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ATTACHMENT 4

TRACE METAL CAPTURE BY VARIOUS SORBENTS DURING FLUIDIZED BED COAL COMBUSTION*

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ABSTRACT

This study investigated the potential of employing suitable sorbents to capture trace metallic substances during fluidized bed coal combustion. The objectives of the study were to demonstrate the capture process, identify effective sorbents, and characterize the capture efficiency.

Experiments were carried out in a 25.4 mm (1") quartz fluidized bed combustor enclosed in an electric furnace. In an experiment, a coal sample was burned in the bed with a sorbent under a specific set of combustion conditions and the amount of metal capture by the sorbent was determined. Three different coal samples from the Illinois Basin Coal Sample Bank were tested in the study. The metals involved were cadmium, lead and chromium, and the sorbents tested included bauxite, zeolite and lime. In addition to the experimental investigations, potential metal-sorbent reactions were also identified through chemical equilibrium calculations based on the minimization of system free energy.

The observed experimental results indicated that metal capture by sorbent can be as high as 96% depending on the metal species and sorbent involved. All three sorbents were observed to be capable of capturing lead in a various degree, zeolite and lime were able to capture chromium, and bauxite was the only sorbent capable of capturing cadmium. Results from thermodynamic equilibrium simulations suggested the formation of metal-sorbent compounds such as $Pb_2SiO_4(s)$, $CdAl_2O_4(s)$ and $CdSiO_3(s)$ under the combustion conditions.

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INTRODUCTION

Toxic trace metallic elements such as arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, mercury, nickel, and selenium are usually contained in coal in various forms and trace amounts (see Table 1). These metals will either stay in the ash or be vaporized during high temperature combustion. Portions of the vaporized metals may eventually be emitted from a combustion system in the form of metal fumes or particulates with diameters less than 1 micron, which are potentially hazardous to the environment (1).

Current practice of controlling trace metal emissions during coal combustion employs conventional air pollution control devices (APCDs), such as electrostatic precipitators and baghouses, to collect fly ash and metal fumes. The control may not always be effective on metal fumes due to their extremely fine sizes (2).

Concern over toxic trace metal emissions from coal-fired combustion sources is growing, especially as the result of the passage of the 1990 Clean Air Act Amendments (CAAA) where eleven metallic elements, i.e., antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, mercury, nickel, and selenium are listed as potential hazardous air pollutants. To address the concern, the US DOE has co-sponsored a workshop jointly with the Electric Power Research Institute (EPRI) and the Energy and Environmental Research Center (EERC) on Trace Elements Transformations in Coal-Fired Power Plants (held in Scottsdale, Arizona, April 19-22, 1993). The objective of the workshop was to evaluate the current level of understanding on metal behavior during coal combustion and to identify potential technologies for improved metal emission control.

This study is to explore the opportunities for improved control of toxic trace metal emissions from coal-fired combustion systems. Specifically, the technology proposed is to employ suitable sorbents to (1) reduce the amount of metal volatilization and (2) capture volatilized metal vapors during fluidized bed coal combustion. The objectives of the study were to demonstrate the capture process, identify effective sorbents, and characterize the capture efficiency.

Metal capture experiments were carried out in a 25.4 mm (1") quartz fluidized bed combustor enclosed in an electric furnace. In an experiment, a coal (or metal-containing wood pellets) sample was burned in the bed with a sorbent under a specific set of combustion conditions and the amount of metal capture by the sorbent was determined. Three different coal samples from the Illinois Basin Coal Sample Bank along with an artificially prepared wood pellets sample were tested in the study. The metals involved were cadmium, chromium and lead, and the sorbents tested included bauxite, zeolite and lime. In addition to the experimental investigations, potential metal-sorbent reactions were also identified through chemical equilibrium calculations based on the minimization of system free energy.

SCIENTIFIC DISCUSSION

During high temperature coal combustion, metals in coal will either stay in the ash or be vaporized in combustion chambers. Most of the vaporized metals will decompose and/or react and eventually recondense during the cooling of flue gas. Two competitive mechanisms are associated with the condensation process, namely, (1) homogeneous nucleation which generates metal fumes (particulates) and creates metal emission problems; and (2) heterogeneous condensation which deposits metals onto available surfaces such as pre-existing fly ash, boiler tubes and combustor walls **(3)**. The proposed technology is to minimize the formation of metal fumes at the hot-end of the coal combustion process, i.e., in the combustion chamber. Specifically, the technology is to employ suitable and effective sorbents to:

(1) reduce the amount of metal volatilization during coal combustion in the combustion chamber through promoting chemical reactions between metals and sorbents to form less-volatile metal compounds at an elevated combustion temperature, and

(2) capture volatilized metal vapors by sorbents through the mechanism of chemisorption and/or heterogeneous deposition.

Chemical absorption reactions between metal vapors and a variety of sorbents at high temperatures have been observed both in a packed bed **(4,5,6,7)** and in a fluidized bed **(8,9,10)**. Most of the captured metals have been observed to be non-leachable through this chemical absorption mechanism. Kaolinite and bauxite have been reported to be suitable sorbents for the removal of alkali vapors and lead compounds through chemical absorption **(4,5,6)**. Calcined limestone and zeolite have also been reported to be an effective sorbent for metal capture **(10)**. The following reactions between metals and sorbents constituents have been confirmed both theoretically and experimentally **(6,7,10)**:

$$2\ PbO + SiO_2 \text{ ----> } Pb_2SiO_4(s) \qquad (A)$$

$$CdO + SiO_2 \text{ ----> } CdSiO_3(s) \qquad (B)$$

$$CdO + Al_2O_3 \text{ ----> } CdAl_2O_4(s) \qquad (C)$$

$$PbCl_2 + Al_2O_3{:}2SiO_2 + H_2O \text{ ----> } PbO{:}Al_2O_3{:}2SiO_2(s) + 2\ HCl(g) \qquad (F)$$

$$CdCl_2 + Al_2O_3 + H_2O \text{ ----> } CdAl_2O_4(s) + 2\ HCl(g) \qquad (G)$$

The metal capture technology, however, has never been evaluated for coal during fluidized bed combustion.

EQUILIBRIUM CALCULATION

Equilibrium composition represents the most stable chemical composition within a system under a specific state. Thermodynamically, this composition is corresponding to the one where the system free energy is minimized. The calculated equilibrium composition would reveal the preferred chemical speciation under a specific state, which in turn, suggest potential chemical reactions which may occur within the system.

In this study, combustion equilibrium was calculated using a PC-based computer software package **(11)** especially developed for predicting equilibrium compositions during fuel or waste combustion. The package incorporated the NASA SP-273 program **(12)** for performing complex chemical equilibrium calculations based on the minimization of system free energy. The simulation would reveal potential metal-sorbent reactions for the proposed metal capture process.

EXPERIMENTAL

Metal capture experiments were carried out semi-batchwise in a 25.4 mm (1") OD quartz fluidized bed coal combustor enclosed in an electric furnace. The metals involved in the study were cadmium, chromium and lead. Three coal samples from the Illinois Basin Coal Sample Bank (IBCSB) and an artificially prepared metal-containing wood sample were tested in the experiments. The corresponding concentration of chlorine, sulfur, and the target metals in each sample was summarized in Table 2. The sorbents tested included bauxite, zeolite and lime. The chemical composition and fluidization properties of the sorbents are listed in Table 3.

For an experimental run, a bed of sorbent was preheated to the desired temperature under the designed operating conditions. A predetermined amount of coal or wood pellets was then charged in the bed at a constant feed rate for combustion. After the combustion was completed, the bed residue including sorbent and ash was discharged for analysis of metal concentration. The experimental parameters and operating conditions associated with the experiments are shown in Table 4.

Chemical Analysis

Metal concentration in the coal, wood pellets, original sorbent, and combustor residue was determined by an atomic absorption spectrophotometer. An HF modified EPA Method 3050 was used to digest metals from the sorbent, which involves the use of HNO_3, HCl and HF acids (13). Toxicity Characteristics Leaching Procedure (TCLP) tests were performed to determine the leachability of the captured metals from sorbents.

Data Analysis

Experimental data were analyzed to determine the characteristics of metal capture under the combustion conditions. The following two metal capture properties were calculated:

Specific Capture Capacity (ϕ)

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

$$\phi_b = C_b - C_o \qquad (1)$$

Percent Capture (ψ)

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

$$\psi_b = \frac{\phi_b \times W_b}{C_w \times W_w} \times 100\% \qquad (2)$$

RESULTS AND DISCUSSION

Simulation Results

Equilibrium calculations were performed to identify thermodynamically preferred metal speciation in a combustion system. Two typical sets of simulation results indicating potential metal-sorbent reactions and the effect of sulfur on metal capture by sorbents are shown in Tables 5 and 6, for lead and cadmium, respectively. The corresponding elemental composition and combustion conditions used in the simulations were: carbon - 71.3 wt%, hydrogen - 5.2 wt%, nitrogen - 1.4 wt%, oxygen - 12.4 to 7.8 wt%, sulfur - 0 to 4.6 wt%, metal concentration - 50 ppm, ash - 9.3 wt%, combustion temperature - 900°C, and percent excess air - 50%.

The results shown in Table 5 indicate that lead will react with both sulfur and silica during combustion. At a temperature below 950°C, $PbSO_4$(s) is the thermodynamically preferred lead compound; however, between 950°C and 1000°C, $PbSiO_4$(s) is the preferred one; and, above 1000°C, PbO(g) is the dominating species. These results suggest that silica is thermodynamically capable of capturing lead. However, the existence of sulfur will affect the capture process especially at a temperature below 950°C. Note that lead does not seem to react with Al_2O_3 according to the equilibrium simulation. It should also be pointed out that lead does not show any reactions with CaO because there are no thermodynamic data available in the literature.

The results shown in Table 6 for cadmium indicate that cadmium will react with Al_2O_3 and SiO_2 to form $CdAl_2O_4$(s) and $CdSiO_3$(s), respectively. It, however, will not react with CaO. The existence of sulfur does not seem to interfere with the reactions according to the equilibrium results shown in the table. These simulation results, again, suggest that silica and alumina have potential to capture cadmium under the combustion conditions. Note that, although not shown, the simulation results for chromium have indicated that the thermodynamically preferred chromium compound under the combustion conditions is exclusively Cr_2O_3 (s) and no chromium-sorbent compounds are observed. The results suggest that, thermodynamically, the tested sorbents are not expected to chemically absorb chromium during combustion.

It is worth pointing out that thermodynamic equilibrium alone is not expected to provide quantitative information regrading the actual metal partitioning among different metal compounds in a combustion system. Other governing laws such as reaction kinetics, and mass and energy transfer operations should also be considered in such prediction.

Experimental Results

Typical experimental results indicating the effectiveness of metal capture by various sorbents are shown in Tables 7, 8 and 9 for lead, cadmium, and chromium, respectively. The combustible materials tested were three coal samples, i.e., IBC-110, IBC-111 and IBC-112, and a wood sample. The sorbents used were bauxite, zeolite and lime. The corresponding metal concentrations in the tested fuel samples and sorbents have been summarized in Tables 2 and 3, respectively.

The results shown in Table 7 for lead indicate that all three sorbents tested in the study are capable of capturing lead during fluidized bed combustion with zeolite being the most effective followed by bauxite and lime. As suggested by equilibrium simulations, the mechanism of lead capture by zeolite appears to be due to the formation of $Pb_2SiO_4(s)$ and the mechanism of capture by bauxite may be due to the formation of the same compound or an alumino-silica compound. The mechanism of lead capture by lime, however, may be due to the "melt capture" as suggested by Linak and Wendt (**14**). These proposed mechanisms, however, could not be analytically confirmed because the concentrations of the potential metal-sorbent compounds are extremely low.

For cadmium capture, the results shown in Table 7 indicate that bauxite is the only sorbent capable of capturing cadmium during coal combustion with the capture efficiency ranging from 62 to 88%. This appears to suggest that the formation of $CdAl_2O_4(s)$ is the dominating reaction during combustion based on equilibrium simulation results. The suggestion, again, could not be confirmed analytically.

The chromium capture results shown in Table 9 indicate that zeolite and lime are both capable of capturing the metal. The mechanism of chromium capture by these sorbents, however, is not clear at this time. Efforts are currently devoted to analytically identify the chromium state in the sorbents. Note that bauxite was not observed to capture any chromium because the original bauxite contained a high concentration of chromium which continued to vaporize during combustion. The net result was that, in contrast to chromium capture, bauxite gave away chromium during the process.

It is essential to point out that, due to the non-uniformity and trace-quantity nature associated with the process, it is still difficult to discuss the effect of fuel type, coal type, and coal properties such as chlorine, sulfur, ash and metal contents on the metal capture process based on the results observed. Efforts are being continued to collect additional experimental data to provide more statistically representative results for better understanding the process.

CONCLUSIONS

This study is to explore the possibility of employing suitable sorbents to capture toxic trace metals during fluidized bed coal combustion. The observed experimental results indicated that metal capture by sorbents can be as high as 96% depending on the metal species and sorbent involved. All three sorbents tested, i.e., bauxite, zeolite and lime, were observed to be capable of capturing lead in a various degree, zeolite and lime were able to capture chromium, and bauxite was the only sorbent capable of capturing cadmium. Results from thermodynamic equilibrium simulations suggested the formation of metal-sorbent compounds such as $Pb_2SiO_4(s)$, $CdAl_2O_4(s)$ and $CdSiO_3(s)$ under the combustion conditions. Additional experiments are being carried out to provide more statistically representative results for better understanding the metal capture process.

NOTATION

C_b	metal concentration in combusted bed sorbent, ppm
C_o	metal concentration in original sorbent, ppm
C_w	metal concentration in coal or wood pellets, ppm
d_p	particle diameter, mm
T	combustor temperature, °C
U	superficial air velocity, cm/s
U_{mf}	minimum fluidization velocity of sorbent, cm/s
W_b	weight of collected combusted bed sorbent, g
W_w	weight of coal or wood pellets, g
ϕ_b	specific capture capacity of bed sorbent, mg/g
ψ_b	percent capture by bed sorbent, %

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Table 1. Trace Metal Concentrations in Selected Coal (ppm)

Metal	Indiana V	Indiana VII	Illinois 6
As	4.7	6.1	3.3
Cd	0.4	0.4	0.3
Cr	11.0	14.0	14.0
Hg	1.8	2.1	0.1
Pb	10.0	18.0	27.0
Se	2.5	1.5	1.6

Table 2. Concentration of Chlorine, Sulfur and Target Metals in Tested Coal Samples and Wood pellets (Units: ppm for metals, % for Cl and S)

Species	IBC-110	IBC-111	IBC-112	Wood*
Cd	<0.4	<0.4	<0.3	5
Cr	11	14	14	20
Pb	10	18	27	30
Cl	0.0%	0.0%	0.2%	0.0%
S	4.6%	2.0%	2.8%	0.0%

*Spiked Metals: Metal Nitrates

Table 3. Major Composition, Trace Metal Concentration and Fluidization Properties of the Three Tested Sorbents

Composition or Property	Bauxite	Zeolite	Lime
SiO_2 (%)	9.0	66.7	0.7
Al_2O_3 (%)	78.0	12.1	0.3
CaO (%)	0.0	3.1	97.2
Cd (ppm)	2.0	3.0	3.6
Cr (ppm)	146	4.0	7.8
Pb (ppm)	43.2	60.4	72.4
d_p (mm)	0.5	0.5	0.5
U_{mf} (cm/s)	3.8	3.5	3.8

Table 4. Experimental Parameters and Operating Conditions

Parameter	Range
Fuel Type	Coal, Wood
Coal Size	0.7 - 1.2 mm
Wood Size	4.8 mm
Fuel Amount	30 g
Fuel Feed Rate	0.1 g/s
Sorbent Type	Bauxite, Zeolite, Lime
Sorbent Size	0.4-0.6 mm
Sorbent Amount	12-15 g
Static Sorbent Height	9 cm
Air Flow Rate	3 U_{mf} of Sorbent
Combustor Temperature	900°C
Combustion Duration	6 hrs

Table 5. Equilibrium Simulation Results for Lead with or without Sulfur

Sorbent Constituent	Metal	With or Without Sulfur	Sulfur-Metal-Sorbent Compound	
SiO_2	Pb	Without S	**Pb_2SiO_4(s)**	<1000°C
			PbO(g)	>1000°C
		With S	**$PbSO_4$(s)**	< 950°C
			Pb_2SiO_4(s)	<1000°C
			PbO(g)	>1000°C
Al_2O_3	Pb	Without S	PbO(s)	< 900°C
			PbO(g)	> 900°C
		With S	**$PbSO_4$(s)**	< 950°C
			PbO(g)	> 950°C
CaO	Pb	Without S	PbO(s)	< 900°C
			PbO(g)	> 900°C
		With S	**$CaSO_4$(s)**	> 500°C
			$PbSO_4$(s)	< 950°C
			PbO(g)	> 950°C

Table 6. Equilibrium Simulation Results for Cadmium with or without Sulfur

Sorbent Constituent	Metal	With or Without Sulfur	Sulfur-Metal-Sorbent Compound	
SiO_2	Cd	Without S	**$CdSiO_3$(s)**	< 850°C
			CdO(s)	< 1000°C
			Cd(g)	> 1000°C
		With S	**$CdSO_4$(s)**	< 800°C
			CdO(s)	< 900°C
			CdS(g)	> 900°C
Al_2O_3	Cd	Without S	**$CdAl_2O_4$(s)**	< 950°C
			CdO(s)	< 1000°C
			Cd(g)	> 1000°C
		With S	**$CdAl_2O_4$(s)**	< 950°C
			CdS(g)	> 950°C
CaO	Cd	Without S	CdO(s)	< 1000°C
			Cd(g)	> 1000°C
		With S	**$CaSO_4$(s)**	> 500°C
			CdO(s)	< 900°C
			CdS(g)	> 900°C

Table 7. Percentage Lead Capture by Sorbents (%)

Fuel Type	Bauxite	Zeolite	Lime
Coal (IBC-110)	50	96	30
Coal (IBC-111)	22	93	26
Coal (IBC-112)	74	81	36
Wood Pellets	59	69	67

Table 8. Percentage Cadmium Capture by Sorbents (%)

Fuel Type	Bauxite	Zeolite	Lime
Coal (IBC-110)	88	0	0
Coal (IBC-111)	79	0	0
Coal (IBC-112)	62	0	0
Wood Pellets	19	43	0

Table 9. Percentage Chromium Capture by Sorbents (%)

Fuel Type	Bauxite	Zeolite	Lime
Coal (IBC-110)	0	10	10
Coal (IBC-111)	0	48	20
Coal (IBC-112)	0	35	70
Wood Pellets	0	54	79