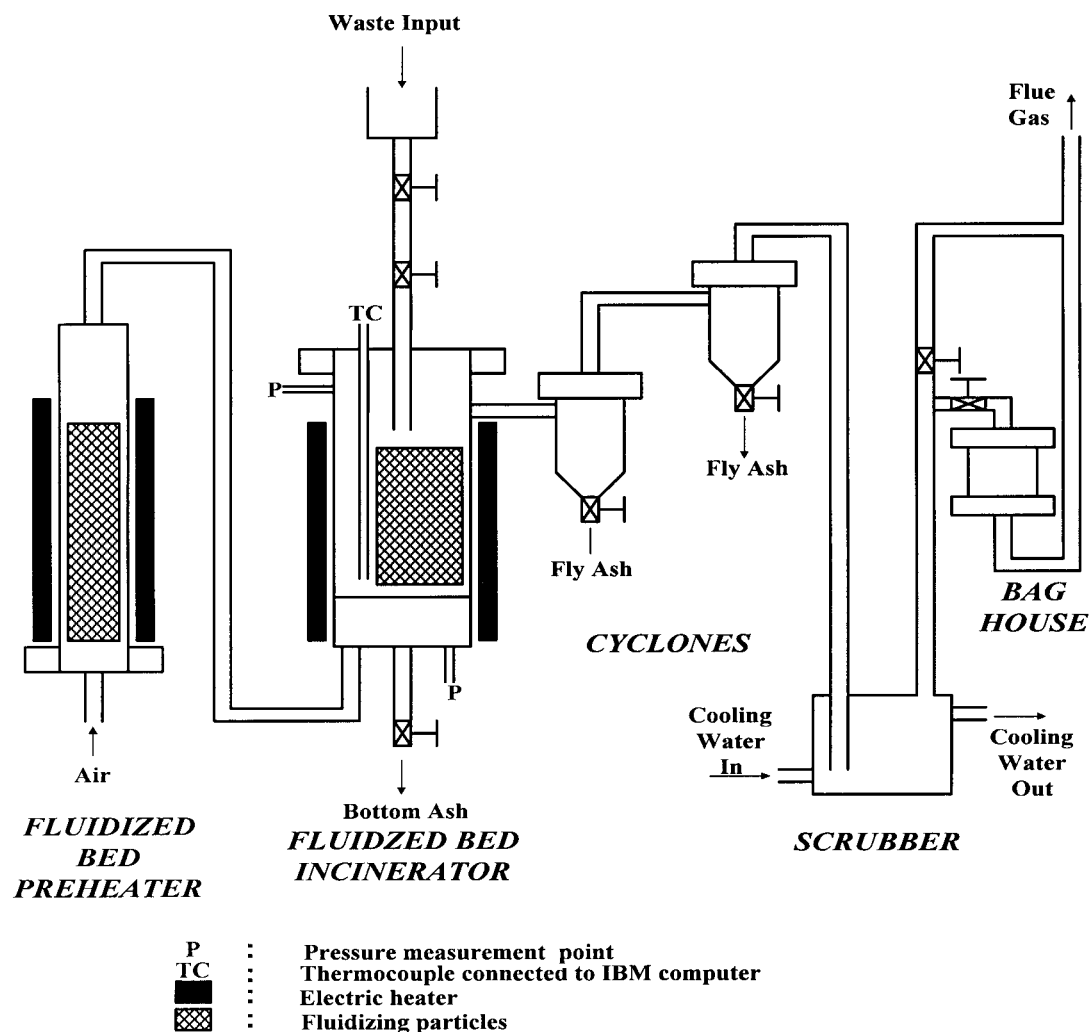


Fig. 1. Experimental setup.

Table 1
Chemical composition of various sorbents (wt.%)

	Bauxite	Zeolite	Limestone
SiO ₂	9	64.7	0.7
Al ₂ O ₃	78	12.6	0.3
Fe ₂ O ₃	8	1.8	0.3
TiO ₂	4	0.2	–
CaO	1	3.3	97.2
MgO	–	1.0	1.5
K ₂ O	–	3.3	–
MnO	–	0.1	–
Na ₂ O	–	0.9	–

sorbent or a sorbent mixture. The procedure was to charge the sorbent into the bed first and then to preheat the bed to the designed combustion condition. The metal-containing wood pellets were then manually charged into the bed in a slow rate to ensure complete combustion. The superficial velocity (U) used for combustion was three times that of U_{mf} of the fluidizing

sorbent particles. The bed sorbent was discharged for chemical analysis at the completion of the combustion process.

3.4. Chemical analysis

Metal concentrations in the original and the combusted sorbents were measured by an atomic absorption spectrophotometer (AAS). An HF modified EPA Method 3050 was used to digest metals from the solid sorbents for subsequent concentration measurement by the AAS. Toxicity Characteristics Leaching Procedure (TCLP) tests were also performed to determine the leachability of the captured metals from sorbents.

3.5. Metal capture analysis

3.5.1. Specific capture capacity (ϕ)

The specific capture capacity is defined to be the amount of metal captured by a unit mass of sorbent. It is calculated as:

Table 2
Properties of fluidized bed particles

Particle (Mesh No.)	d_p (mm)	ρ (g/cm ³)	U_{mf} (cm/s) 600°C	U_{mf} (cm/s) 750°C	U_{mf} (cm/s) 900°C
Limestone (30–40)	0.51	1.5	5.9	5.4	5.0
Bauxite (30–40)	0.51	1.68	6.7	6.0	5.6
Zeolite (30–40)	0.51	1.39	5.5	5.0	4.6

$$\phi = M_b - M_o \quad (8)$$

3.5.2. Percent capture (ψ)

The percent capture is defined to be the percentage of metal capture by fluidized bed sorbents over the total amount of metal charged. It is calculated by the following equation:

$$\Psi = [(W_b \times \phi) / (W_w \times M_w)] \times 100\% \quad (9)$$

It should be noted that the percent capture represents the efficiency of the metal capture process.

4. Results and discussion

Both equilibrium simulations and experimental measurements were performed in this study. The results are reported below.

4.1. Equilibrium simulation results

Typical sets of equilibrium simulation results indicating potential metal–sulfur–lime or metal–sulfur–silica reactions are displayed in Figs. 2–4 for Pb–S–CaO and Pb–S–SiO₂

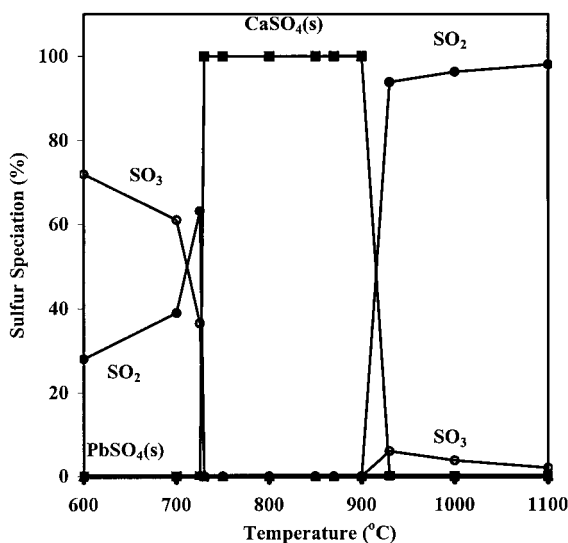


Fig. 2. Equilibrium sulfur speciation in a Pb–S–CaO system.

systems. The corresponding simulation conditions are: carbon — 41.9 wt.%, hydrogen — 4 wt.%, nitrogen — 1 wt.%, oxygen — 5 wt.%, sulfur — 4 wt.%, lead — 0.1 wt.%, ash — 4 wt.%, moisture — 10 wt.%, CaO (or SiO₂) — 30 wt.%, and percent excess air — 50%.

The results shown in Fig. 2 for sulfur speciation in a Pb–S–CaO system indicate that, at temperatures below about 730°C, most sulfur will react with oxygen to form either SO₂(g) or SO₃(g); between 730 and 910°C, most sulfur will react with CaO to form CaSO₄(s); and above about 930°C, sulfur will be in the form of SO₂(g). Note that the results also indicate that a small amount of sulfur will react with lead to form PbSO₄(s) at temperatures below about 730°C. For lead speciation in the same simulation, the results shown in Fig. 3 indicate that most lead will react with sulfur to form PbSO₄(s) at

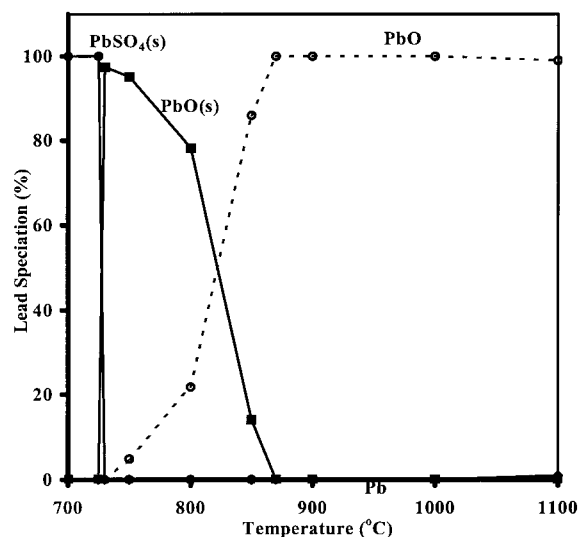


Fig. 3. Equilibrium lead speciation in a Pb–S–CaO system.

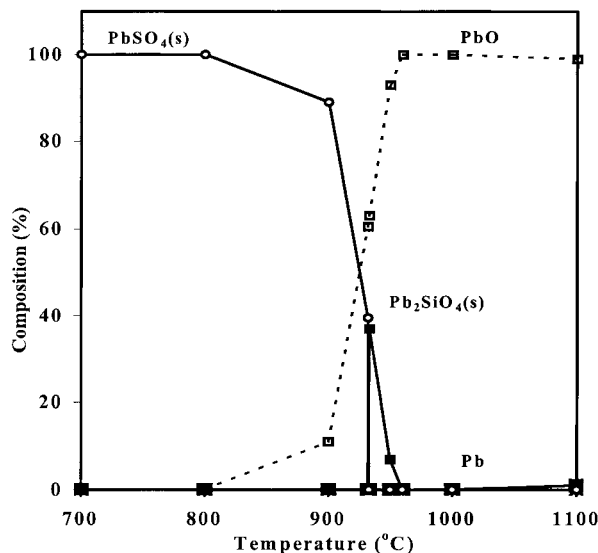


Fig. 4. Equilibrium lead speciation in a Pb–S–SiO₂ system.

temperatures below about 730°C; between 730 and 820°C, most lead will form PbO(s) ; and above 820°C, lead will be in the form of PbO(g) .

It is worth pointing out that the above simulation results do not indicate any reactions between lead and CaO , which implies that lead is not expected to be chemically absorbed by lime. This implication, however, may not be absolutely correct due to the possibility of incomplete thermodynamic data being available for the simulation. Similar equilibrium results were observed for other metal–sulfur–lime systems and are not reported. For SiO_2 and Al_2O_3 systems, typical simulation results showing lead speciation in a Pb-S-SiO_2 system are displayed in Fig. 4. These results suggest that silica is thermodynamically capable of chemically absorbing lead through the formation of $\text{Pb}_2\text{SiO}_4\text{(s)}$ between 950 and 1000°C as indicated in the figure. Although not shown, the equilibrium simulations have also suggested the formation of $\text{CdSO}_4\text{(s)}$, $\text{CdAl}_2\text{O}_4\text{(s)}$ and $\text{CdSiO}_3\text{(s)}$.

4.2. Experimental results

It has been generally observed that, depending on metal species, sorbent type and combustion temperature, the percent capture may range from a low of 20% up to a high of close to 100%. The capture process is found to be especially effective for lead and chromium at high temperatures; it, however, is less effective for cadmium at high temperatures. Among the sorbents tested, calcined limestone has been observed to be capable of simultaneously capturing sulfur and chlorine effectively. Typical experimental results on metal capture are displayed in Figs. 5–13 to demonstrate the following observations: effect of metal format, effect of sorbent mixture, effect

of temperature, effect of sulfur, and effect of chlorine. These observations are discussed below.

4.2.1. Effect of metal blend

One of the experimental parameters examined in this study was the effect of metal blend on metal capture. In the test, two identical combustion experiments were carried out; one involved with a single metal at 1000 ppm and the other involved with the identical metal and concentration, however, coexisting with other metals, i.e. in a metal blend. It has been observed that the percent capture is always higher when the metal is in a metal blend format. Typical sets of such results are shown in

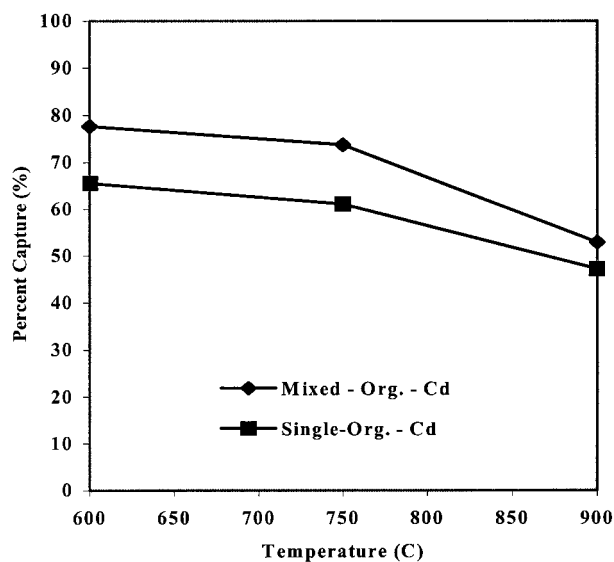


Fig. 6. Comparison of organic cadmium capture by the sorbent mixture [metal: 1000 ppm of $\text{Cd}(\text{CH}_3\text{CO}_2)$ in a mixed or single metal format].

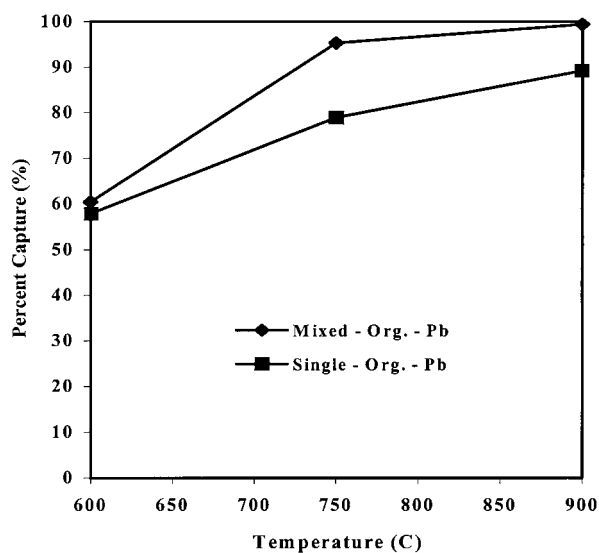


Fig. 5. Comparison of organic lead capture by the sorbent mixture [metal: 1000 ppm of $\text{Pb}(\text{CH}_3\text{CO}_2)$ in a mixed or single metal format].

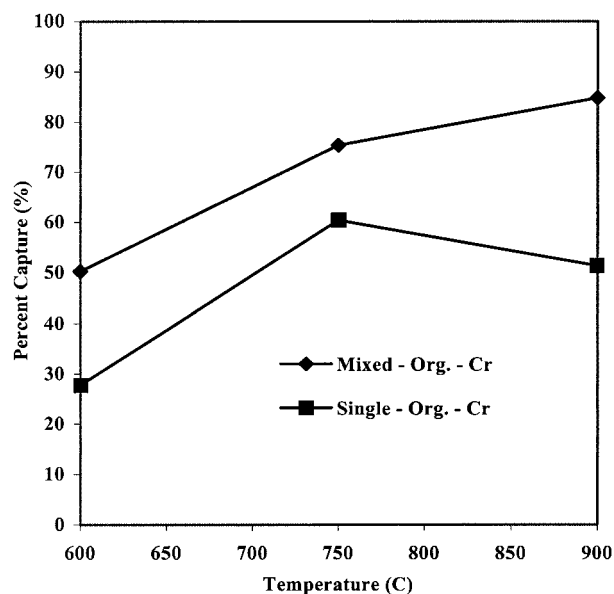


Fig. 7. Comparison of organic chromium capture by the sorbent mixture [metal: 1000 ppm of $\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_3$ in a mixed or single metal format].

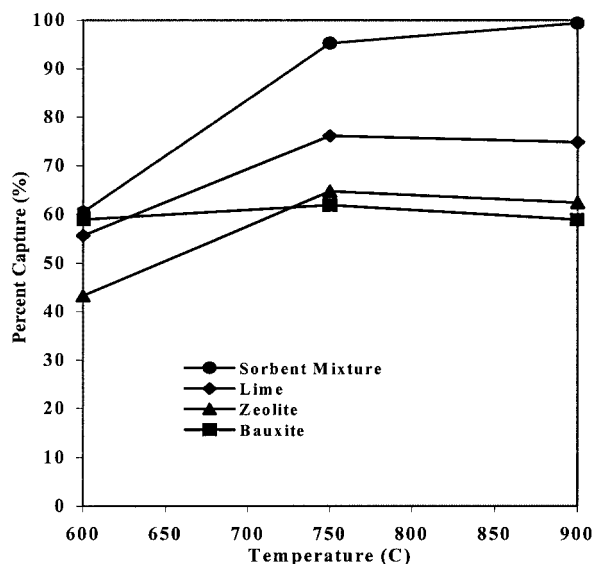


Fig. 8. Comparison of organic lead capture by various sorbents [metal: 1000 ppm of $\text{Pb}(\text{CH}_3\text{CO}_2)$ in a metal blend].

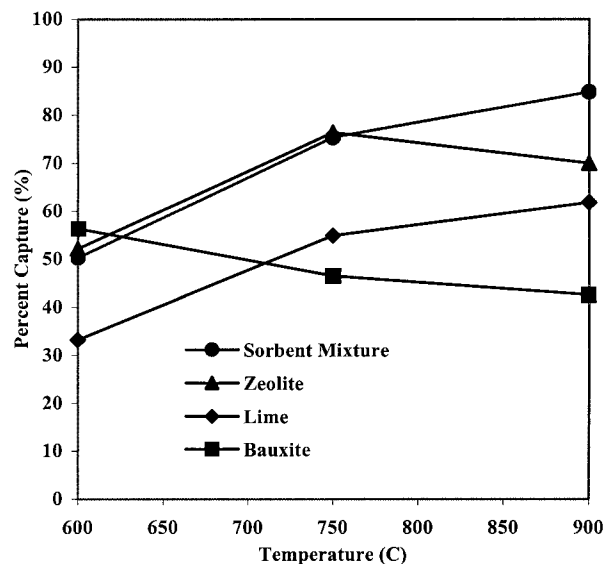


Fig. 10. Comparison of organic chromium capture by sorbent mixtures [metal: 1000 ppm of $\text{Cr}(\text{C}_{15}\text{H}_{21}\text{O}_6)$ in a metal blend].

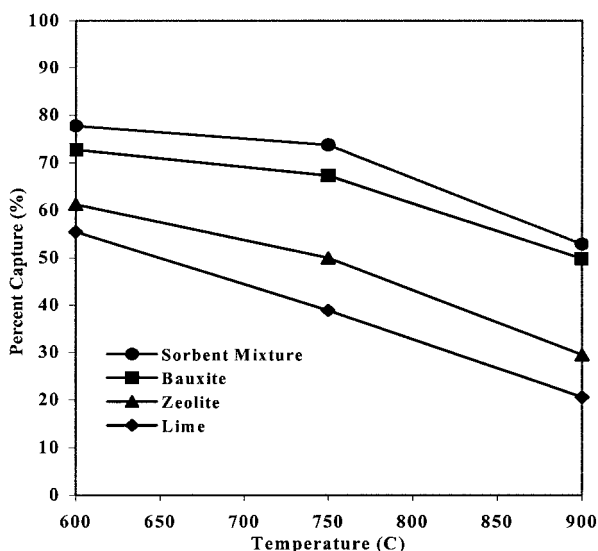


Fig. 9. Comparison of organic cadmium capture by various sorbents [metal: 1000 ppm of $\text{Cd}(\text{CH}_3\text{CO}_2)$ in a metal blend].

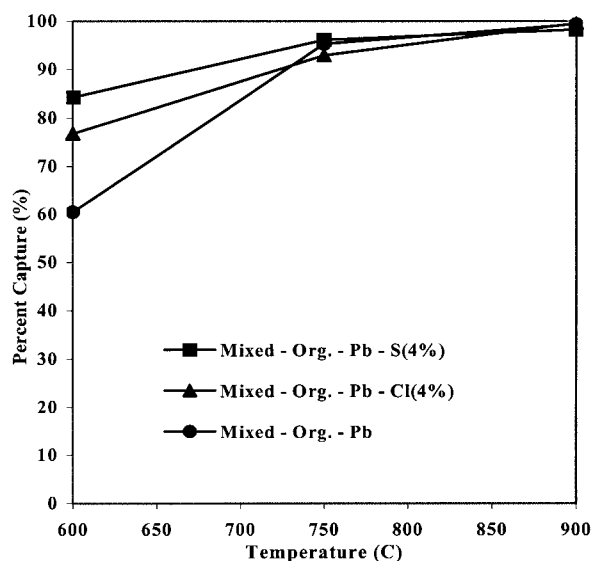


Fig. 11. Effect of sulfur and chlorine on organic lead capture by the sorbent mixture [metal: 1000 ppm of $\text{Pb}(\text{CH}_3\text{CO}_2)$ in a metal blend].

Figs. 5–7 for Pb, Cd and Cr, respectively. These results indicate that the percent capture is approximately 20% higher with metals in a mixed-metal format (coexistence of the three metals at 1000 ppm each) than those in a single-metal format (a single metal of lead acetate, cadmium acetate or chromium acetylacetonate at 1000 ppm) especially at high temperatures. One explanation to the observed results is that the coexistence of the metals creates additional metal reactions which enhance the capture of metals by sorbents.

4.2.2. Effect of sorbent mixture

Another experimental parameter examined in the study was the use of sorbent mixture in addition to single

sorbents for metal capture. It has been observed that the sorbent mixture (one third by weight each of lime, bauxite and zeolite) is more effective in capturing metals in the experiments. It may create more than 30% higher percent capture than that generated by any of the single sorbents. Typical sets of such results are shown in Figs. 8–10 where the capture efficiencies are seen to be the highest when the sorbent mixture was used. The observation, however, is expected because the use of the sorbent mixture is likely to involve all capture mechanisms, e.g. chemisorption and particulate scrubbing, offered by each single sorbent.

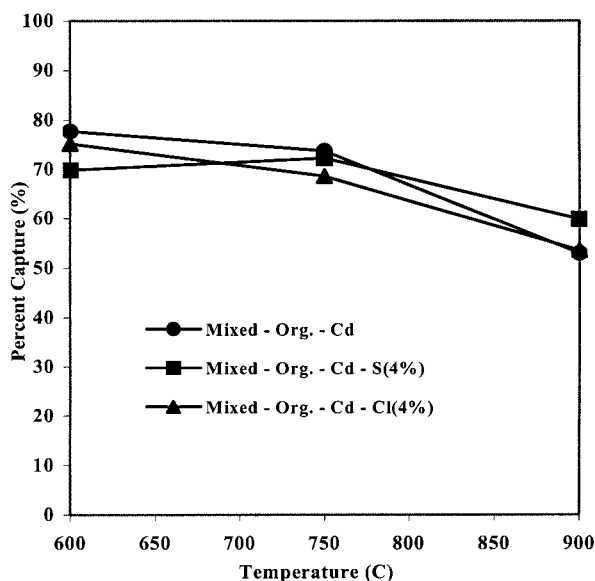


Fig. 12. Effect of sulfur and chlorine on organic cadmium capture by the sorbent mixture [metal: 1000 ppm of $\text{Cd}(\text{CH}_3\text{CO}_2)$ in a metal blend].

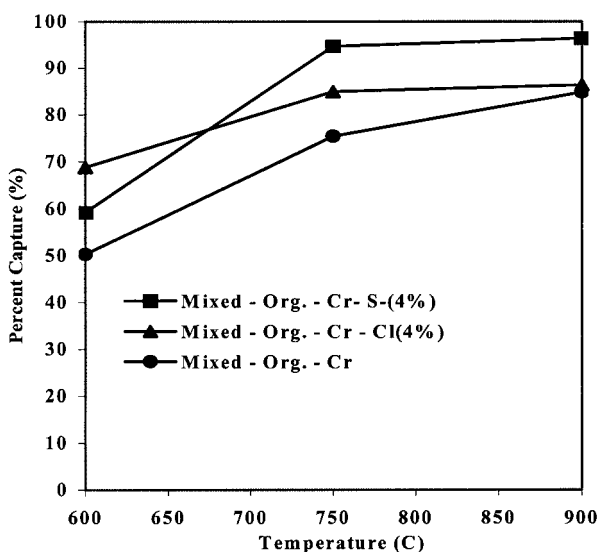


Fig. 13. Effect of sulfur and chlorine on organic chromium capture by the sorbent mixture [metal: 1000 ppm of $\text{Pb}(\text{CH}_3\text{CO}_2)$ in a metal blend].

4.2.3. Effect of temperature

Figs. 11–13 are plots of metal capture efficiency versus temperature for lead, cadmium and chromium capture, respectively, by the sorbent mixture. Also on the plots are the effect of the coexistence of sulfur and chlorine. As indicated, for lead and chromium, the capture efficiency is seen to be higher at a higher temperature; however, for cadmium, it is seen to be higher at a lower temperature. The observations are in good agreement with the results observed previously [2,3].

4.2.4. Effect of sulfur

The existence of sulfur always enhances the lead and chromium capture as can be seen in Figs. 11–13, especially

at a high temperature for lead and at a low temperature for chromium. The effect, however, is less obvious for cadmium capture by sorbents. The results suggest that the reactivity of sulfur with metals and sorbents plays an important role in the metal capture process.

4.2.5. Effect of chlorine

As indicated in the same three figures, chlorine is also observed to enhance the metal capture process in the same manner as sulfur does for lead and chromium capture. Its effect on cadmium capture, again, is less obvious.

5. Conclusions

This study investigated the characteristics of simultaneous sulfur and metal capture by sorbents and sorbent mixtures during fluidized bed incineration of metal-containing waste. The observed experimental results have indicated that the capture efficiency ranges from 20 to 99% depending on metal and sorbent species and operating conditions. The capture mechanisms appear to include particulate scrubbing and chemisorption depending on the type of sorbents. Metals in a metal mixture format have been observed to create higher capture efficiencies than those in a single metal format. In addition, sorbent mixtures appear to generate the highest capture efficiencies. The existence of sulfur and chlorine almost always enhances the metal capture process especially for lead and chromium capture. Results from equilibrium simulations have suggested the formation of metal–sulfur–sorbent compounds such as PbSO_4 (s), CdSO_4 (s), CaSO_4 (s), Pb_2SiO_4 (s), CdAl_2O_4 (s) and CdSiO_3 (s) under the combustion conditions.

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