

FINAL TECHNICAL REPORT

(July 1, 1994 through December 31, 1997)

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for the Project

CONTROL OF TRACE METAL EMISSIONS DURING COAL COMBUSTION

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Project Title: **CONTROL OF TRACE METAL EMISSIONS DURING COAL COMBUSTION**
DOE Grant Number: DE-FG22-94PC94221
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ABSTRACT

Emissions of toxic trace metals in the form of metal fumes or submicron particulates from a coal-fired combustion source have received greater environmental and regulatory concern over the past years. Current practice of controlling these emissions is to collect them at the cold-end of the process by air-pollution control devices (APCDs) such as electrostatic precipitators and baghouses. However, trace metal fumes may not always be effectively collected by these devices because the formed fumes are extremely small.

The proposed research is to explore the opportunities for improved control of toxic trace metal emissions, alternatively, at the hot-end of the coal combustion process, i.e., in the combustion chamber. The technology proposed is to prevent the metal fumes from forming during the process, which would effectively eliminate the metal emission problems. Specifically, the technology is to employ suitable sorbents to (1) reduce the amount of metal volatilization during combustion and (2) capture volatilized metal vapors. The objectives of the project are to demonstrate the technology and to characterize the metal capture process during coal combustion in a fluidized bed combustor.

This final technical report details the work performed, the conclusions obtained, and the accomplishments achieved over the project performance period from July 1, 1994 through December 31, 1997. Specifically, this report consists of the following five chapters:

- Chapter 1. Executive Summary;
- Chapter 2. Metal Capture by Various Sorbents;
- Chapter 3. Simultaneous Metal and Sulfur Capture;
- Chapter 4. Sorption and Desorption of Mercury on Sorbents; and
- Chapter 5. Project Conclusions.

In summary, the metals involved in the project were arsenic, cadmium, chromium, lead, mercury and selenium and the sorbents tested included bauxite, zeolite and calcined limestone. The three sorbents have been found to have various degree of metal capture capability on arsenic, cadmium, chromium and lead. Among them, calcined limestone is capable of simultaneously capturing metals and sulfur. Mercury and selenium, however, can not be effectively retained by these sorbents under the combustion conditions. Mercury adsorption by sorbents at low temperatures was also investigated and the developed mass transfer model for mercury absorption appears to describe reasonably well the experimental results. Overall, the project has generated 18 presentations and/or publications in professional conferences and journals.

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CHAPTER 1. EXECUTIVE SUMMARY

PROJECT OBJECTIVE

Toxic (or potentially toxic) trace metallic elements such as barium, beryllium, boron, cadmium, chromium, lead, mercury, nickel, selenium, strontium, vanadium, zinc and zirconium are usually contained in coal in various forms. 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. Most of the emitted metals will be in the form of metal fumes or particulates with diameters less than 1 micron and are potentially hazardous to the environment. The U.S. EPA has reported that metals account for almost all of the identified risks from waste incineration systems.

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). To address the concern, the U.S. DOE has recently 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. 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.

Current practice of controlling trace metal emissions during coal combustion employs conventional air pollution control devices (APCDs), e.g., venturi scrubbers, electrostatic precipitators, baghouses etc., to collect fly ash and metal fumes. This type of control is essentially a cold-end technology because metals are allowed to vaporize and condense before being collected. The control may not always be effective on metal fumes due to their extremely fine sizes.

An alternative technology for metal emission control is to minimize the formation of metal fumes at the hot-end of the coal combustion process, i.e., in the combustion chamber. The technology proposed is to prevent the metal fumes from forming during the process, which would effectively eliminate the metal emission problems. Specifically, the technology is to employ suitable sorbents to (1) reduce the amount of metal volatilization during combustion and (2) capture volatilized metal vapors. The objectives of the project are to demonstrate the technology and to characterize the metal capture process during coal combustion in a fluidized bed combustor.

SUMMARY OF WORK PERFORMED

The detailed work performed and the corresponding major conclusions obtained are reported in the following three chapters:

- Chapter 2. Metal Capture by Various Sorbents;
- Chapter 3. Simultaneous Metal and Sulfur Capture; and
- Chapter 4. Sorption and Desorption of Mercury .

In Chapter 2, the characteristics of metal capture by various sorbents during fluidized bed coal combustion are reported. Metal capture experiments were carried out in a 25.4 mm quartz

fluidized bed combustor enclosed in an electric furnace. The metals involved were cadmium, lead, chromium, arsenic, and selenium, and the sorbents tested included bauxite, zeolite, and calcined limestone. 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 sorbents can be as high as 88% depending on the metal species and sorbent involved. Results from thermodynamic equilibrium simulations suggested the formation of metal-sorbent compounds such as $\text{Pb}_2\text{SiO}_4(\text{s})$, $\text{CdAl}_2\text{O}_4(\text{s})$ and $\text{CdSiO}_3(\text{s})$ under the combustion conditions.

In Chapter 3, the characteristics of simultaneous sulfur and metal capture by calcined limestone during fluidized bed coal combustion are reported. Experimental results on seven coal samples have indicated that the capture process can be effective. Good fluidization, however, is essential in achieving the optimum capture efficiency which was observed to range from 93% to 15% in the order of cadmium, sulfur, lead, chromium, arsenic, and selenium. Also reported are capture mechanism, effect of metal concentration in coal, and effect of bed temperature.

In the above experiments, mercury concentrations in the spent sorbents and the combusted coal fly ash were also measured. It was found that neither of them contained any mercury. The preliminary conclusion was therefore that mercury would not react with any of the tested sorbents during high temperature coal combustion in the combustion chamber. In several follow-up experiments, mercury was intentionally diffused into sorbents and the mercury-loaded sorbents were placed in a high temperature furnace to test the reactivity between mercury and the tested sorbents at elevated temperatures. Unlike most of the other tested metals where various percentages of the metals were reactively retained by the sorbents, none of the initially-loaded mercury was found to be reactively retained by the sorbents. All the mercury was observed to have completely vaporized at about 500°C. This confirms the preliminary conclusion that mercury can not be retained by the tested sorbents at elevated temperatures. The conclusion appears to be supported by equilibrium calculations where $\text{Hg}^0(\text{g})$ is determined to be the thermodynamically preferred species at high temperatures and no potential reactions can be identified between $\text{Hg}^0(\text{g})$ and any other species. Effective mercury emission control, however, can be accomplished at low temperatures during the cooling of combustion flue gas. Two promising methods are sorbent injection and fixed bed adsorption using effective sorbents, such as activated carbon.

In Chapter 4, the adsorption/desorption characteristics of mercury on various sorbents at elevated temperatures are reported. Experiments were carried out in a 25.4 mm (1") ID fixed bed absorber. The mercury compounds involved were mercury chloride and elemental mercury, and the sorbents tested included bauxite, zeolite, lime, alumina and activated carbon. Experimental parameters were air flow rate, vaporization temperature, sorbent bed temperature, sorbent bed height, and sulfur impregnation. The Toxicity Characteristics Leaching Procedure (TCLP) tests were also performed to evaluate the leachability of the retained mercury. The results indicated that different sorbents have different mercury sorption capacity. Bauxite and activated carbon were found to be more effective than other tested sorbents for mercury retention. Besides experimental investigations, potential mercury reactions during the experiments were identified through equilibrium simulations and a model based on the mass transfer control mechanism was proposed to simulate the mercury sorption process. The proposed sorption model appeared to describe reasonably well the experimental results.

CONCLUDING REMARKS ON METAL EMISSION CONTROL

Toxic trace heavy metals are generally classified into three groups, namely volatile, semi-volatile, and refractory. Among the 11 metals listed in the Clean Air Act Amendments of 1990, i.e., Sb, As, Be, Cd, Cr, Co, Pb, Hg, Mn, Ni, and Se, mercury and selenium are classified as volatile; arsenic, cadmium and lead are semi-volatile; and the rest of the metals are refractory.

For coal combustion, the most troublesome metals are mercury and selenium because they tend to stay in gas phase and are less reactive with sorbents at high temperatures as reported in this project. Additional control technologies such as low temperature sorbent injection/carbon adsorption or acid scrubbing are required to effectively control their emissions. The semi-volatile metals, i.e., arsenic, cadmium and lead, also tend to volatilize during combustion and, if not reactively retained by sorbents, will eventually recondense during flue gas cooling to form metal fumes or to deposit on fine particular matter (PM). The efficient collection of fine particular matter, micron and sub-micron in size, is therefore extremely crucial to control the emissions of these metals. These metals, however, are found to be relatively reactive and can be effectively retained by sorbents at high temperatures as demonstrated in the current project. The refractory metals are thermally stable and most of them will stay in bed ash or fly ash without being vaporized. The effective control of fly ash emission therefore controls the emissions of these metals. In this group of metals, the behavior of chromium during coal combustion often receives more attention because chromium has potential to transform into chromium (+6) which is more volatile and more toxic than chromium (+3).

LIST OF PROJECT PRESENTATIONS/PUBLICATIONS

Overall, the project has generated 18 presentations and/or publications in professional conferences and journals. They are listed below:

1. Ho et al., "Transformation of Chromium from Cr(III) to Cr(VI) in a Simulated Wet Scrubber," Proceedings of the 1995 International Incineration Conference held in Bellevue, Washington, pp. 569-573, May 8-12, 1995.
2. Ho et al., "Lead and Cadmium Capture by Various Sorbents During Fluidized Bed Combustion/Incineration," Proceedings of the 8th International Fluidization Conference held in Tours, France, pp. 899-906, May 14-19, 1995.
3. Ho et al., "Metal Behavior During Fluidized Bed Thermal Treatment of Soil," Waste Management, **15**, 325 (1995).
4. Ho, T.C., "Control of Trace Metal Emissions During Coal Combustion," paper presented at the 1995 DOE Review of Fossil Energy Advanced Research Projects Conference held in Nashville, TN, June 13-15, 1995.

5. Ho et al., "Effect of Chlorine and Sulfur on Metal Capture by Sorbents During Fluidized Bed Incineration," Proceedings of the 1996 International Incineration Conference held in Savannah, George, pp. 415-422, May 6-10, 1996.
6. Ho, T.C., "Control of Trace Metal Emissions During Coal Combustion," paper presented at the 1996 DOE Annual UCR Contractors Review Conference held in Pittsburgh, PA, June 4-5, 1996.
7. Ho et al., "Trace Metal Capture by Various Sorbents During Fluidized Bed Coal Combustion," paper presented at the 212th ACS National Meeting held in Orlando, Florida, August 25-30, 1996.
8. Lee and Ho et al., "Dynamic Volatilization Characteristics of Heavy Metals During the Thermal Treatment of Contaminated Soil," Proceedings of the Fifth Asian Conference on Fluidized-Bed & Three-Phase Reactors held in Hsitou, Taiwan, pp. 200-206, December 16-20, 1996.
9. Ho et al., "Trace Metal Capture by Various Sorbents During Fluidized Bed Coal Combustion," Proceedings of the Fifth Asian Conference on Fluidized-Bed & Three-Phase Reactors held in Hsitou, Taiwan, pp. 207-212, December 16-20, 1996.
10. Ho et al., "Trace Metal Capture by Various Sorbents During Fluidized Bed Coal Combustion," pp. 877-888, Proceedings of the 22nd International Conference on Coal Utilization & Fuel Systems held in Clearwater, FL, March 16-19, 1997.
11. Ho et al., "Metal Vaporization and Metal Binding by Additives or Sorbents During High Temperature Thermal Treatment," pp. 761-768, Proceedings of the 1997 Incineration Conference held in Oakland, CA, May 12-16, 1997.
12. Ho, T.C., "Trace Metal Capture by Various Sorbents During Fluidized Bed Coal Combustion," paper presented at the 1997 DOE Annual UCR Contractors Review Conference held in Pittsburgh, PA, June 3-4, 1997.
13. "Effect of Temperature on Mercury Desorption from Sorbents in a Packed Bed Absorber," paper presented at the 1997 AIChE Los Angeles Annual Meeting, November 16-21, 1997.
14. Ho et al., "Simultaneous Sulfur and Metal Capture by Lime During Fluidized Bed Combustion," paper accepted for publication at the AIChE Symposium Series on Fluidization and Fluid Particle Systems (1998).
15. Ho et al., "Adsorption and Desorption of Mercury on Sorbents at Elevated Temperatures," paper presented at the 5th International Congress on Toxic Combustion By-Products held at the University of Dayton, June 25-27, 1997 and accepted by Combustion Sci. & Tech. for publication (1998).

16. Ho et al., "Multipollutants Air Emission Control During Fluidized Bed Combustion," paper accepted for presentation at the 28th Annual Meeting of the Fine Particle Society to be held in Dallas, TX, April 1-3, 1998.
17. Ho et al., "Characterization of Mercury Desorption from Spent Sorbents During Regeneration at Elevated Temperature," paper accepted for presentation at the 1998 Incineration Conference to be held in Salt Lake City, Utah, May 11-15, 1998.
18. Ho et al., "Simultaneous Sulfur and Metal Capture by Lime During Fluidized Bed Coal Combustion," paper accepted for presentation at the 9th International Fluidization Conference to be held at Durango, CO, May 17-22, 1998.

CHAPTER 2. METAL CAPTURE BY VARIOUS SORBENTS

ABSTRACT

In this chapter, the project investigated the potential of employing suitable sorbents to capture toxic trace metals during fluidized bed coal combustion. Metal capture experiments were carried out in a 25.4 mm quartz fluidized bed combustor enclosed in an electric furnace. The metals involved were cadmium, lead, chromium, arsenic, and selenium, and the sorbents tested included bauxite, zeolite, and calcined limestone. 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 sorbents can be as high as 88% depending on the metal species and sorbent involved. 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.

INTRODUCTION

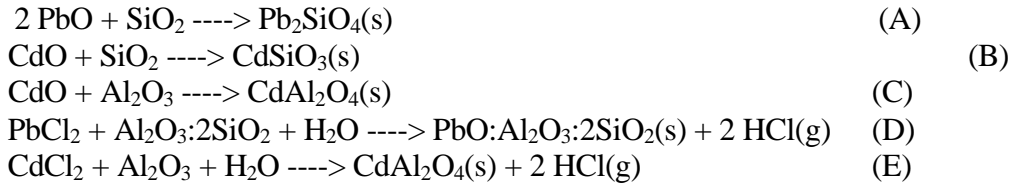
Toxic trace metallic elements such as arsenic, cadmium, chromium, lead, mercury, and selenium are usually contained in coal in various forms and trace amounts. Portions of these metals may eventually be emitted from a combustion system in the form of metal fumes or particulates with diameters less than 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. 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 work were to demonstrate the capture process, identify effective sorbents, and characterize the capture efficiency.

SCIENTIFIC DISCUSSION

Metal-Sorbent Reactions

Chemical absorption reactions between metal vapors and a variety of sorbents at high temperatures have been observed both in a packed bed and in a fluidized bed (3-6). The following reactions between metals and sorbent constituents have been confirmed both theoretically and experimentally:



Note that the technology of metal capture by sorbents during fluidized bed coal combustion has never been evaluated. Due to the trace concentration and the nonuniformity nature of metals in coal, statistical approaches are essential in the evaluation.

Chemical Equilibrium

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's 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 (7) especially developed for predicting equilibrium compositions during fuel or waste combustion.

EXPERIMENTAL

Facilities and Procedure

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. A schematic diagram of the fluidized bed coal combustion system is shown in Figure 1. Seven coal samples from the Illinois Basin Coal Sample Bank (IBCSB) were tested in the experiments. The concentrations of sulfur, chlorine, and the target metals in these samples are summarized in Table 1. The sorbents tested included bauxite, zeolite and lime. Their chemical composition and the corresponding minimum fluidization velocity (U_{mf}) at 900°C are listed in Table 2.

In an experimental run, a bed of sorbent (normally 6 cm bed height) was preheated to the desired temperature under the designed operating conditions (normally 900°C and 3 U_{mf}). A predetermined amount of coal (normally 60 g) 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 and separated for analysis of metal concentration. The experimental parameters and operating conditions are summarized in Table 3.

Metal concentration in coal, 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 HNO₃, HCl and HF acids (8). Toxicity Characteristics Leaching Procedure (TCLP) tests were also performed to determine the leachability of the captured metals from sorbents.

Data Analysis

Specific Capture Capacity (ϕ) - This is defined to be the amount of metal captured by a unit mass of bed (or fly ash) sorbent. It was calculated as:

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

or

$$\phi_f = C_f - C_o \quad (2)$$

Percent Capture (ψ) - This is defined to be the percent of metal captured by fluidized bed sorbents (or fly ash sorbents) relative to the total amount of metal charged. It was calculated as:

$$\psi_b = \frac{\phi_b \times W_b}{C_c \times W_c} \times 100\% \quad (3)$$

or

$$\psi_f = \frac{\phi_f \times W_f}{C_c \times W_c} \times 100\% \quad (4)$$

All chemical symbols used in the equations are defined at the end of this chapter.

RESULTS AND DISCUSSION

Simulation Results

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 4 and 5 for lead and cadmium, respectively. The corresponding elemental compositions 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 4 indicate that lead will react with both sulfur and silica during combustion. At a temperature below 950°C, PbSO₄(s) is the thermodynamically preferred lead compound; however, between 950°C and 1000°C, PbSiO₄(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 Al₂O₃ 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 5 for cadmium indicate that cadmium will react with Al₂O₃ and SiO₂ to form CdAl₂O₄(s) and CdSiO₃(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.

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.

Detailed simulation results on Pb-S-SiO₂, Cd-S-SiO₂, and Cd-S-Al₂O₃ systems are also shown in Figures 2 through 4. They clearly indicate the effect of temperature on metal speciation during coal combustion with sorbents. It is worth pointing out again that literature data to date indicate that lead, cadmium and chromium will not react with CaO. For arsenic and selenium, efforts are currently ongoing to collect the necessary thermodynamic data for equilibrium simulations. The results will be reported in the near future in the open literature.

Experimental Results

Typical experimental results indicating the effectiveness of metal capture by various sorbents are shown in Tables 6 through 10 for lead, cadmium, chromium, arsenic and selenium, respectively. Note that the results reported in these tables include only the amount captured by bed sorbents, i.e., the amount captured by fly ash sorbents is not included. It is worth pointing out at this point that the amount captured by fly ash sorbents can be significant especially for lime.

The results shown in Table 6 for lead capture indicate that all three sorbents tested are capable of in-bed capturing lead during fluidized bed coal combustion with the average capture efficiency ranging from 44% to 69%. Bauxite and zeolite appear to have better "bed sorbent" capture efficiencies than lime. Lime, however, has greater "fly ash sorbent" capture efficiency as compared to zeolite and bauxite which will be discussed later. 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 lead capture by bauxite could be due to the formation of the same compound and/or alumino-silica compounds. The mechanism of lead capture by lime, however, is suspected to be due to the "melt capture" as suggested by Linak and Wendt (9).

For cadmium capture, the results shown in Table 7 indicate that the average "bed sorbent" capture efficiencies associated with the sorbents are similar to those of lead capture by bed sorbents. All three sorbents are seen to be relatively effective with an average capture efficiency being around 60%. The effectiveness of cadmium capture by bauxite and zeolite appears to suggest the formation of CdAl_2O_4 (s) and CdSiO_3 (s) as revealed from equilibrium simulations. The formation of these compounds, however, could not be analytically confirmed due to their low concentrations in the sorbents.

The chromium capture results shown in Table 8 indicate that zeolite and lime are both capable of capturing the metal. The average capture efficiencies are seen to be 31 and 30% which are much lower than those of lead and cadmium capture by the two sorbents. The mechanisms of chromium capture by these sorbents, however, are 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. For arsenic and selenium capture, the results shown in Tables 9 and 10 indicate that the average capture efficiencies of these two metals by sorbents are generally in the ranges of 13 to 34%, which are relatively low as compared to those of lead and cadmium capture.

One observation worth reporting is that the observed results strongly indicated that the amount of lead, cadmium and arsenic capture by a unit mass of sorbents was roughly proportional to the concentration of the metal in coal. Typical sets of results indicating this trend are shown in Figures 5 through 7. This trend, however, was not observed for chromium and selenium (see Figures 8 and 9). Note that, the observed results have not clearly indicated the effects of sulfur and other coal properties on capture efficiency of the metal capture process. A typical set of results is shown in Figure 10.

As mentioned previously, the results reported in the tables and figures include only the amount of capture by bed sorbents. It was observed that metal capture by "fly ash sorbent" can be very significant for lime and is insignificant for zeolite and bauxite. The results have indicated that, for lime, this "fly ash sorbent capture" can be as high as 200% as compared to the "bed sorbent capture" especially on arsenic and selenium. The complete results regarding this capture will be reported in the near future. It is also worth reporting that good fluidization is essential in the metal capture process. The metal capture efficiencies were observed to be much lower when the bed was operated under slugging regimes or near fixed bed conditions.

CONCLUSIONS

This study investigated the potential of employing suitable sorbents to capture toxic trace metals during fluidized bed coal combustion. The observed experimental results indicated that good fluidization operations are essential in the metal capture process. Metal capture by sorbents can be as high as 88% depending on the metal species and sorbent involved. All three sorbents tested, i.e., bauxite, zeolite and lime, were observed to be capable of effectively capturing lead and cadmium, and zeolite and lime were able to capture chromium. Arsenic and selenium capture by bed sorbents was found to be relatively ineffective. Among the three sorbents tested, lime appears to have the best overall performance when cyclone capture is also considered. 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.

NOTATION

C_b	metal concentration in bed sorbent, ppm
C_c	metal concentration in coal, ppm
C_f	metal concentration in cyclone sorbent, ppm
C_o	metal concentration in original sorbent, ppm
d_p	particle diameter, mm
T	combustion temperature, °C

U	air superficial velocity, cm/s
U_{mf}	minimum fluidization velocity, cm/s
W_b	weight of collected bed sorbent, g
W_f	weight of collected fly ash sorbent, g
W_c	weight of coal, g
ϕ_b	specific capture capacity of bed sorbent, mg/Kg
ϕ_f	specific capture capacity of fly ash sorbent, mg/Kg
ψ_b	percent capture by bed sorbent, %
ψ_f	percent capture by fly ash sorbent, %

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Table 1. Sulfur, Chlorine and Target Metals in Coal Samples
 (% for S and Cl; ppm for metals)

Coal*	S	Cl	Cd	Cr	Pb	As	Se
IBC-101	4.4	0.1	1.1	31	8	2	1.5
IBC-102	3.3	0.0	0.8	7	149	32	1.3
IBC-106	3.8	0.0	0.2	10.4	6	4.1	2.0
IBC-109	1.2	0.4	<0.3	13	18	6.9	1.5
IBC-110	4.6	0.0	<0.4	11	10	4.7	2.5
IBC-111	2.0	0.0	<0.4	14	18	6.1	1.5
IBC-112	2.8	0.2	<0.3	14	27	3.3	1.6

* IBC = Illinois Basin Coal

Table 2. 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 ₂ O ₃ (%)	78.0	12.1	0.3
CaO (%)	0.0	3.1	97.2
As (ppm)	1.2	0.0	0.0
Cd (ppm)	2.0	3.0	3.6
Cr (ppm)	146	4.0	7.8
Pb (ppm)	43.2	60.4	72.4
Se (ppm)	1.0	0.8	0.9
d _p (mm)	0.5	0.5	0.5
U _{mf} (cm/s)	3.8	3.5	3.8

Table 3. Experimental Parameters and Operating Conditions

Parameter	Range
Coal Size	2.0 - 2.8 mm
Coal Amount	60 g
Coal Feed Rate	0.15-0.3 g/min
Sorbent Size	0.4 - 0.6 mm
Sorbent Amount	22.5 - 30 g
Static Sorbent Height	3-9 cm
Air Flow Rate	1.2-5 U_{mf} of Sorbent
Combustor Temperature	900°C
Combustion Duration	4.5 hrs

Table 4. 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	Pb₂SiO₄(s)	<1000°C
			PbO(g)	>1000°C
		With S	PbSO₄(s)	< 950°C
			Pb₂SiO₄(s)	<1000°C
			PbO(g)	>1000°C
Al ₂ O ₃	Pb	Without S	PbO(s)	< 900°C
			PbO(g)	> 900°C
		With S	PbSO₄(s)	< 950°C
			PbO(g)	> 950°C
CaO	Pb	Without S	PbO(s)	< 900°C
			PbO(g)	> 900°C
		With S	CaSO₄(s)	> 500°C
			PbSO₄(s)	< 950°C
			PbO(g)	> 950°C

Table 5. 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	CdSiO₃(s)	< 850°C
			CdO(s)	<1000°C
			Cd(g)	>1000°C
		With S	CdSO₄(s)	< 800°C
			CdO(s)	< 900°C
			CdS(g)	> 900°C
Al ₂ O ₃	Cd	Without S	CdAl₂O₄(s)	< 950°C
			CdO(s)	<1000°C
			Cd(g)	>1000°C
		With S	CdAl₂O₄(s)	< 950°C
			CdS(g)	> 950°C
CaO	Cd	Without S	CdO(s)	<1000°C
			Cd(g)	>1000°C
		With S	CaSO₄(s)	> 500°C
			CdO(s)	< 900°C
			CdS(g)	> 900°C

Table 6. Percentage Lead Capture by Bed Sorbents (ψ_b)

Coal\Sorbent	Bauxite	Zeolite	Lime
IBC-101	64	74	75
IBC-102	80	68	16
IBC-106	77	57	67
IBC-109	62	47	49
IBC-110	73	51	36
IBC-111	49	62	32
IBC-112	74	44	22

Average	69	58	42

Table 7. Percentage Cadmium Capture by Bed Sorbents (ψ_b)

Coal\Sorbent	Bauxite	Zeolite	Lime
IBC-101	54	52	56
IBC-102	50	58	58
IBC-106	76	72	70
IBC-109	71	88	50
IBC-110	47	58	61
IBC-111	56	30	73
IBC-112	55	49	50
Average	58	58	60

Table 8. Percentage Chromium Capture by Sorbents (ψ_b)

Coal\Sorbent	Bauxite	Zeolite	Lime
IBC-101	0	4	2
IBC-102	0	26	30
IBC-106	0	22	9
IBC-109	0	37	26
IBC-110	0	66	44
IBC-111	0	10	47
IBC-112	0	54	51
Average	0	31	30

Table 9. Percentage Arsenic Capture by Sorbents (ψ_b)

Coal\Sorbent	Bauxite	Zeolite	Lime
IBC-101	57	24	27
IBC-102	23	7	31
IBC-106	28	14	23
IBC-109	34	13	12
IBC-110	32	19	28
IBC-111	28	18	23
IBC-112	43	22	24
Average	34	17	24

Table 10. Percentage Selenium Capture by Sorbents (ψ_b)

Coal\Sorbent	Bauxite	Zeolite	Lime
IBC-101	29	28	24
IBC-102	18	9	16
IBC-106	9	8	10
IBC-109	43	11	12
IBC-110	12	3	12
IBC-111	18	24	22
IBC-112	8	10	12
Average	20	13	15

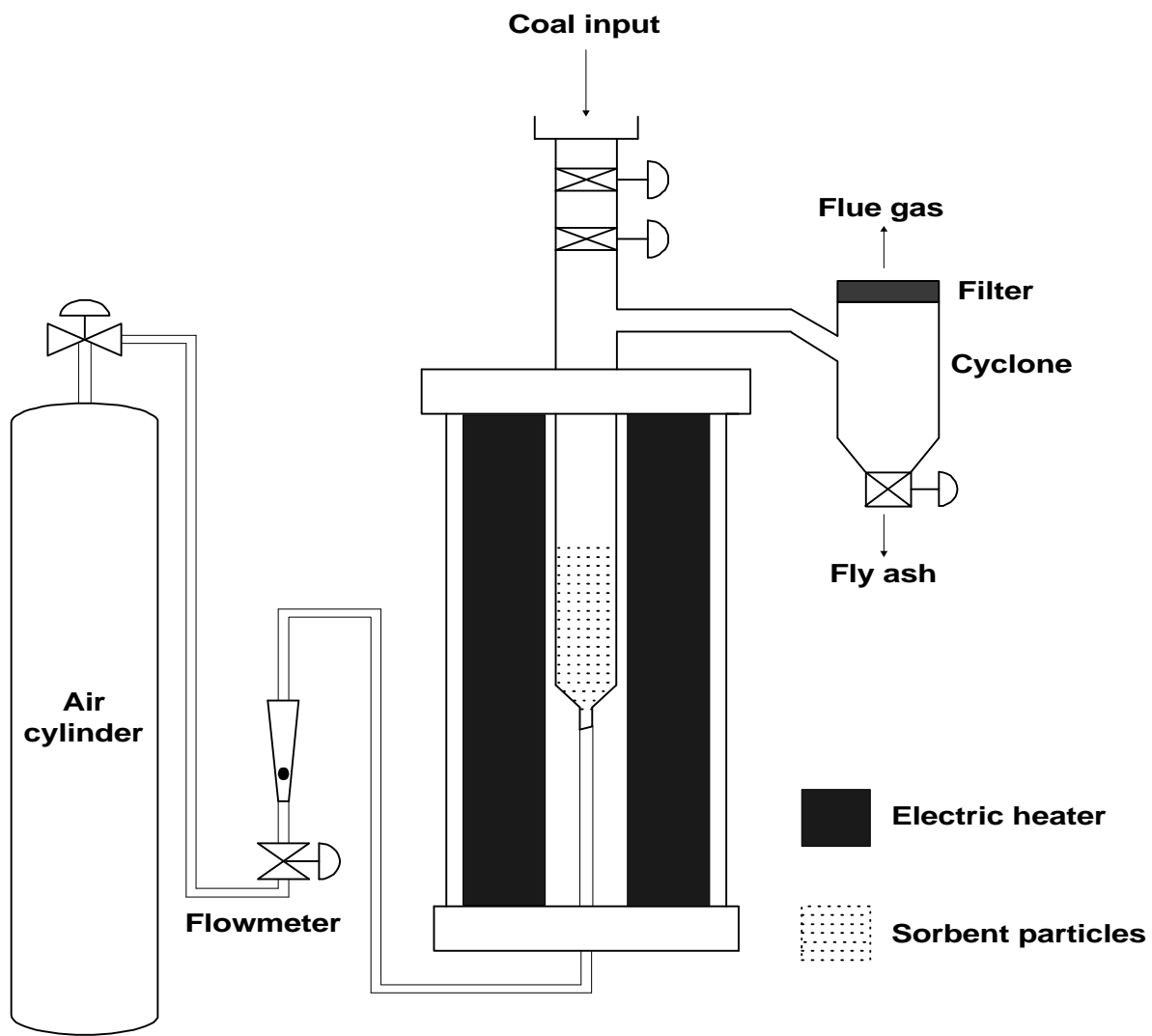


Fig. 1. Fluidized bed coal combustion system.

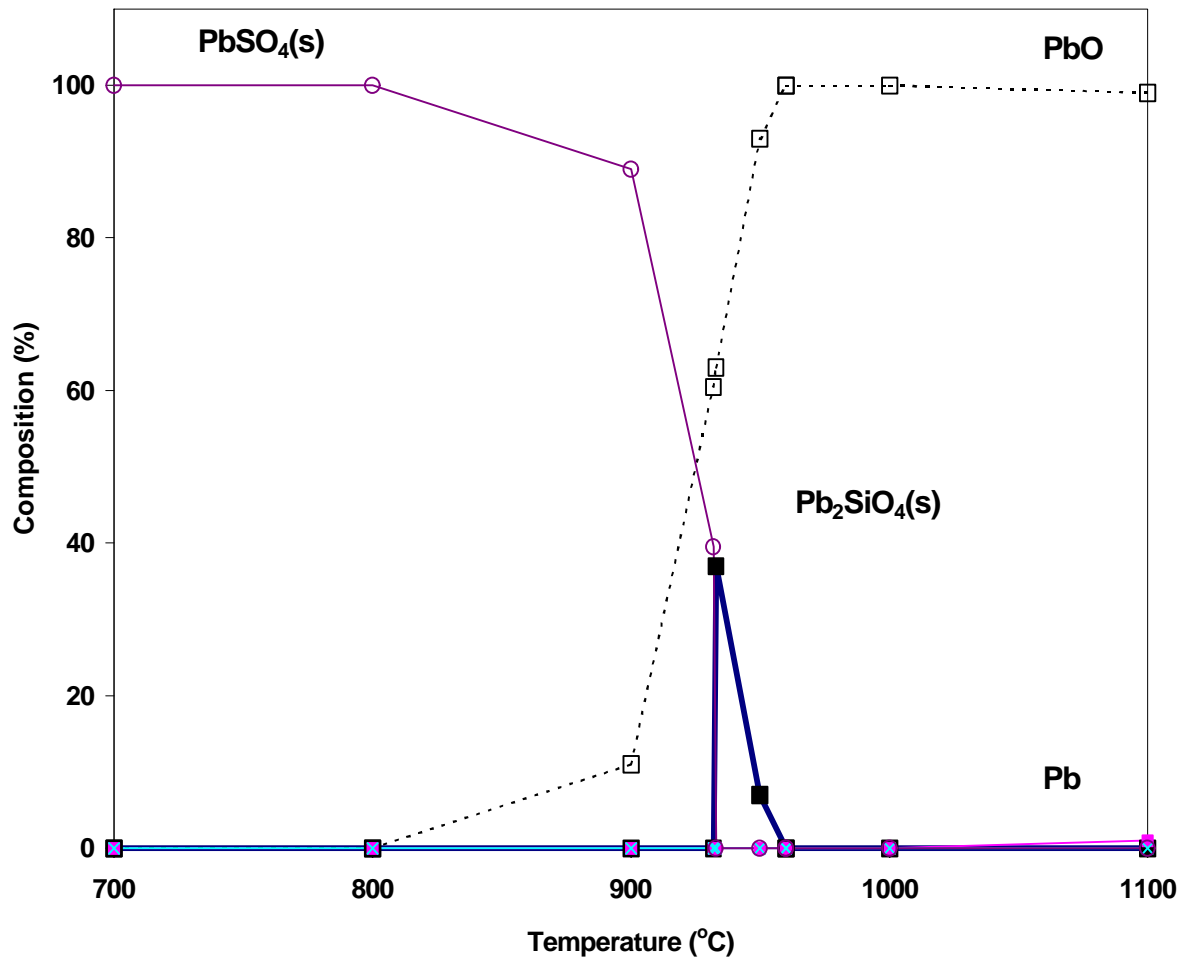


Fig. 2. Simulated lead speciation (System: Pb-S-SiO₂).

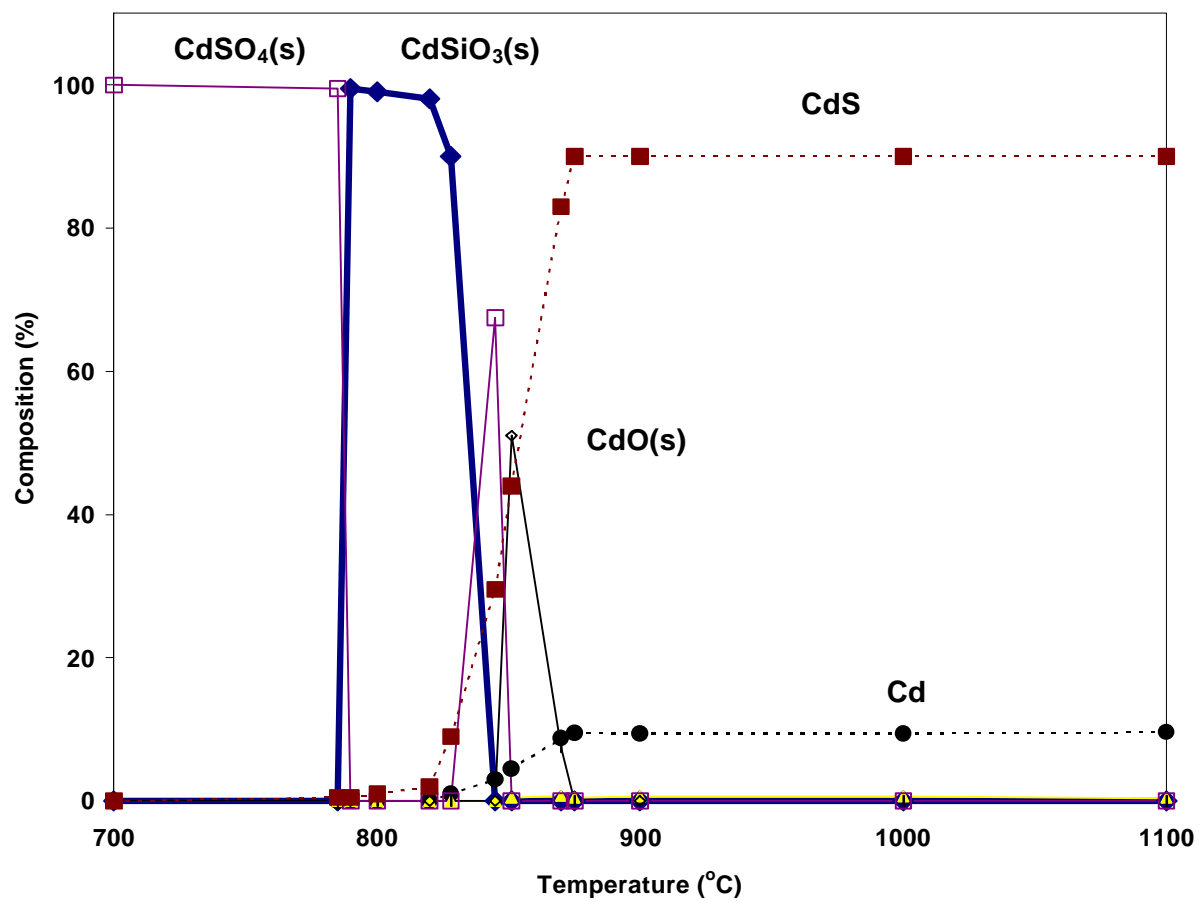


Fig. 3. Simulated cadmium speciation (System: Cd-S-SiO₂).

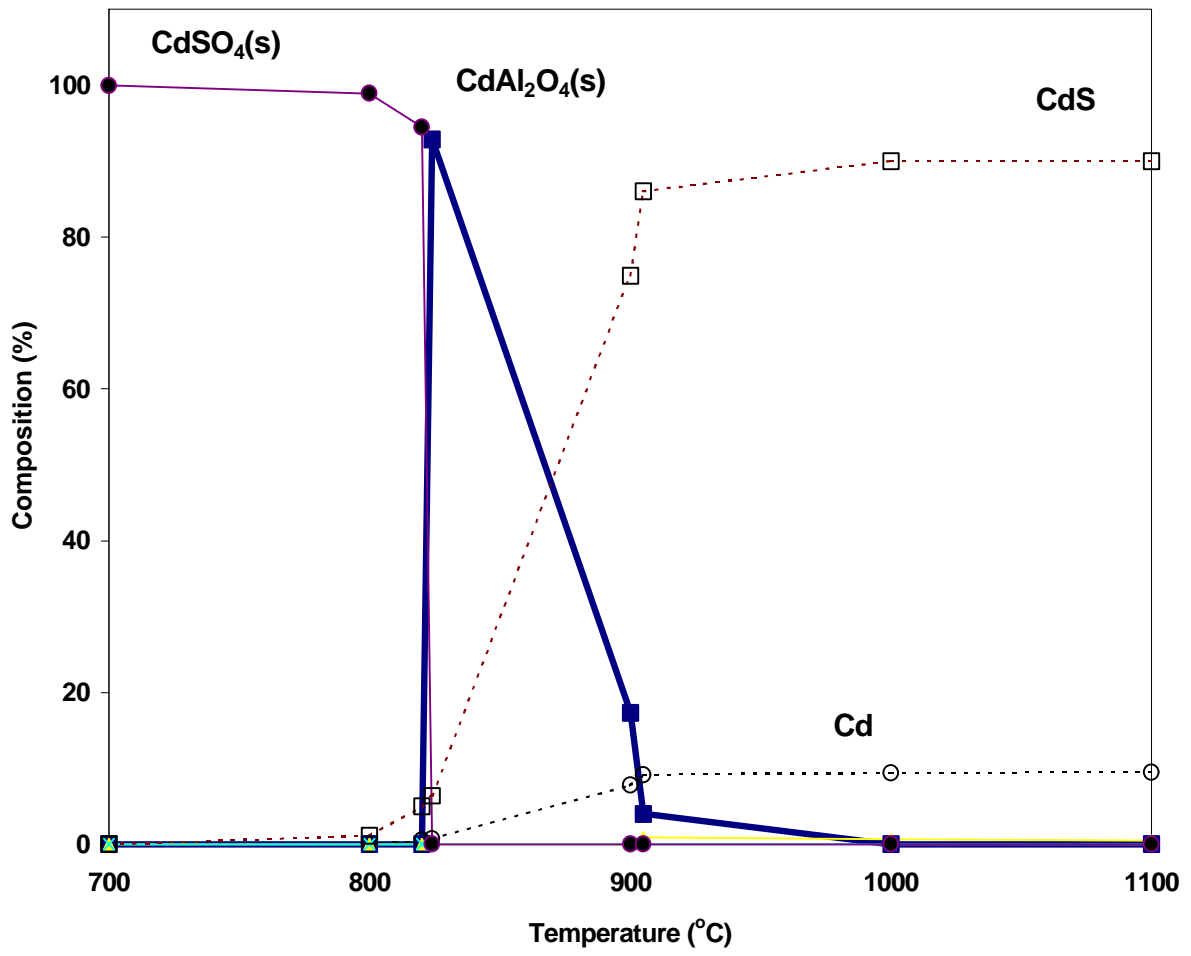


Fig. 4. Simulated cadmium speciation (System: Cd-S-Al₂O₃).

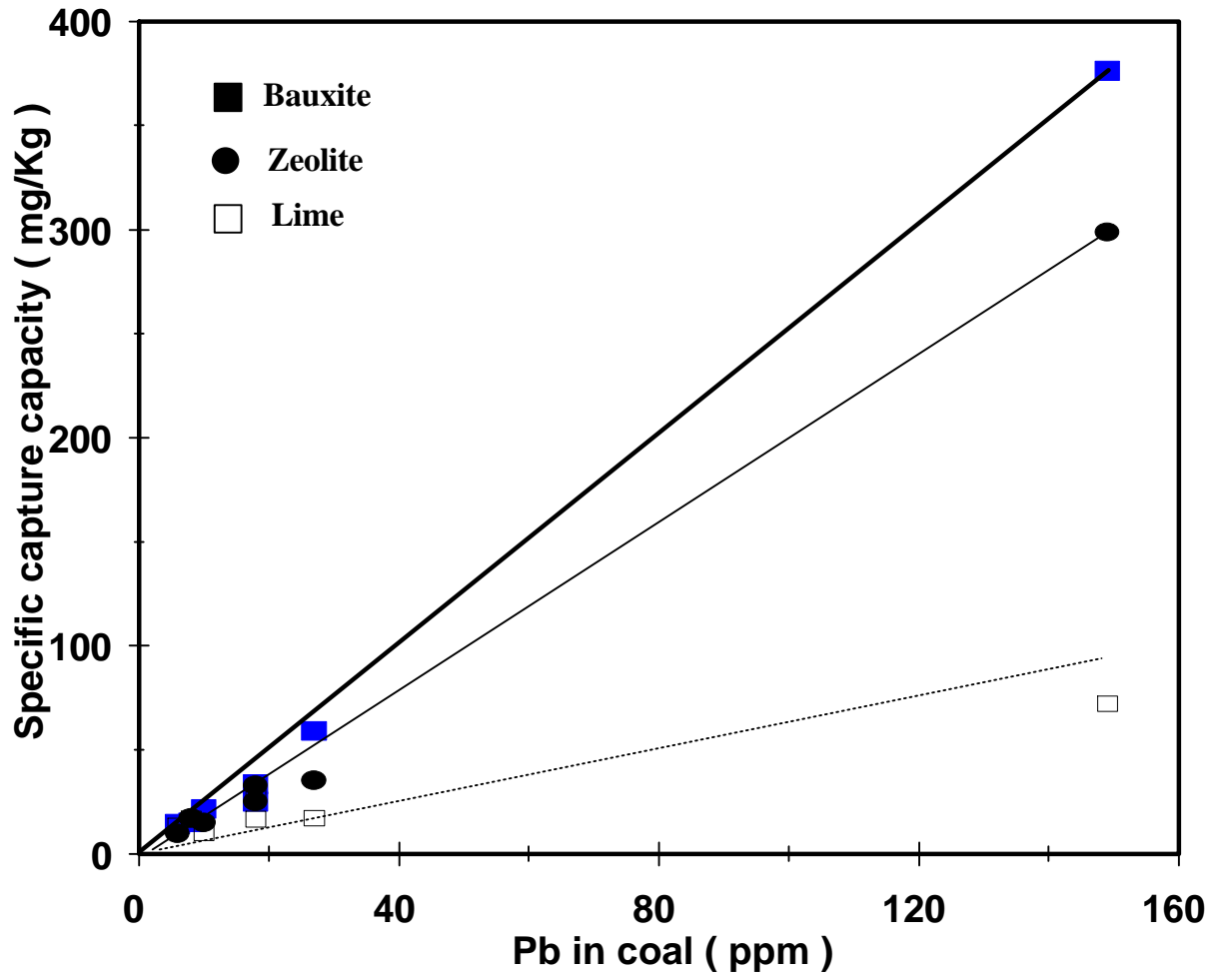


Fig. 5. Specific capture capacity of Pb by bed sorbents (ϕ_b).

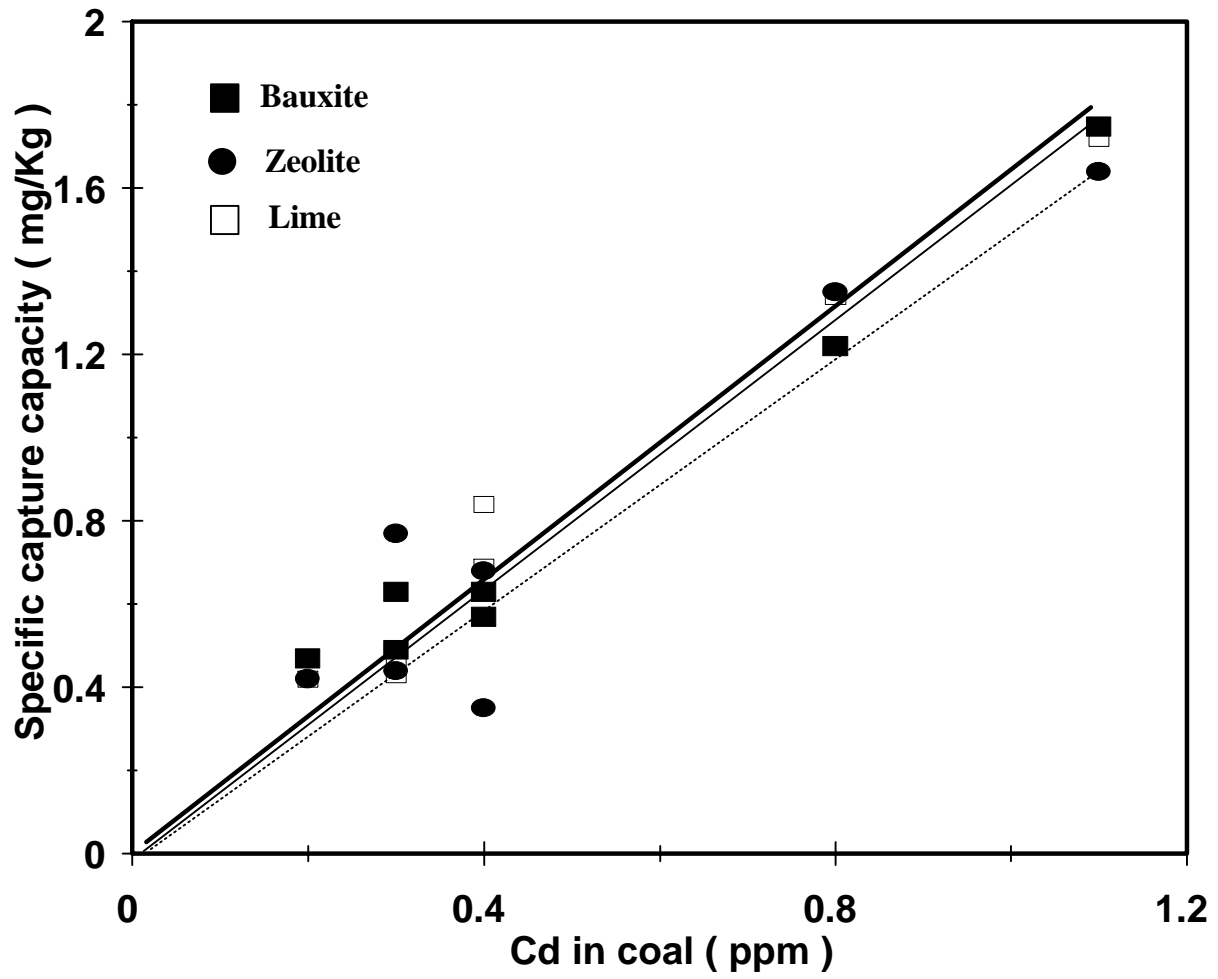


Fig. 6. Specific capture capacity of Cd by bed sorbents (ϕ_b).

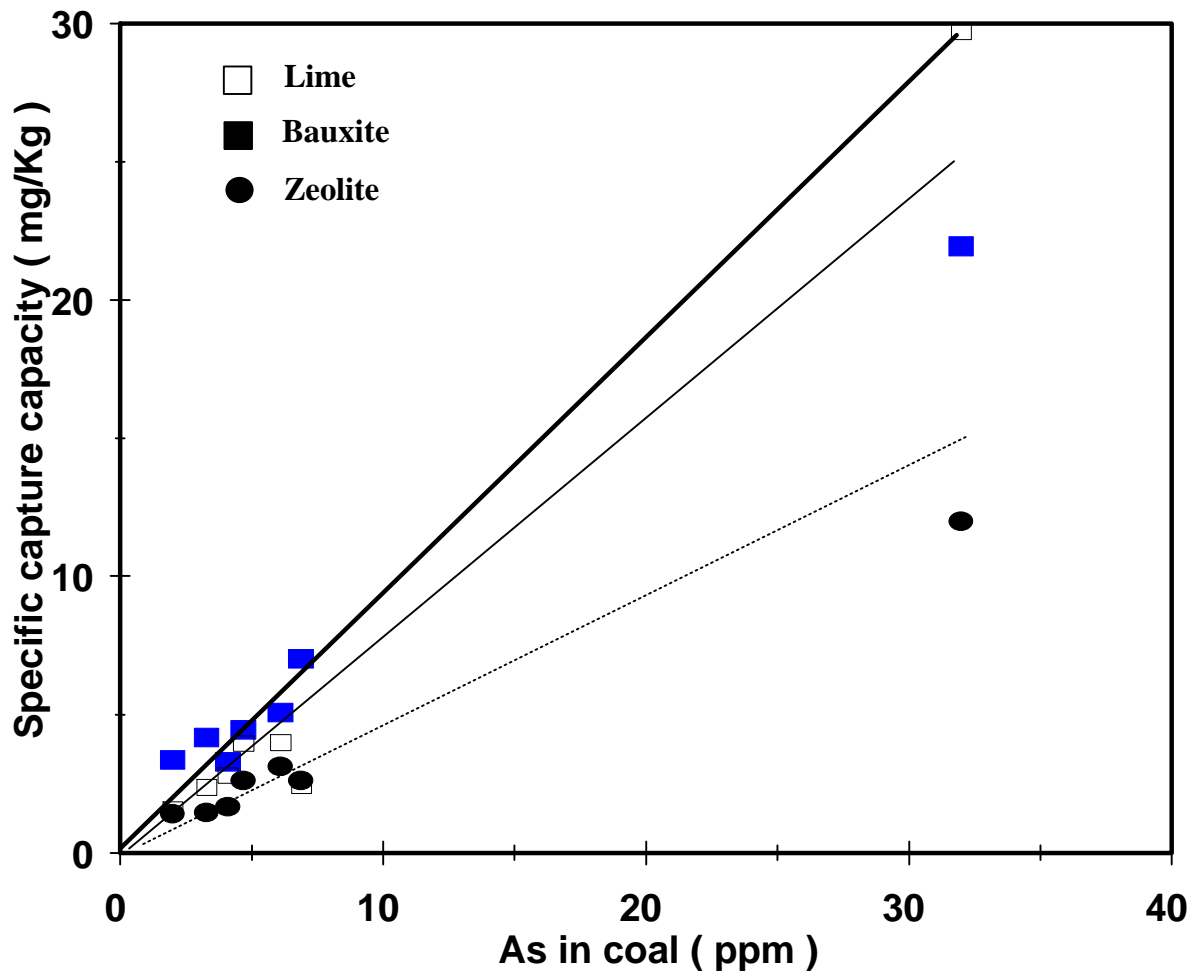


Fig. 7. Specific capture capacity of As by bed sorbents (ϕ_b).

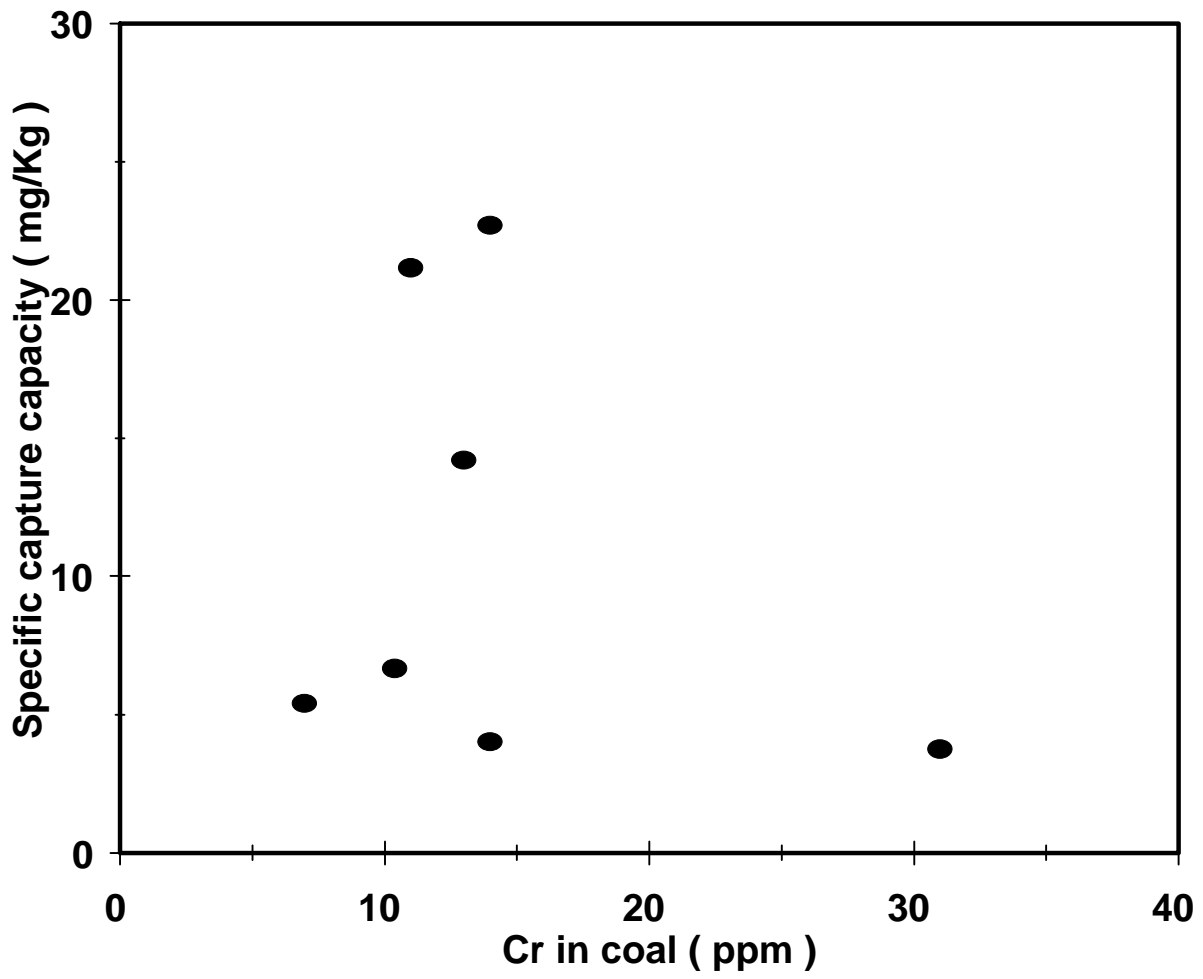


Fig. 8. Specific capture capacity of Cr by Zeolite (ϕ_b).

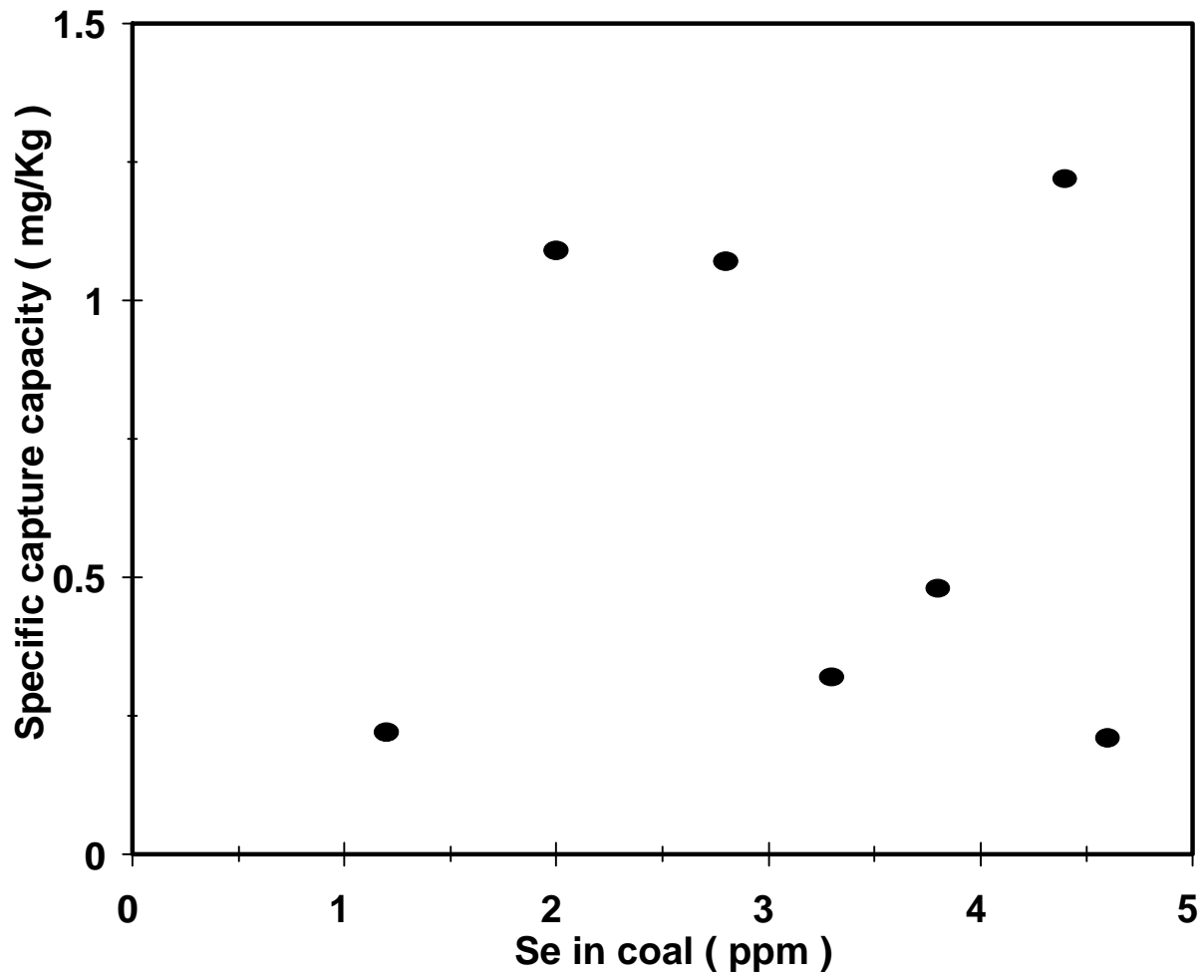


Fig. 9. Specific capture capacity of Se by Zeolite (ϕ_b).

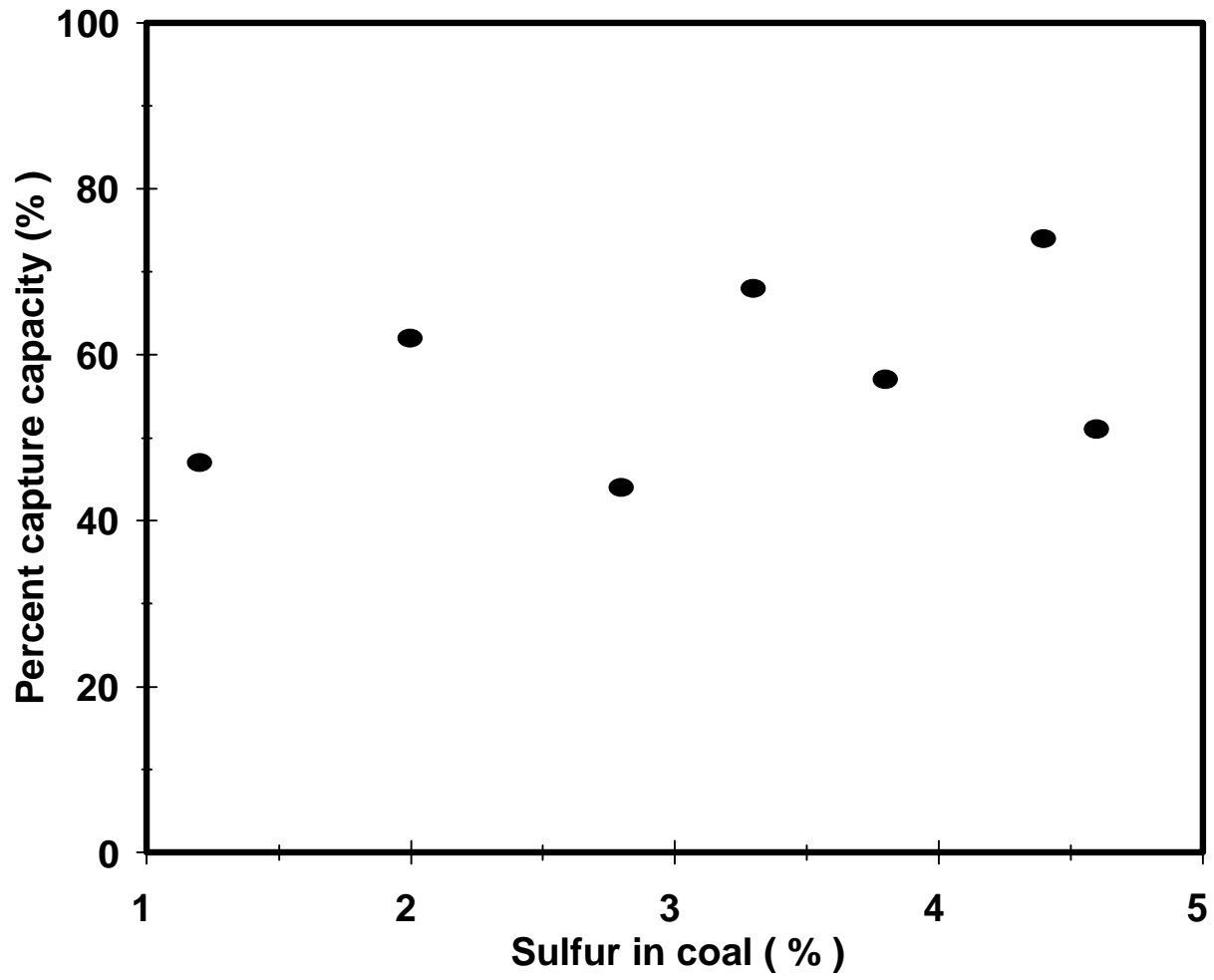


Fig. 10. Percent Capture of Pb by Zeolite (ψ_b).

CHAPTER 3. SIMULTANEOUS SULFUR AND METAL CAPTURE

ABSTRACT

This chapter reports a more in-depth investigation on the characteristics of simultaneous sulfur and metal capture by calcined limestone during fluidized bed coal combustion. Experimental results on seven coal samples have indicated that the capture process can be effective. Good fluidization, however, is essential in achieving the optimum capture efficiency which was observed to range from 93% to 15% in the order of cadmium, sulfur, lead, chromium, arsenic, and selenium. Also reported are capture mechanism, effect of metal concentration in coal, and effect of bed temperature.

INTRODUCTION

Toxic trace metallic elements such as As, Ad, Cr, Pb, Hg, and Se are usually contained in coal in various forms and trace amounts. These metals will not be destroyed during coal combustion. Instead, a fraction of these metals may be emitted as toxic metal fumes (1). The US EPA has reported that metals can account for almost all of the identified cancer risks from waste incineration systems (2).

Concern over trace metal emissions from coal-fired combustion sources is growing, especially since the passage of the 1990 Clean Air Act Amendments (CAAA) where eleven metallic elements, i.e., Sb, As, Be, Cd, Cr, Co, Pb, Mn, Hg, Ni, and Se are listed as potential hazardous air pollutants. Current practice of controlling trace metal emissions during coal combustion employs conventional air pollution control devices, 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). The objective of this study was to explore the potential of employing calcined limestone for simultaneous sulfur and metal emission control during fluidized bed coal combustion.

SCIENTIFIC DISCUSSION

Metals can be chemically absorbed by suitable sorbents at high temperatures. The following metal-sorbent reactions have been reported (see, e.g., 3, 4):



Metal capture by lime (CaO) or calcined limestone has also been reported to be effective during waste incineration (4, 5). The capture, however, has been attributed to "melt capture" instead of chemisorption (5). The potential use of lime for capturing trace metals during fluidized bed coal

combustion where the concentration of metals are extremely small, however, has never been systematically investigated. For lime to capture SO₂, the following reaction has been well-recognized:



EXPERIMENTAL

Experiments of simultaneous metal and sulfur capture by calcined limestone were carried out semi-batchwise in a 25.4 mm (1") OD quartz fluidized bed coal combustor enclosed in an electric furnace (Fig. 1). Seven coal samples of size 2.0 to 2.8 mm from the Illinois Basin Coal Sample Bank (IBCSB) were tested in the experiments along with calcined limestone of 0.5 mm in size. The metals examined were Pb, Cd, Cr, As, and Se. The concentrations of sulfur, chlorine, and the target metals in coal samples and calcined limestone (lime) are summarized in Table 1. The experimental parameters and operating conditions are summarized in Table 2.

After each experiment, the lime and coal ash in the collected combustion residue either from the bed or cyclone were separated through selective digestion of lime in dilute acetic acid solutions. Metal concentration in coal, original lime, combusted lime, and burned coal ash was measured by an atomic absorption spectrophotometer (AAS). An HF modified EPA Method 3050 was used to digest metals from particles for subsequent concentration measurement by the AAS. The collected lime and coal ash particles were also analyzed through scanning electron microscopy (SEM) coupled with x-ray diffraction (XRD).

RESULTS AND DISCUSSION

Equilibrium Simulation Results

Equilibrium calculations were performed based on the minimization of system's free energy. Typical sets of equilibrium simulation results indicating potential metal-sulfur-lime or metal-sulfur-silica reactions are displayed in Figs. 2 through 4 for Pb-S-CaO and Pb-S-SiO₂ 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%.

For the Pb-S-CaO system, the simulation results shown in Figs. 2 and 3 have identified two essential reactions, i.e., the formation of CaSO₄(s) between 730°C and 900°C and the formation of PbSO₄(s) below 730°C. No chemical reactions between lead and CaO, however, are identified. For comparison purpose, the results shown in Figure 4 for the Pb-S-SiO₂ system indicate that, without the existence of CaO, lead will predominately be in the form of PbSO₄(s) up to about 950°C. It then will either decompose to form PbO(g) or react with SiO₂(s) to form Pb₂SiO₄(s), which strongly implies the metal capture reaction of PbO(g) by SiO₂(s).

Experimental Results

General Observations

As described previously, metal and sulfur capture experiments were carried out in a 25.4 mm quartz fluidized-bed coal combustor at various lime static bed heights and air flow rates. The transparent quartz bed was used because it allowed for visual observation of the combustion phenomena. Although the size of the bed may appear to be small, the various experimental conditions were able to create different fluidization operations and generate distinctive experimental results. The use of this small size bed, nevertheless, allowed for more experiments from the limited supply of high quality coal samples.

The static bed height was found to affect noticeably the metal and sulfur capture efficiency. In a relatively deep bed with static bed heights greater than about 9 cm, the bed tended to operate in a slugging bed regime where the charged coal particles were observed to burn on top of a moving slug without being able to penetrate into the lime bed freely. This less-than-perfect mixing between a burning coal and the bed lime significantly reduced the efficiency of metal and sulfur capture. On the other hand, in a relatively shallow bed with bed heights less than about 3 cm, the capture efficiency was also lowered due to an insufficient contact time between the bed lime and the volatilized metal or sulfur species. The optimum bed height was found to be around 6 cm where good fluidization was easily obtained.

With the static lime bed height at 6 cm, it was found that the capture efficiency is maximized and insensitive to superficial air velocity (U) as long as the fluidization quality is good, roughly in the range of $2.0 < U/U_{mf} < 5.0$. At $U < 2.0 U_{mf}$, the bed tended to operate near a fixed-bed regime while, at $U > 5.0 U_{mf}$, it tended to be in a turbulent bed regime. In both operating regimes, the capture efficiencies were found to drop noticeably from their optimum values.

Optimum Capture Efficiency

The optimum capture efficiencies reported below are based on the experiments with 6 cm static bed height and $3 U_{mf}$ superficial air velocity. For these experiments, the original lime charged in the bed was 26 g and the average amounts of bed residue (lime and coal ash in the bed after combustion) and cyclone residue (lime and coal fly ash in the cyclone after combustion) collected were around 20 g and 7 g, respectively, for 750°C experiments and around 19 g and 8 g for 900°C experiments. For the collected bed residue, less than 10% was coal ash; however, for the collected cyclone residue, approximately 36-50% was coal fly ash. The duration of the combustion was about 4.5 hours and the average amount of lost mass (lime and coal ash escaped from the cyclone and lost to the surroundings) was around 5 g.

The experimentally observed average capture efficiency for the species examined are summarized in Fig. 5. As indicated, the overall capture efficiency as well as the proportion between the capture by bed residue (bed capture) and that by cyclone residue (cyclone capture) varies with species and temperature. The overall capture efficiency is seen to range from 93% to 47% in the order of cadmium, sulfur, lead, chromium, and arsenic. Although not shown, selenium capture by lime was found to be inefficient with capture efficiency mostly less than 15%.

It should be pointed out that most of the reported bed capture came from bed lime capture because the amount of coal ash in the bed residue was not significant. The reported cyclone capture, however, includes that captured by cyclone lime and cyclone coal fly ash. An analysis of the cyclone coal fly ash has revealed that: (1) sulfur concentration was close to zero indicating complete volatilization of sulfur from coal during combustion; (2) chromium concentration was relatively high indicating little chromium volatilization during coal combustion; and (3) concentration of lead, cadmium and arsenic was detectable but various indicating partial volatilization of these metals during coal combustion. An SEM (Scanning Electron Microscopy) analysis on cyclone lime has revealed that lime is capable of capturing small particles with size ranging from sub-micron to a few microns.

Capture Mechanism

The observed results appear to suggest the following three major mechanisms on the retention of metals and sulfur during the experiments, i.e., (1) capture of volatilized metals and sulfur either in gas or particulate phases by lime through chemisorption or physical adsorption; (2) capture of micron or sub-micron size coal fly ash by lime through particle coagulation; and (3) retention of unvolatilized metals in coal ash or coal fly ash. They have indicated that the capture of sulfur is exclusively through the first mechanism, the capture of lead, cadmium and arsenic is also mainly through the first mechanism but with about 10 to 20% of the capture through the second mechanism, and the capture of chromium is mainly through the second and the third mechanisms due to its low volatility.

Effect of Metal Concentration in Coal

It was observed that, except for chromium and selenium, the specific capture of a metal by the bed or cyclone residue (amount of capture per unit mass of residue) is roughly proportional to the concentration of that metal in coal among different coal samples, i.e., the capture efficiency is approximately constant among different coal samples. A typical set of such results are shown in Fig. 6 where the average specific capture is seen to be approximately a straight line passing through the origin with the slope representing the capture efficiency.

Effect of Bed Temperature

As indicated in Fig. 5, the bed temperature does not affect significantly the metal capture efficiency; however, it affects noticeably the sulfur capture efficiency. The results shown in Fig. 5 indicate that, at 750°C, the overall sulfur capture efficiency is high and the majority of the capture is by the bed lime. However, at 900°C, the overall sulfur capture efficiency is lower and the capture by the cyclone lime is more significant as compared to those at 750°C. This observation is further detailed by the results shown in Figs. 7 and 8 where it is seen that, at 750°C, the specific capture of sulfur by the bed lime (mole sulfur/mole bed CaO) is higher than that by the cyclone lime; however, at 900°C, the trend is reversed. The observation is believed to be due to the equilibrium effect, i.e., the formation of $\text{CaSO}_4(\text{s})$ is not thermodynamically dominating at a high bed temperature around 900°C as indicated in Fig. 2. A slightly cooled temperature above the bed or in the cyclone, instead, is thermodynamically favored for the sulfur capture reaction.

CONCLUSIONS

The results from this study have indicated that simultaneous sulfur and metal capture by calcined limestone during fluidized bed coal combustion can be effective. Good fluidization, however, is essential in achieving optimum capture efficiency which was observed to range from 93% to 15% in the order of Cd, S, Pb, Cr, As, and Se. All of the sulfur capture and most of the capture of Cd, Pb, and As were observed to come from lime either in the bed or cyclone. For chromium, most of the capture was from the coal fly ash collected in the cyclone. Except for Cr and Se, the overall capture efficiency was observed to be roughly constant among different coal samples. Except for sulfur capture, the two combustor temperatures tested, i.e., 750°C and 900°C, was found to produce similar metal capture efficiencies.

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Table 1. Sulfur, Chlorine and Target Metals in Coal Samples and in Lime (% for S and Cl; ppm for metals)

Coal*/Lime	S	Cl	Cd	Cr	Pb	As	Se
IBC-101	4.4	0.1	1.1	31	8	2	1.5
IBC-102	3.3	0.0	0.8	7	149	32	1.3
IBC-106	3.8	0.0	0.2	10.4	6	4.1	2.0
IBC-109	1.2	0.4	<0.3	13	18	6.9	1.5
IBC-110	4.6	0.0	<0.4	11	10	4.7	2.5
IBC-111	2.0	0.0	<0.4	14	18	6.1	1.5
IBC-112	2.8	0.2	<0.3	14	27	3.3	1.6
Lime	0.0	0.0	3.6	7.8	72	0.0	0.9

* IBC = Illinois Basin Coal

Table 2. Experimental Parameters and Operating Conditions

Parameter	Range
Static Bed Height	3, 6, 9 cm
Coal Amount (each bed height)	30, 60, 90 g
Lime Amount (each bed height)	13, 26, 39 g
Air Superficial Velocity (U)	1.5 - 6 U_{mf}
Combustor Temperature	750°C, 900°C
Lime Bed U_{mf} (750°C, 900°C)	4.9, 4.5 cm/sec
Combustion Duration	4.5 hrs (60 g coal)

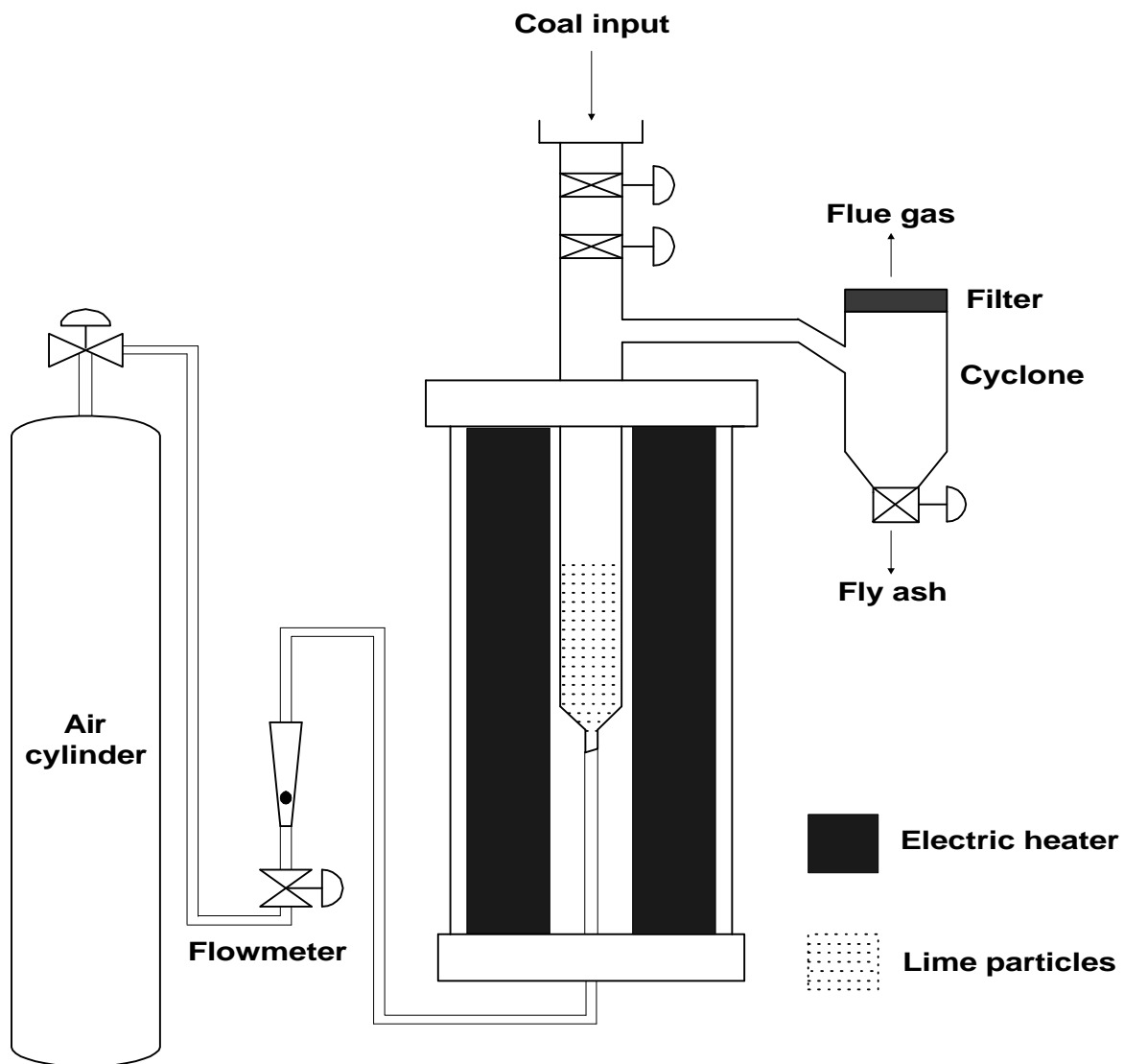


Fig.1. Fluidized bed coal combustion system.

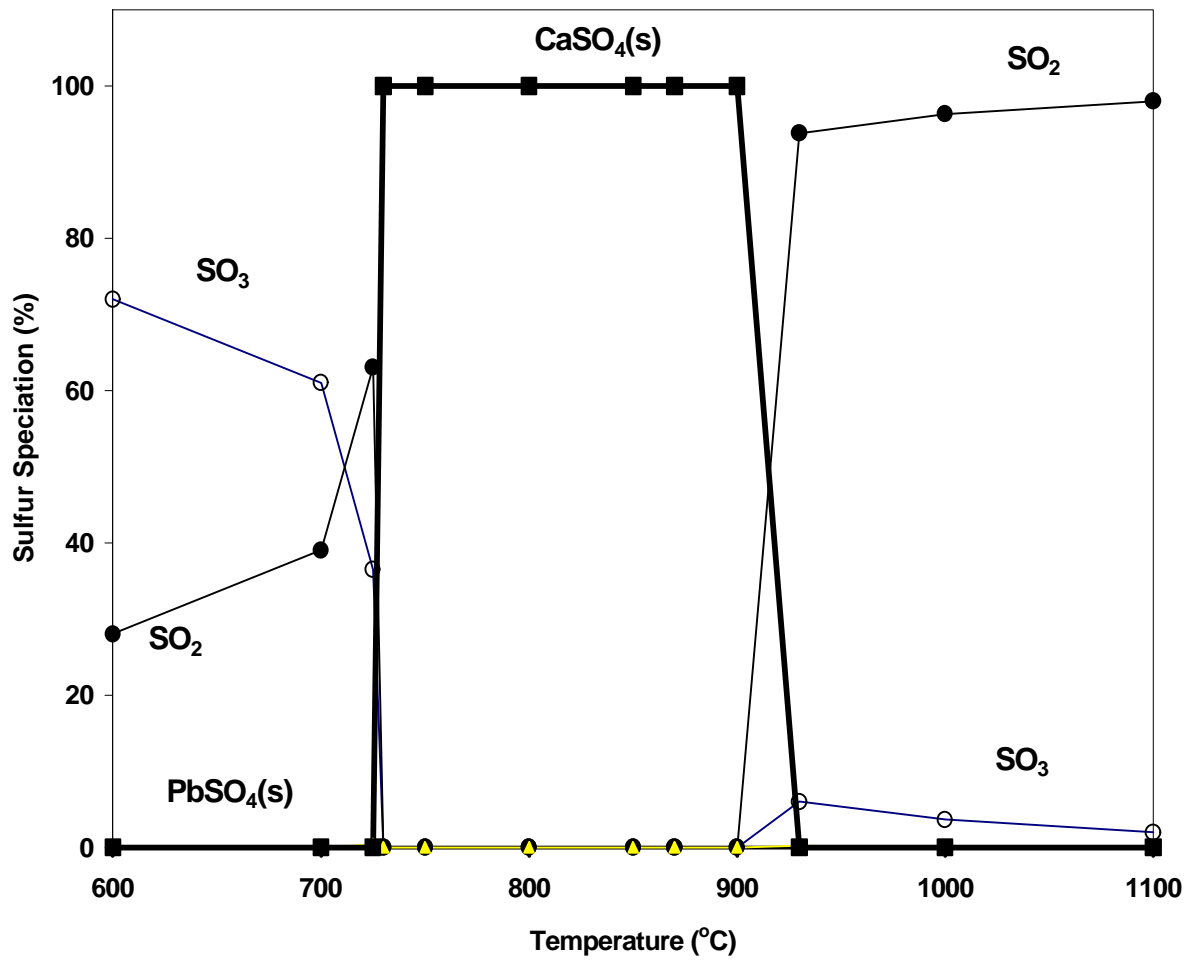


Fig.2. Equilibrium sulfur speciation in a Pb-S-CaO system.

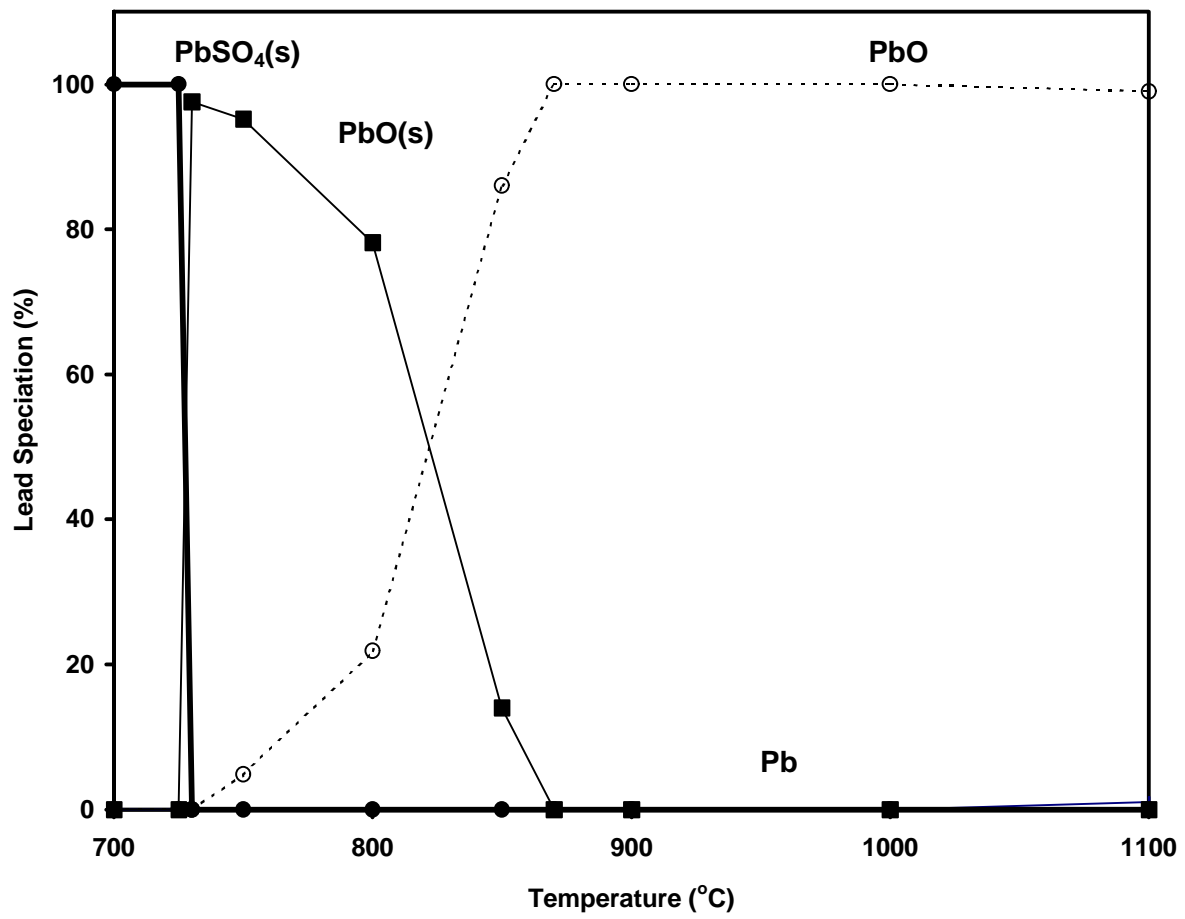


Fig.3. Equilibrium lead speciation in a Pb-S-CaO system.

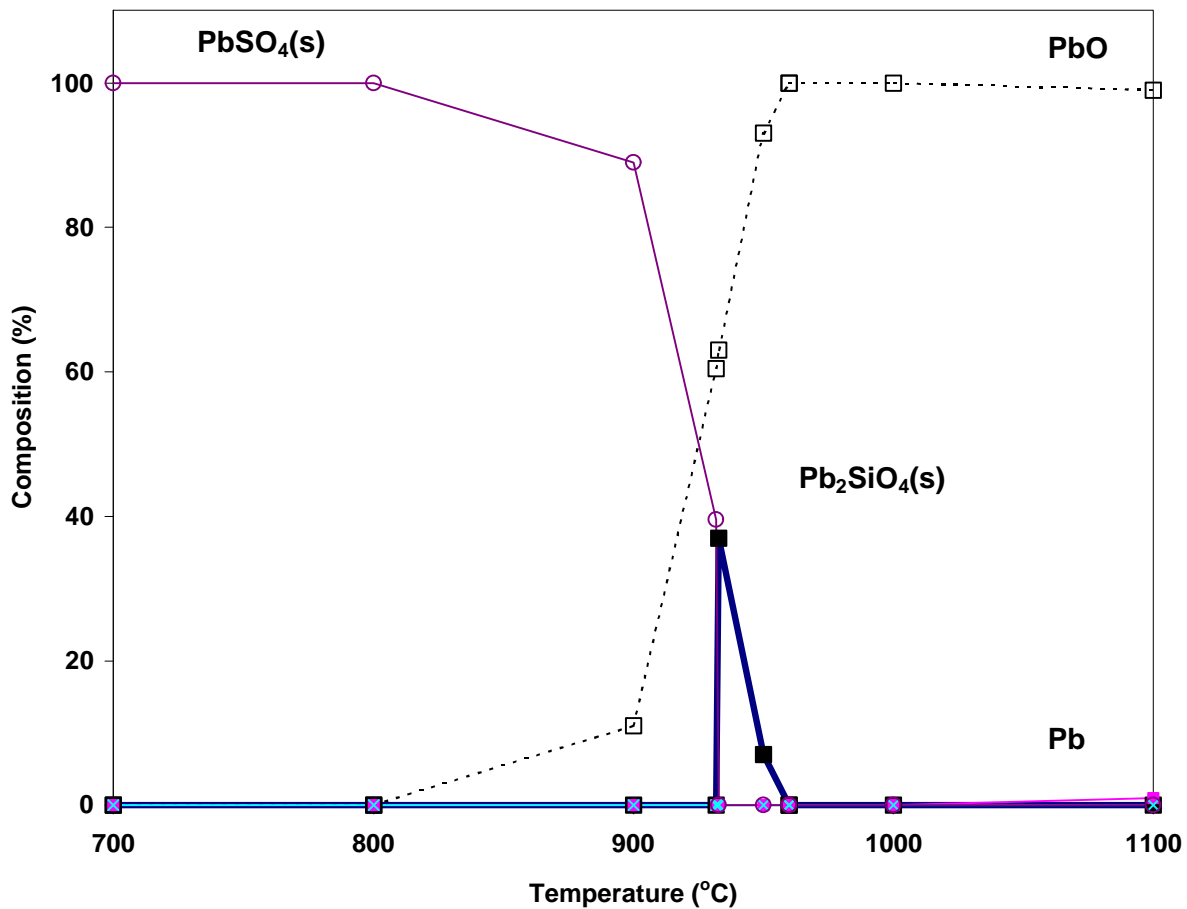


Fig.4. Equilibrium lead speciation in a Pb-S-SiO₂ system.

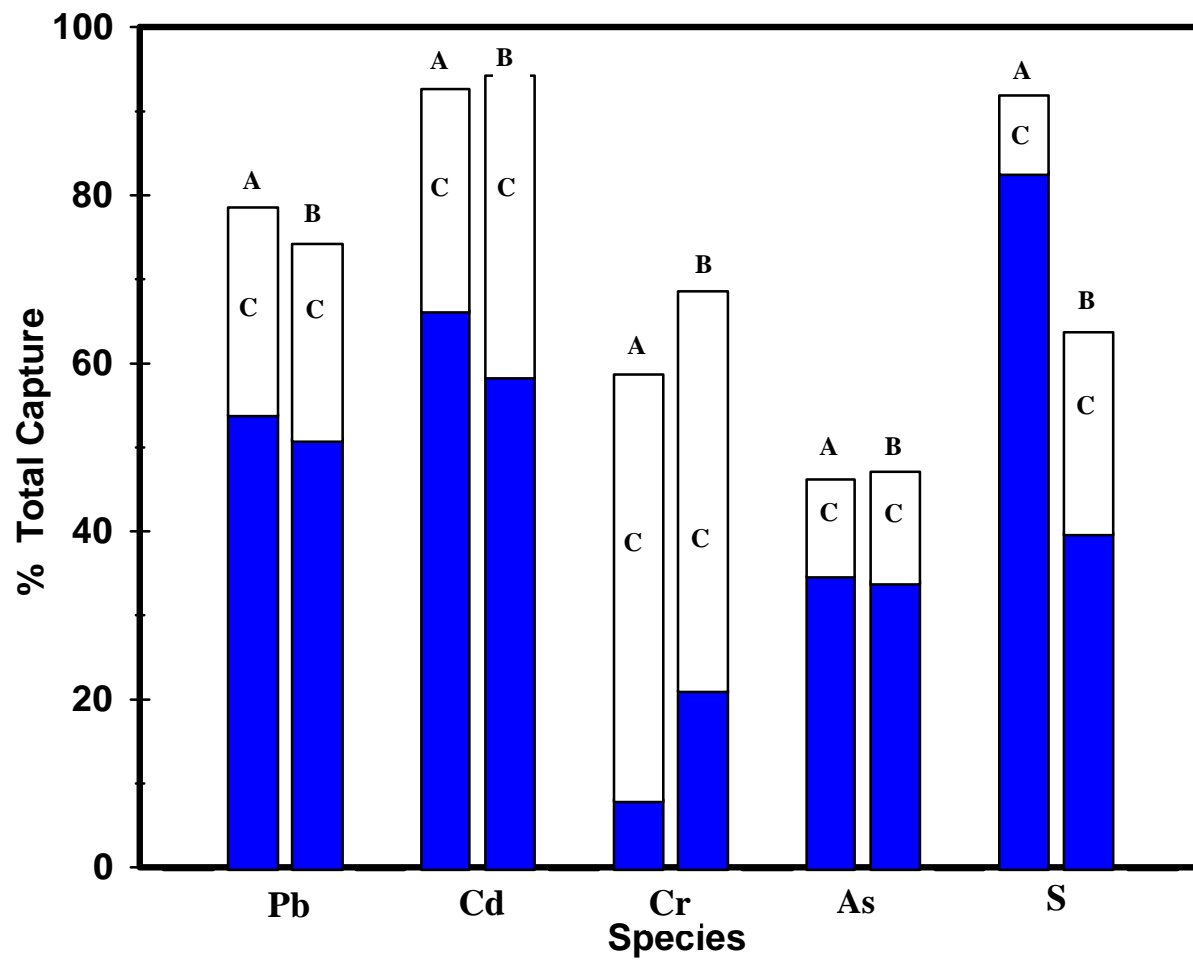


Fig.5. Average capture efficiency by bed and cyclone residue (A:750°C, B:900°C, C:Cyclone Capture, Dark Area: Bed Capture).

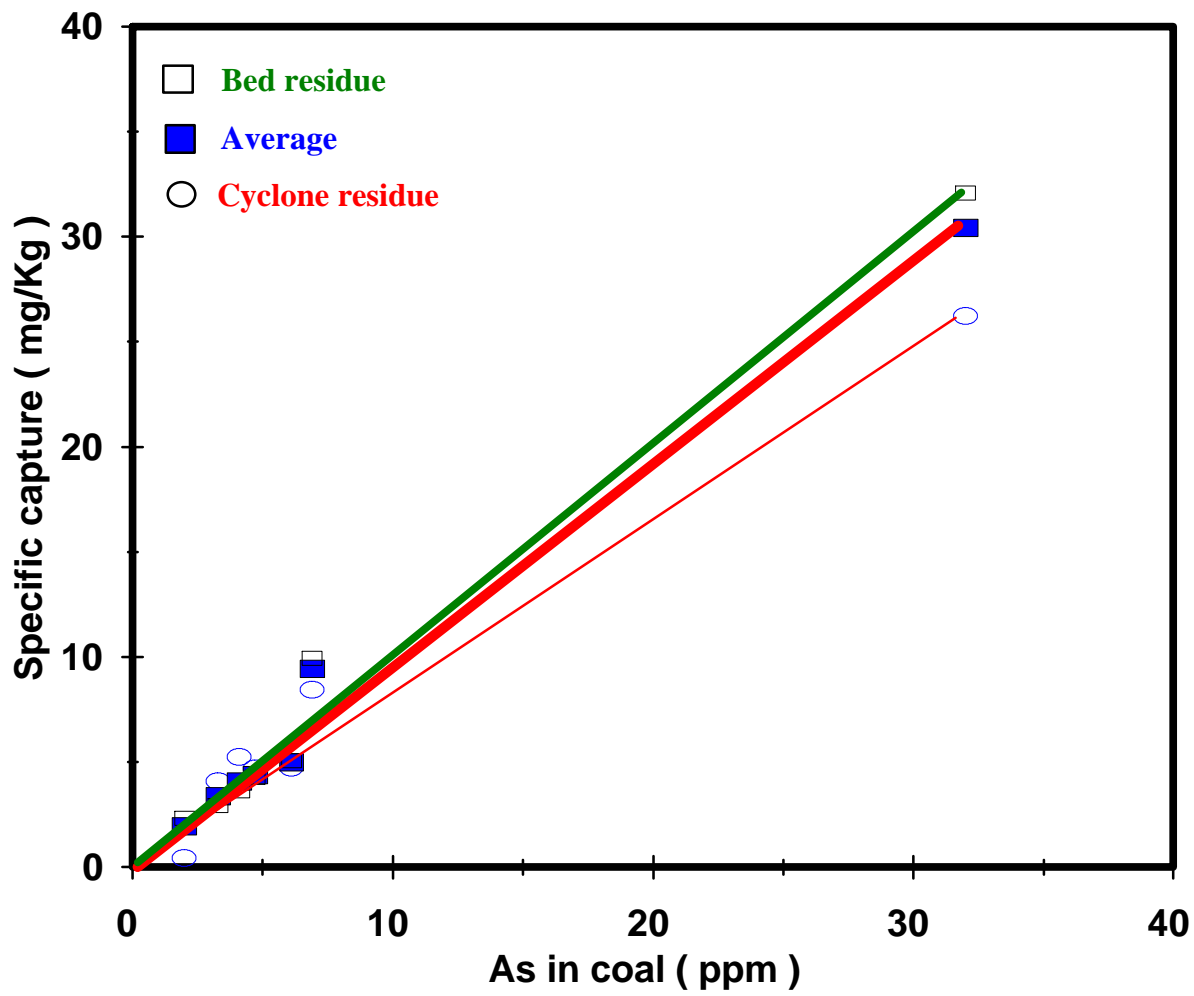


Fig.6. Arsenic capture by bed and cyclone residue at 900°C.

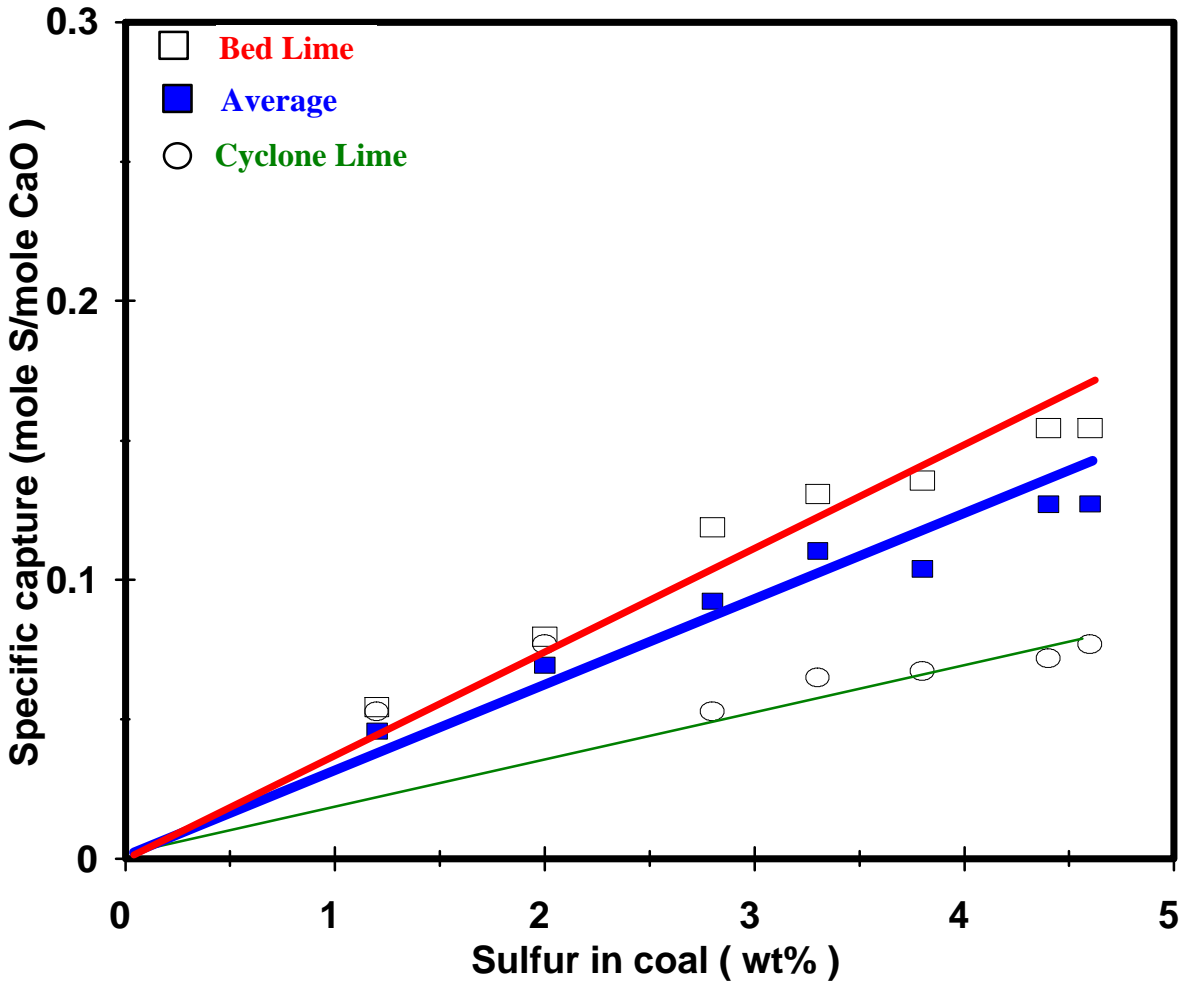


Fig.7. Sulfur capture by bed and cyclone lime at 750°C.

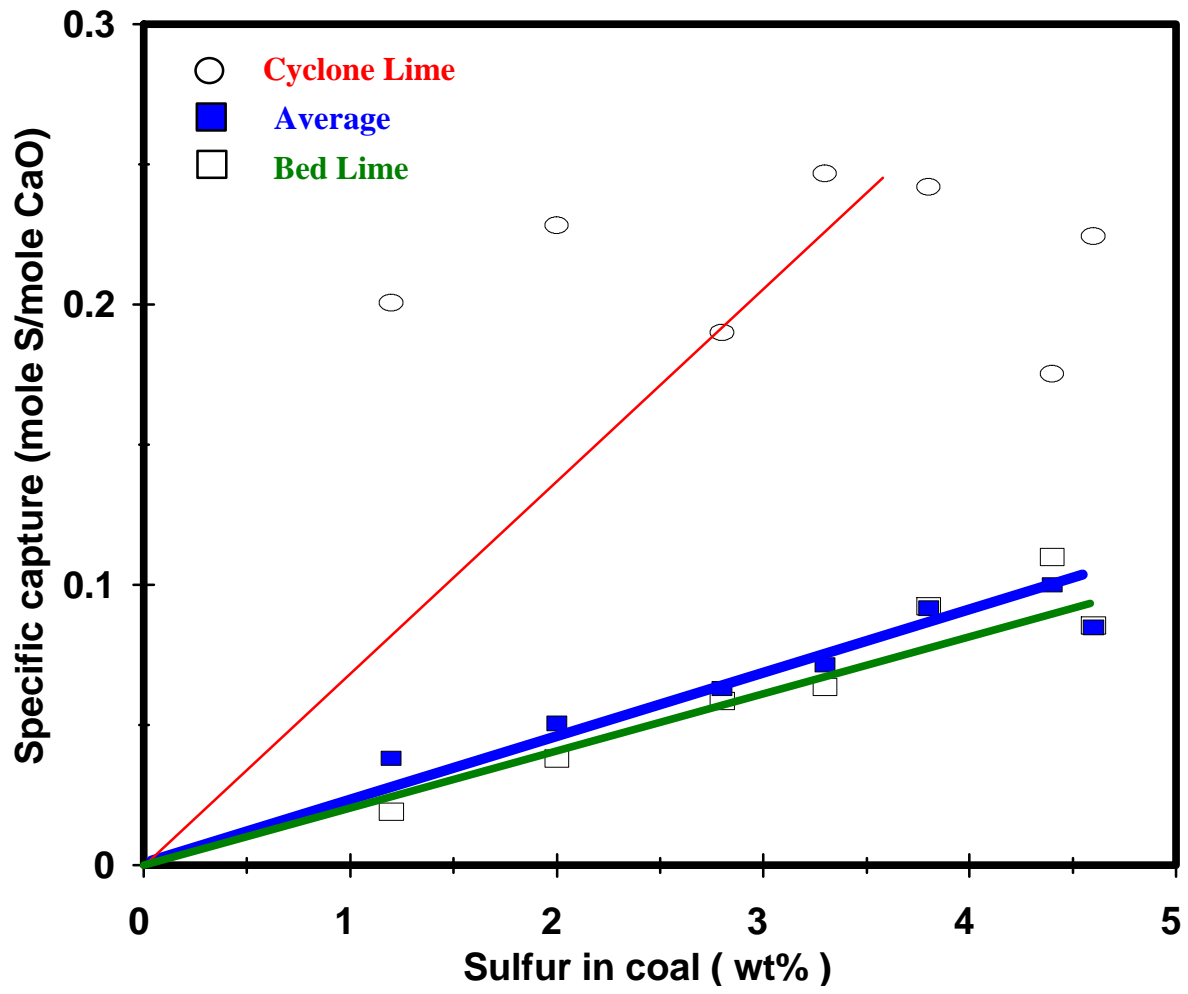


Fig.8. Sulfur capture by bed and cyclone lime at 900°C.

CHAPTER 4. ADSORPTION AND DESORPTION OF MERCURY

ABSTRACT

This chapter reports an investigation on the adsorption/desorption characteristics of mercury on various sorbents at elevated temperatures. Experiments were carried out in a 25.4 mm (1") ID fixed bed absorber. The mercury compounds involved were mercury chloride and elemental mercury, and the sorbents tested included bauxite, zeolite, lime, alumina and activated carbon. Experimental parameters were air flow rate, vaporization temperature, sorbent bed temperature, sorbent bed height, and sulfur impregnation. The Toxicity Characteristics Leaching Procedure (TCLP) tests were also performed to evaluate the leachability of the retained mercury. The results indicated that different sorbents have different mercury sorption capacity. Bauxite and activated carbon were found to be more effective than other tested sorbents for mercury retention. Besides experimental investigations, potential mercury reactions during the experiments were identified through equilibrium simulations and a model based on the mass transfer control mechanism was proposed to simulate the mercury sorption process. The proposed sorption model appeared to describe reasonably well the experimental results.

INTRODUCTION

The concern over mercury emissions from waste combustion/incineration systems and coal-burning utilities has been growing especially since the passage of the Clean Air Act Amendments of 1990 where 189 substances are listed as hazardous air pollutants, including mercury and ten other trace metallic species. Unlike most other trace elements, mercury is highly volatile and exists almost exclusively in the vapor phase of combustion flue gases, either in the form of elemental mercury or mercury salts such as HgCl_2 , HgO , HgS and HgSO_4 . As flue gases cool, it is possible that a fraction of the mercury in the gas phase may nucleate or be adsorbed on residual carbon or other fly ash particles.

The performance standards imposed by federal and state agencies for mercury emissions have been tightening in recent years. Current proposed federal standards on mercury emission for hazardous waste incinerators, cement kilns burning hazardous waste, and lightweight aggregate kilns burning hazardous waste are 40, 72, and 47 $\mu\text{g}/\text{dscm}$ (corrected to 7 % oxygen), respectively. Similar standards are expected to be proposed for municipal waste incinerators and coal-fire utility combustors. It is generally reported (1) that without additional modifications, conventional flue gas desulfurization systems are capable of removing mercury to some extent. However, to achieve high removal efficiencies to meet the expected emission standards, modifications such as packed bed absorption by effective absorbents or dry sorbent injection with activated-carbon-impregnated lime are required.

Activated carbons with or without chemical impregnation have been reported to be relatively effective for the sorption of mercury chloride and elemental mercury (2,3,4). It is generally observed that mercury chloride is more easily adsorbed by non-chemically-impregnated activated carbons than elemental mercury (5). However, chemically-impregnated activated carbons have been found to dramatically enhance elemental mercury sorption (6). Sulfur, iodine, and chlorine are commonly used as the chemical agents for chemical impregnation (3). Other chemical

agents evaluated include hydrogen chloride and the chlorides of aluminum, zinc, iron and copper (7).

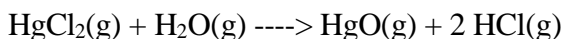
The mechanisms of mercury sorption by various sorbents have also been investigated and both chemisorption and physisorption have been reported (4,7,8). It is generally reported that the rate of mercury sorption by sorbents vary with temperature, gas flow rate, mercury form, sorbent type, sorbent amount, and sorbent properties such as particle size, surface area, pore size distribution, and chemical impregnation procedures (9). Despite all the previous investigations, the mercury sorption process is still far from being adequately understood. In addition, the desorption of mercury from the host absorbents has not been systematically investigated especially at elevated temperatures. The information is essential for sorbent selection and regeneration.

In this study, the adsorption and desorption characteristics of mercury on and from various sorbents at elevated temperatures were experimentally investigated in a 25.4 mm (1") ID fixed bed absorber. The mercury compounds involved were mercury chloride and elemental mercury, and the sorbents tested included bauxite, zeolite, lime and activated carbon. In an experiment, a known amount of mercury was vaporized into a hot air stream which flowed upwards through a bed of a specific sorbent with a controlled temperature profile. The amount of mercury retained by the sorbent was determined by analyzing the concentration of mercury in the sorbent at the conclusion of the experiment. Experimental parameters were air flow rate, vaporization temperature, sorbent bed temperature, sorbent bed height, and sulfur impregnation. The Toxicity Characteristics Leaching Procedure (TCLP) tests were also performed to evaluate the leachability of the retained mercury. In addition to the experimental investigations, equilibrium and kinetic models were derived to describe the sorption process.

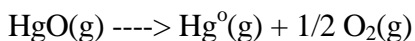
THEORETICAL

Mercury Speciation

At low temperatures, the commonly encountered stable forms of mercury are $\text{HgSO}_4(\text{s})$, $\text{HgCl}_2(\text{s})$, $\text{HgS}(\text{s})$, $\text{HgO}(\text{s})$, and $\text{Hg}^0(\text{l})$. As the temperature increases, these mercury species may vaporize, decompose, or react with chlorine to form $\text{HgO}(\text{g})$, $\text{Hg}^0(\text{g})$ and $\text{HgCl}_2(\text{g})$. Depending on chlorine concentration, the $\text{HgCl}_2(\text{g})$ may be the most dominate form of mercury at temperatures up to about 450°C . With further increasing the temperature, $\text{HgCl}_2(\text{g})$ may react with $\text{H}_2\text{O}(\text{g})$ to form $\text{HgO}(\text{g})$ according to the following equation (10):



At higher temperatures, the formed $\text{HgO}(\text{g})$ will decompose to $\text{Hg}^0(\text{g})$ according to:



Consequently, elemental mercury is the most dominant form of mercury at high temperatures. In this study, equilibrium calculations were systematically performed to determine the thermodynamically preferred mercury speciation under the experimental conditions. The results are discussed in RESULTS AND DISCUSSION.

Sorption Modeling

The effective rate of gas-solids adsorption or desorption is determined by one or more of several rate controlling steps. The performance of a fixed bed absorber containing large numbers of sorbent particles will depend both on local particle behavior and on the size and overall arrangement of the bed. In general, the rate controlling steps may include:

1. Mixing, or lack of mixing, in the bulk gas stream;
2. Mass transfer from the gas phase to the external surfaces of the sorbent particles;
3. Pore diffusion in the gas phase within the sorbent particles;
4. Reaction at the gas-solids phase boundary; and
5. Diffusion in the solids state (or particle-phase diffusion).

Systems with low total gas-phase concentration are more likely to be controlled by gas-phase effects (i.e., steps 1, 2, and 3).

External Mass Transfer Control

Under the mass transfer control mechanism described in Step 2 above, the transport rate for solute between the bulk of the fluid phase and the outer surfaces of the sorbent granules is given by (11): (All symbols in the following equations are defined at the end of the Chapter.)

$$dn/dt = K_g S_{ex} (C - C^i) \quad (1)$$

For a segment of a fixed-bed absorption/desorption system shown in Figure 1, the following material balance principle must be satisfied:

$$dn/dt = F_i C_i - F_e C_e \quad (2)$$

Equations 1 and 2 can be combined to yield:

$$K_g S_{ex} (C - C^i) = F_i C_i - F_e C_e \quad (3)$$

With the assumption that the segment of the bed acts like a complete stirred tank reactor (i.e., $C = C_e$), Equation 3 may be rearranged to yield

$$C = (K_g S_{ex} C^i + F_i C_i) / (K_g S_{ex} + F_e) \quad (4)$$

Equation 4 describes the concentration of solute in a segment of the bed at any bed location shown in Figure 1.

Tank-in-Series Model

A five-tank-in-series model, considering the external mass transfer as the controlling mechanism, was proposed to simulate the fixed bed mercury sorption process. In the model, the bed was composed of five equally-divided complete stirred tank absorbers with each operating at its

own temperature. The solute concentration in the gas stream in each tank is described by Equation 4 and the rate of absorption/desorption is described by Equation 1, where C_i in Equation 4 is the solute concentration either in the exit stream from the preceding tank or in the process input stream.

Since the temperature in each tank may be different, the parameters appearing in Equations 1 and 4, e.g., K_g , C^i , F_i , and F_e , may have different values in different tanks. In model simulations, the mercury concentration at gas-solids interphase, i.e., C^i appearing in Equation 4, was estimated based on the following ideal gas law expression:

$$C^i = P^i/RT \quad (5)$$

where P^i was estimated by the Henry's Law expressed as:

$$P^i = x H^* \quad (6)$$

EXPERIMENTAL

Experiments on mercury sorption and desorption were carried out in a fixed bed absorber. A schematic diagram of the experimental apparatus is shown in Figure 2. It includes a preheater, a mercury holding assembly, a 25.4 mm ID inconel bed assembly enclosed in a tube furnace, a temperature measurement assembly, a filter, and six impingers. The mercury holding assembly consists of a platinum cup and a sliding tract for placing the cup in the hot gas stream. The bed assembly includes a 300 mm long column, a distributor, and cooling coils in the bed. The temperature measurement assembly includes two thermocouple probes. The bottom probe, with one thermocouple embedded in it, measures the temperature at the platinum cup location. The top probe, with four thermocouple sensors embedded in it, measures the bed temperatures simultaneously at four different bed locations above the distributor. The solution in the impingers contained either 1:1 HNO₃ or 0.5 % KMnO₄ in 1 N H₂SO₄ aqueous solution.

Procedure

In each experiment, a specific amount of a sorbent was charged in the bed. The carrier gas, which was air in this study, was preheated to the designated temperature. The temperature in the sorbent bed was then established with the adjustments of cooling water and the tube furnace surrounding the bed. After the temperatures were stabilized, the platinum cup with a known amount of mercury in it was moved into the hot air stream to allow the mercury to vaporize. The hot air stream carried the vaporized mercury into the sorbent bed where a fraction of the mercury was absorbed/adsorbed by the bed sorbent and the rest of it might condense on cooling coils or bed walls, or exit the bed with the gas stream. The mercury in the exit stream was finally captured by the filter or the impinger solutions. The experimental parameters were vaporization and bed temperatures, air flow rate, form of mercury, sorbent type, sorbent amount, sulfur impregnation and experimental duration. The ranges of these parameters are summarized in Table 1.

Test Materials

Two forms of mercury were used in the experiments, i.e., elemental mercury and mercury chloride, with boiling points of 357°C and 304°C, and melting points of -38.9 °C and 277 °C, respectively. The vapor pressure of these two forms of mercury can be estimated by:

For Hg⁰

$$\log_{10}P^* = 7.7042 - 2976/(T + 260) \quad (T: 100-400^\circ\text{C}) \quad (7)$$

For HgCl₂

$$\log_{10}P^* = 10.888 - 4441/(T + 273) \quad (T: 100-130^\circ\text{C}) \quad (8)$$

$$\log_{10}P^* = 10.094 - 4118/(T + 273) \quad (T: 130-270^\circ\text{C}) \quad (9)$$

$$\log_{10}P^* = 8.409 - 3187/(T + 273) \quad (T: 275-400^\circ\text{C}) \quad (10)$$

Five types of sorbents were tested in the study. They were: activated carbon, bauxite, lime, alumina, and zeolite. The size of the sorbents were mostly between 20 and 40 mesh which is equivalent to about 0.5 mm in diameter. Other selected physical properties of the sorbents are listed in Table 2. It is worth noting that activated carbon and bauxite have relatively larger surface areas than the other tested sorbents.

Mercury Analysis

A Buck Scientific Model 400A Cold Vapor Mercury Analyzer was used to measure the mercury concentration in the bed sorbents and the process components (i.e., bed wall, cooling coils, distributor, platinum cup, and acid solutions in the impingers). In the analysis, the mercury in bed sorbents was first digested into a solution following EPA Method 7471A involving repeated heating and cooling steps in aqua regia, potassium persulphate, and sodium chloride-hydroxylamine sulfate solutions. The leachability of mercury from sorbents was examined by performing the Toxicity Characteristics Leaching Procedure (TCLP) tests.

Percent Sorption

The percent sorption of mercury by sorbents is defined to be the amount of mercury absorbed over that vaporized. It is expressed as

$$\Phi = (m_a/m_v) \times 100\% \quad (11)$$

RESULTS AND DISCUSSION

Equilibrium Simulation

Figures 3 through 6 display four sets of equilibrium simulation results corresponding to the current experimental systems, namely HgCl₂-Air, HgCl₂-Air-Sulfur, Hg⁰-Air, and Hg⁰-Air-Sulfur

systems. Note that the thermodynamic data used in the simulation were derived from the JANAF Thermochemical Tables (12).

HgCl₂ Systems

The results shown in Figure 3 for a HgCl₂-Air system indicate that HgCl₂(g) is the dominate form of mercury for temperatures between 150 and 650°C. At lower temperatures, HgCl₂(s) is the main form of mercury; and, at temperatures above 650°C, elemental mercury gradually becomes the thermodynamically preferred mercury species. With the existence of sulfur in the system, the results in Figure 4 indicate that, HgSO₄(s) is the predominant form of mercury at low temperatures below 200°C; HgCl₂(g) remains to be the dominate mercury species at temperatures between 300 and 650°C; and, elemental mercury again will gradually become the main mercury form at higher temperatures. These simulation results strongly suggest that, in the current experiments involving mercury chloride, HgCl₂(g) is exclusively the predominant species in the system at temperatures between 250 and 500°C and no chemical reactions involving mercury chloride are expected to occur during the experiments. However, as the bed temperature cools down, HgCl₂(s) or HgSO₄(s) may form depending on the temperature and the existence of sulfur.

Hg⁰ Systems

When elemental mercury is involved and sulfur is not present, the simulation results shown in Figure 5 for a Hg⁰-Air system indicate that HgO(s) is the main mercury species in the system at low temperatures below about 250°C. As the temperature increases, elemental mercury becomes the dominant form of mercury coexisting with a small fraction of HgO(g). With the existence of sulfur, the results shown in Figure 6 for a Hg⁰-Air-Sulfur system indicate that HgSO₄(s) will be the main form of mercury at temperatures up to about 400°C. As the temperature increases, it will vaporize and decompose to form Hg⁰ with a small fraction reacting with oxygen to form HgO(g). These simulation results suggest that, in the current experiments involving elemental mercury, the main form of mercury in the system may be Hg⁰, HgSO₄(s) or HgO(s) depending on the operating temperature and the existence of sulfur. This definitely implies that chemical reactions will occur during most of the current sorption experiments involving Hg⁰. As discussed previously, chemical reactions may only occur at low temperatures with sulfur during the experiments involving HgCl₂. It is worth pointing out that the equilibrium simulation results observed in this work are generally consistent to the results reported in the literature (13).

Experimental Observation

The results reported in this sub-section include Bed Temperature Profile, General Sorption Results, Effect of Sorbent Type, Effect of Parameters, and Mercury Leachability.

Bed Temperature Profile

The temperature profile in the sorbent bed during sorption experiments varied with the vaporization temperature (temperature at the platinum cup) and the use of cooling water. Typical

temperature profiles recorded in bauxite beds are shown in Figure 7. These profiles indicate that, without the use of cooling water, the bed temperature decreases approximately linearly with the bed location. A temperature drop from 420°C to 280°C is observed when the vaporization temperature is at 500°C; from 330°C to 240°C at 400°C; and from 240°C to 180°C at 300°C. However, with the use of cooling water, the bed temperature is observed to drop much faster in the bed. The exit temperatures were below 100°C at all of the vaporization temperatures studied (i.e., 500, 400 and 300°C). Note that the bed temperature profiles in beds with other sorbents were observed to be similar to those shown in Figure 7.

General Sorption Results

The amount of mercury retention by sorbents was generally observed to decrease with time due to mercury desorption from the sorbents. Typical results on dynamic mercury sorption/desorption on bauxite and activated carbon are displayed in Figures 8 and 9, for HgCl₂ and Hg⁰ sorption, respectively. These results represent the sorption experiments involving the vaporization of a batch of 100 mg of HgCl₂(s) (or approximately 200 mg of Hg⁰(l)) in a stream of 400°C air flowing at 4.7 x 10⁻⁴ scmm (standard cubic meter per min) into a sorbent bed of 100 mm bed height for a duration of 60, 120, and 180 minutes. Note that, in these experiments, most of the mercury in the holding cup was observed to have vaporized within about 10 minutes of the experiment, the recorded data at 60, 120, and 180 minutes, therefore, essentially represent the desorption of mercury from the sorbents.

The results shown in Figure 8 for HgCl₂ sorption indicate that the amount of mercury retention by both bauxite and activated carbon decreases with time, with the rate of desorption being roughly the same for all four sets of experiments. Since, according to equilibrium predictions, no chemical reactions are expected to occur in the sorption process involving mercury chloride at these bed temperatures between 100 and 400°C, the sorption results observed in Figure 8 apparently represent the physical sorption/desorption of mercury chloride on the sorbents. Under the experimental conditions, bauxite is seen to be more effective in the sorption of mercury chloride than activated carbon. Without the use of cooling water, the sorption efficiencies for bauxite are around 70, 60 and 50% at the duration of 60, 120, and 180 minutes, respectively; while for activated carbon, the efficiencies are around 30, 23, and 16%. The results in Figure 8 also indicate that, for both bauxite and activated carbon, sorption efficiencies are higher in beds without cooling water (i.e., in beds with higher bed temperatures). This observation appear to suggest that the sorption process is not controlled by the adsorption mechanism on the sorbent surfaces. Instead, the main mechanism governing the sorption/desorption of mercury chloride on sorbents could be the mass transfer between the bulk gas phase and the external sorbent surfaces under the experimental conditions.

For the sorption of elemental mercury, the results shown in Figure 9 again indicate that the amount of mercury retention by sorbents decreases with time representing desorption of mercury from sorbents. Bauxite again is observed to be more effective in retaining mercury. The desorption rates of mercury from activated carbon, however, are lower than those from bauxite. However, the results shown in Figure 9 indicate that, especially for bauxite, the high sorption efficiencies are in beds with cooling water, which appears to be opposite to that observed for mercury chloride. One explanation to this observation is that elemental mercury may react with oxygen to form mercury

oxide during the experiments and, according to the equilibrium results shown in Figure 5, the formed HgO is in solid phase when the bed temperatures are below about 250°C (i.e., in beds with cooling water). The results appear to suggest that $\text{HgO}(\text{s})$ is more easily retained by bauxite than Hg° . This phenomenon, however, is not obvious for activated carbon possibly due to its low sorption capacity for both elemental mercury and mercury oxide.

Effect of Sorbent Type

Bauxite and activated carbon were observed to be more effective in mercury sorption among the sorbents tested. A typical set of comparison is shown in Figure 10 where the sorption capacity of bauxite and activated carbon is seen to be around 1.5 mg/g sorbent; while for other sorbents, it is less than 0.9 mg/g . Since bauxite and activated carbon happen to have the highest surface areas among the sorbents tested (see Table 2), it is apparent that the surface area of the sorbents plays an important role in the mercury sorption process. However, for sorbents with sufficient surface area, surface area may not be the controlling factor for the sorption process. The observation that bauxite has much less surface areas and yet a slightly higher sorption capacity than activated carbon appears to support this statement. Similar results were observed under different experimental conditions for both HgCl_2 and Hg° sorption.

It is worth pointing out that, although bauxite and activated carbon have similar sorption capacity in the milli-gram mercury per gram sorbent basis, the sorption capacity for bauxite in the milli-gram mercury per volume sorbent basis is much greater than that for activated carbon. This explains the results observed in Figures 8 and 9 that the percent retention of mercury by bauxite is much greater than that by activated carbon at the same sorbent bed height of 100 mm.

Effect of Other Parameters

Other experimental parameters were vaporization temperature, use of cooling water, sulfur impregnation, sorbent size, and air flow rate. In general, the percent sorption of mercury is higher at a lower vaporization temperature for both mercury chloride and elemental mercury. A typical set of such observations is shown in Figure 11 where sorption of mercury chloride at a duration of 60 minutes is seen to decrease slightly from 75 to 60% when the vaporization temperature increases from 200 to 500°C . The results are expected since the Henry's Law Constant is expected to be lower at a lower temperature. The lower constant would result in a lower mercury concentration at the gas-solid interphase which, in turn, would enhance the rate of mass transfer of mercury from the gas phase to the gas-solid interphase according to Equation 1. The observation that the percent sorption decreases only slightly with temperature suggests that the Henry's Law constant is not a strong function of temperature under the experimental conditions.

Typical results on the effects of cooling water and sulfur impregnation are shown in Figures 12 and 13, where the percent sorption of HgCl_2 and Hg° by bauxite at a duration of 60 minutes is compared under different operating conditions. The results shown in Figure 12 for HgCl_2 sorption indicate that, at the vaporization temperature of 500°C , the highest mercury retention occurred when cooling water was not used (i.e., at highest bed temperatures). When cooling water was used, the amount of mercury retention decreased slightly, from 1.75 to 1.70 g/g bauxite. As discussed previously, this suggests that the controlling mechanism for mercury sorption in the current

experiments could be the mass transfer from bulk gas phase to the gas-solid interphase instead of adsorption at sorbent surfaces because the latter would favor low temperature operations. The observation that bauxite, having smaller pore sizes but retaining more mercury than activated carbon as shown in Figure 10, appears to suggest that internal diffusion is not the controlling mechanism.

The results shown in Figure 12 also indicate that sulfur impregnation did not seem to affect the HgCl_2 sorption process when cooling water was used; however, it decreased the percent sorption noticeably when cooling water was not used. Since sulfur is not expected to react with mercury chloride at high bed temperatures, the observed decrease in mercury retention when cooling water was not used seem to indicate that the existence of sulfur simply blocks the available sites for mercury sorption and therefore, reduces the sorption capacity of the sorbent. However, at low bed temperatures when cooling water was used, sulfur on bauxite could react with mercury chloride to form $\text{HgSO}_4(\text{s})$ which was observed to be retained by bauxite as efficiently as mercury chloride.

For elemental mercury retention by bauxite, the results shown in Figure 13 indicate that the effects of cooling water and sulfur impregnation are different from those for mercury chloride shown in Figure 12. Percent mercury sorption is relatively high in beds with cooling water and with sulfur impregnation. The observed phenomena are believed to be due to potential mercury reactions in the bed as discussed previously. According to the equilibrium results shown in Figures 5 and 6, $\text{HgO}(\text{s})$ or $\text{HgSO}_4(\text{s})$ can be the dominant species in the system when cooling water or sulfur impregnation was involved. The results shown in Figure 13 apparently suggest that bauxite can retain $\text{HgO}(\text{s})$ and $\text{HgSO}_4(\text{s})$ more efficiently than elemental mercury.

Smaller size sorbents and higher air flow rates were found to slightly enhance the rate of the mercury sorption/desorption process. The effect of these two parameters, however, was insignificant within the ranges tested.

Mercury Leachability

Mercury leachability was examined through Toxicity Characteristic Leaching Procedure (TCLP) tests. The test results have indicated that mercury chloride on bauxite is the only mercury-sorbent pair with significant mercury leachability, where the leachable amount is around 60%. The leachability of mercury in other mercury-sorbent pairs is insignificant, mostly less than 2%.

Model Prediction

The proposed five-tank-in-series model as described earlier was used to simulate the mercury sorption process carried out in the experiments. In the model, the Henry's Law Constant for mercury chloride and elemental mercury was empirically proposed to have the following form:

$$H^* = H_0 + (P^*)^{0.1} \quad (12)$$

This proposed form was based on the current experimental observation that an increase in temperature only slightly decreases the rate of sorption. The form, however, may be modified based

on additional observations. Furthermore, the effect of temperature on mercury diffusivity was assumed to have the following form (14):

$$(D_1/D_2) = (T_1/T_2)^{1.823} \quad (13)$$

Model Simulation

In model simulations, selected values of $K_g S_{ex}$ in Equation 1 and H_o in Equation 12 were first assigned and Equations 1, 4, 5, and 6 coupled with Equations 12 and 13 were sequentially solved to predict mercury sorption at any bed locations and duration of time. The optimal values of $K_g S_{ex}$ and H_o were then determined by statistically comparing the simulation predictions and experimental results. Note that, in the simulation, the value of $K_g S_{ex}$ for activated carbon was fixed at 27.5% of that for bauxite under the same experimental conditions. This ratio was estimated based on the amount, density, and particle size of the two sorbents.

Model Prediction

Three typical sets of model predictions of mercury sorption by sorbents are plotted against the experimentally observed data in Figures 14 through 16 for $HgCl_2$ and Hg^0 sorption by bauxite and activated carbon. The values of $K_g S_{ex}$ and H_o used in generating these model predictions are listed in Table 3. The results in these figures indicate that the proposed mass transfer control model approximately predicts the sorption processes under these experimental conditions. It is generally observed that the sorption of mercury chloride is better described by the model than that of elemental mercury. The higher deviations for elemental mercury are expected because, due to the lack of data on mercury speciation, the current simulation does not account for the effect of potential chemical reactions between elemental mercury and oxygen to form $HgO(s)$ under the experimental conditions. The model, however, can be modified to account for the effect once the data become available.

It is worth pointing out that the values of $K_g S_{ex}$ generated from model simulations are approximately one order of magnitude smaller than those estimated from multiplying the total exterior surfaces of sorbent particles (S_{ex}) and the K_g estimated from the following literature available equation for well-dispersed particles (14), i.e.,

$$(K_g d_p y/D) = 2 + 0.6(Sc)^{0.33}(Re)^{0.5} \quad (14)$$

These lower values of $K_g S_{ex}$ from model simulation, however, are expected since S_{ex} in fixed bed operations would not involve all the exterior surfaces of the particles. Furthermore, the channeling and non-ideal mixing in the bed would also lower the values of $K_g S_{ex}$ predicted from model simulations.

It should also note that the simulated H_o value for each mercury-sorbent pair represents the sorption capacity of that specific sorbent on the corresponding mercury. A higher value of H_o implies a lower sorption capacity and vice versa. The H_o values listed in Table 3 appear to indicate that the mercury sorption capacity of activated carbon is in general less than that of bauxite. This conclusion is in agreement with current experimental observations.

Effect of Bed Location

The model was able to predict the dynamic concentration of mercury on sorbents in each simulated tank. A typical set of simulation results are shown in Figure 17. These results indicate that the sorbent particles in the lower parts of the bed will absorb/adsorb mercury from the gas stream in the first 10 minutes when mercury is still vaporizing from the cup. They then will desorb mercury to the gas stream once the mercury in the cup is completely vaporized. The particles in the higher parts of the bed, however, may continue to absorb/adsorb mercury from the gas stream due to the desorption of mercury from sorbent particles in the lower parts of the bed. The effect of bed height on mercury sorption was also simulated and reasonable agreement is observed between the experimental and simulation results as indicated in Figure 18.

CONCLUSIONS

The adsorption and desorption of mercury on and from several selected sorbents at elevated temperature were experimentally and theoretically studied. The mercury species involved were mercury chloride and elemental mercury and the sorbents tested were bauxite, activated carbon, lime, alumina and zeolite. Bauxite and activated carbon were found to retain more mercury than other sorbents tested in the study, possibly due to their higher available surface areas. However, the mercury sorption capacity of bauxite was found to be slightly higher than that of activated carbon at the tested temperatures despite the fact that bauxite has less surface areas than activated carbon. The experimental parameters examined (i.e., vaporization temperature, use of cooling water, sulfur impregnation, sorbent particle size, and air flow rate) were found to affect the sorption process moderately or marginally. The proposed mercury sorption model based on the external mass transfer mechanism appeared to describe reasonably well the experimental observations.

NOTATIONS

C	solute concentration in gas phase, Kg-mole/m ³
C_e	solute concentration in exit stream, Kg-mole/m ³
C_i	solute concentration in inlet stream, Kg-mole/m ³
C^i	solute concentration at gas-solid interphase, Kg-mole/m ³
D	diffusivity of solute, m ² /min
D_1	diffusivity of solute at T_1 , m ² /min
D_2	diffusivity of solute at T_2 , m ² /min
d_p	particle size, mm
F	volumetric flow rate, m ³ /min
H^*	Henry's Law Constant of solute-sorbent pair, mm Hg
H_o	constant in Eq. 12 for Henry's Law Constant expression, mm Hg
K_g	mass transfer coefficient, m/min
m_a	mass of solute absorbed/adsorbed by sorbent, mg
m_v	mass of solute vaporized, mg
n	moles of solute, Kg-mole
P	pressure, mm Hg
P^i	partial pressure of solute at gas-solid interphase, mm Hg

P^*	vapor pressure of solute, mm Hg
R	gas constant, 1.08×10^{-4} (mmHg m ³)/(Kg-mole °K)
Re	Reynolds number, -
Sc	Schmidt number, -
S_{ex}	total external surfaces of sorbent particles, m ²
T	Temperature, °C
T	Temperature, °K
t	time, min
x	solute mole fraction in sorbent, -
y	solute mole fraction in gas phase, -
Φ	percent sorption by sorbent, %

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Table 1. Ranges of Experimental Parameters

Parameter	Ranges
Mercury Form	Hg ⁰ , HgCl ₂
Vaporization Temp.	200, 300, 400, 500°C
HgCl ₂ Amount/Batch	100 mg
Hg ⁰ Amount/Batch	150-250 mg
Sorbent Size	0.35-0.70 mm
Sorbent Bed Height	20-140 mm
Air Flow Rate	2.3-7.0 x 10 ⁻⁴ scmm *

* standard cubic meter per minute

Table 2. Physical Properties of the Tested Sorbents

Sorbent	Bulk Density (Kg/m ³)	Surface Area (m ² /g)
Activated Carbon	360	665
Bauxite	900	175
Zeolite	770	45
Lime	730	8
Alumina	1850	0.5

Table 3. Simulated Values of $K_g S_{ex}$ and H_o

Mercury-Sorbent Pair	$K_g S_{ex}$ (@25°C) (m ³ /min)	H_o (mm Hg)
HgCl ₂ -Bauxite	8.7×10^{-6}	50
HgCl ₂ -Activated Carbon	2.4×10^{-6}	550
Hg ⁰ -Bauxite	8.7×10^{-6}	190
Hg ⁰ -Activated Carbon	2.4×10^{-6}	700

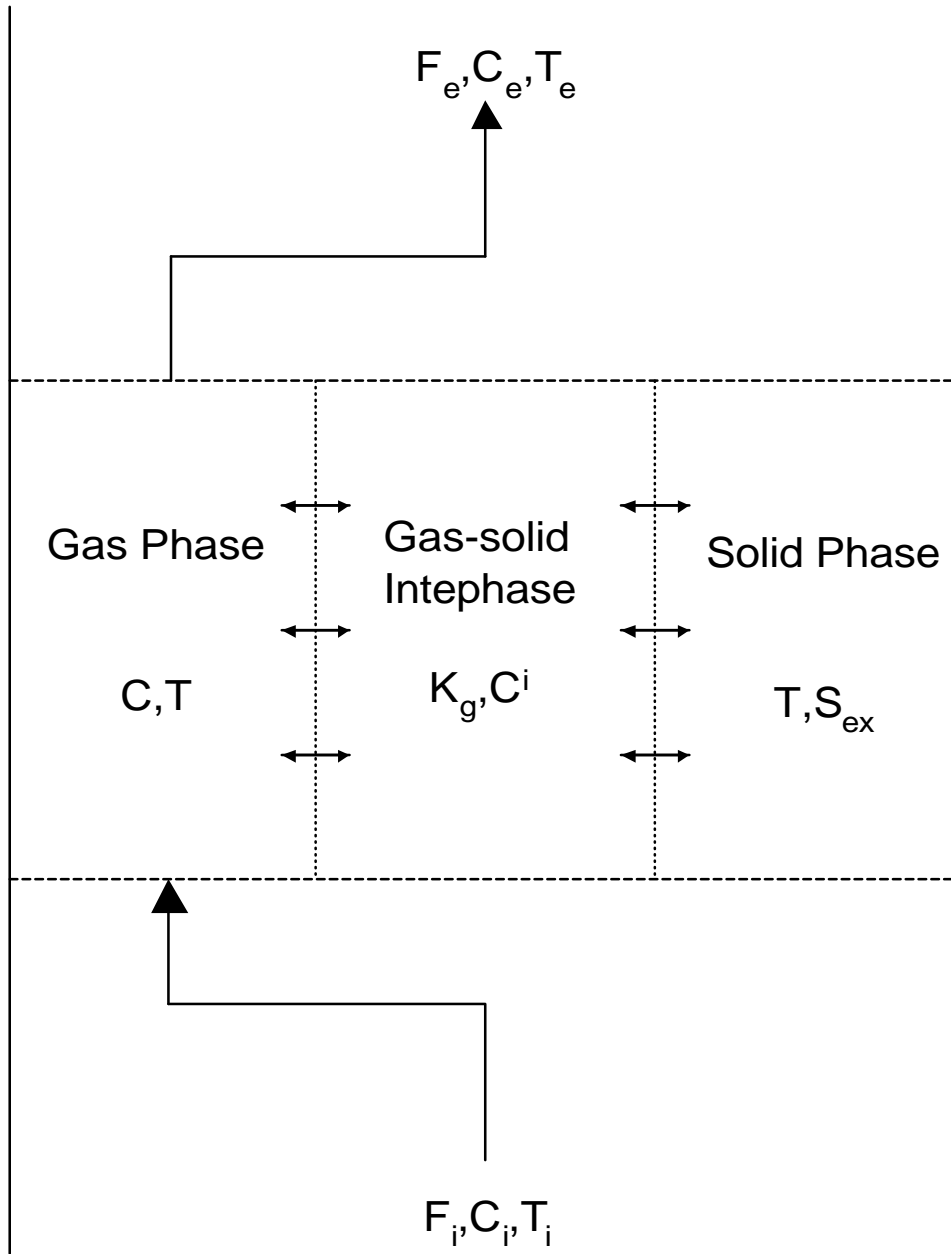


Figure 1. Conceptual sketch of the proposed sorption model.

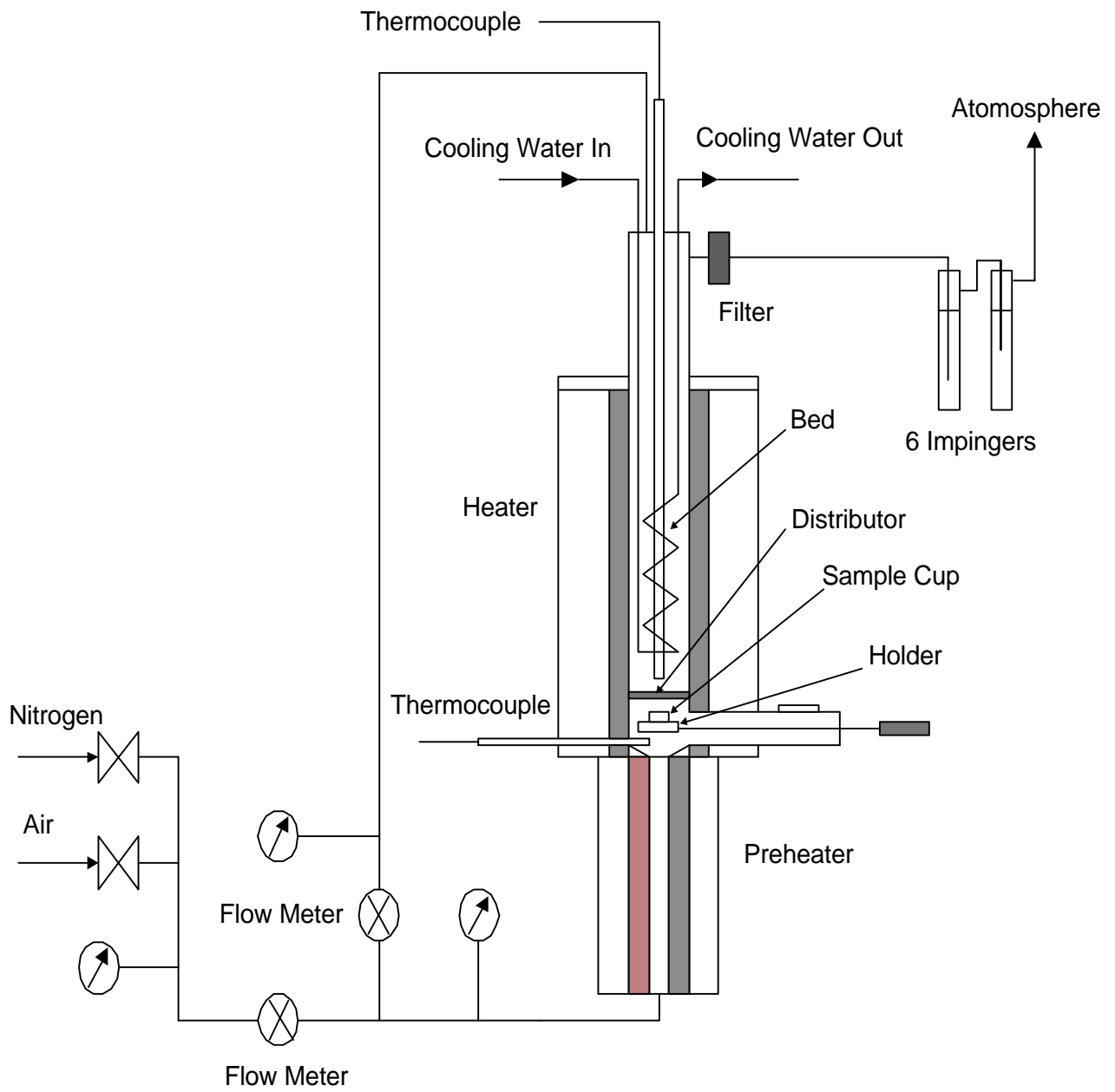


Figure 2. Experimental apparatus.

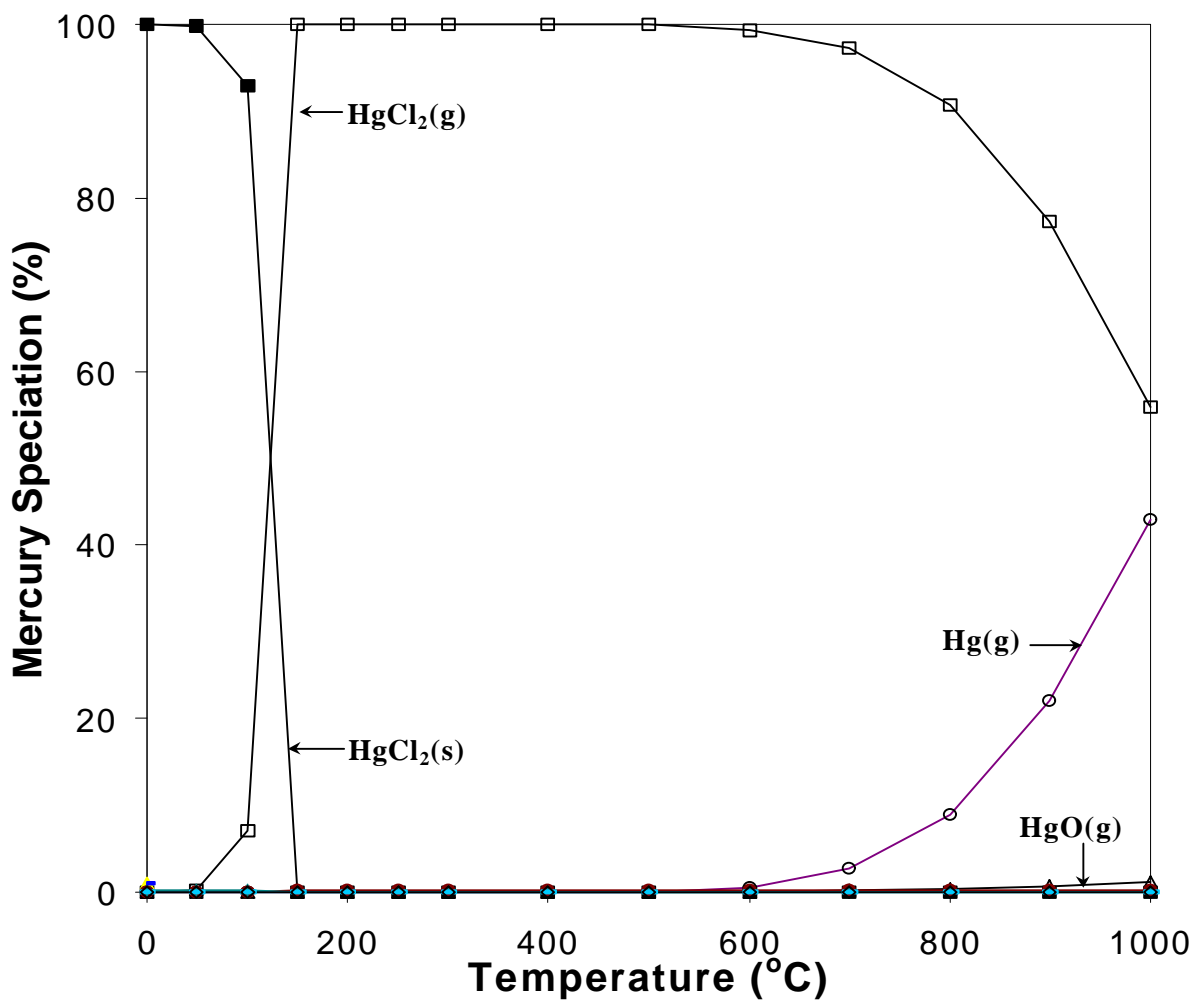


Figure 3. Equilibrium mercury speciation in a HgCl₂-Air system (HgCl₂: 1.6 wt%; Air: 98.4 wt%).

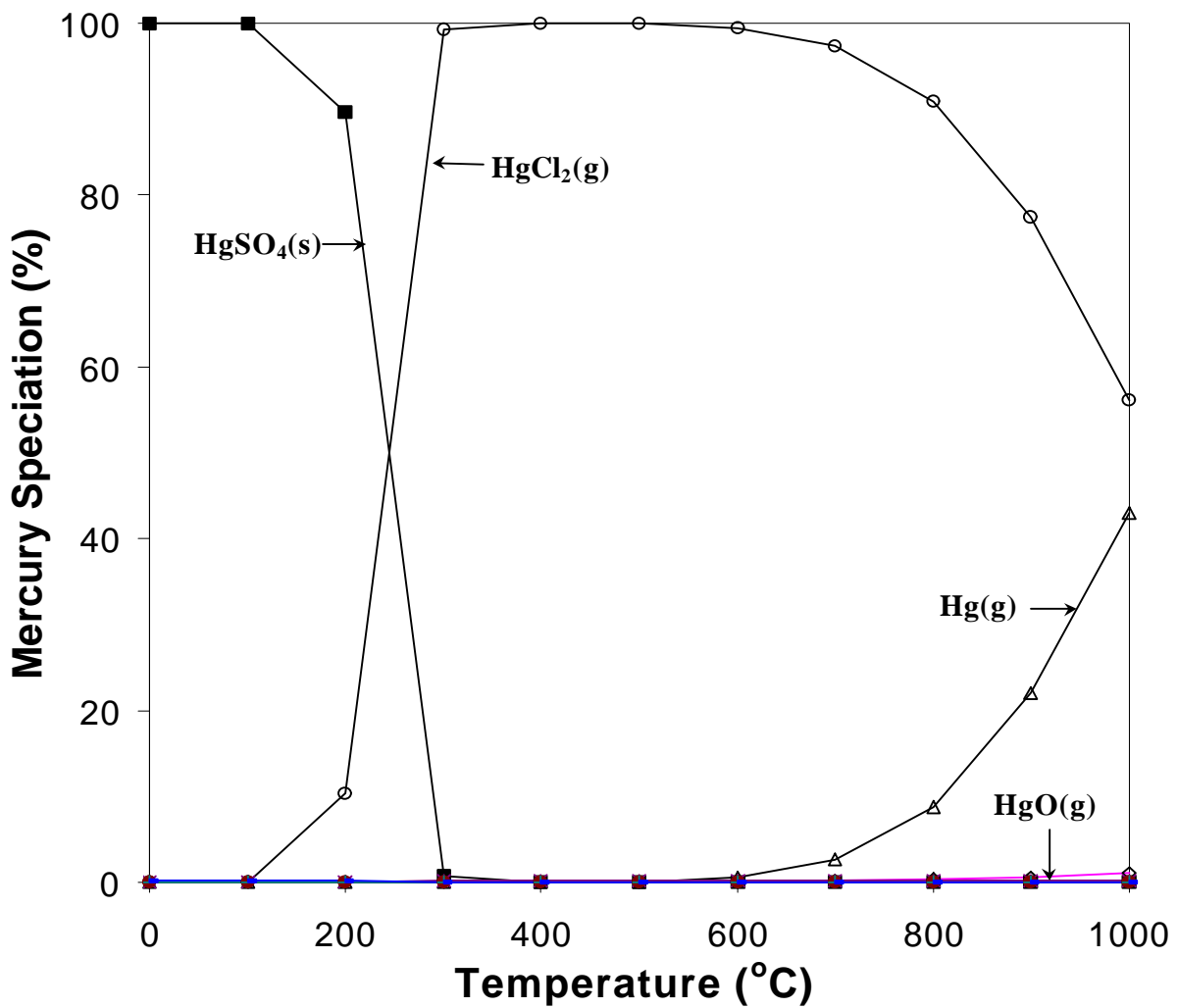


Figure 4. Equilibrium mercury speciation in a HgCl₂-Air-Sulfur system (HgCl₂: 1.5 wt%; Air: 94.5 wt%; Sulfur: 4.0 wt%).

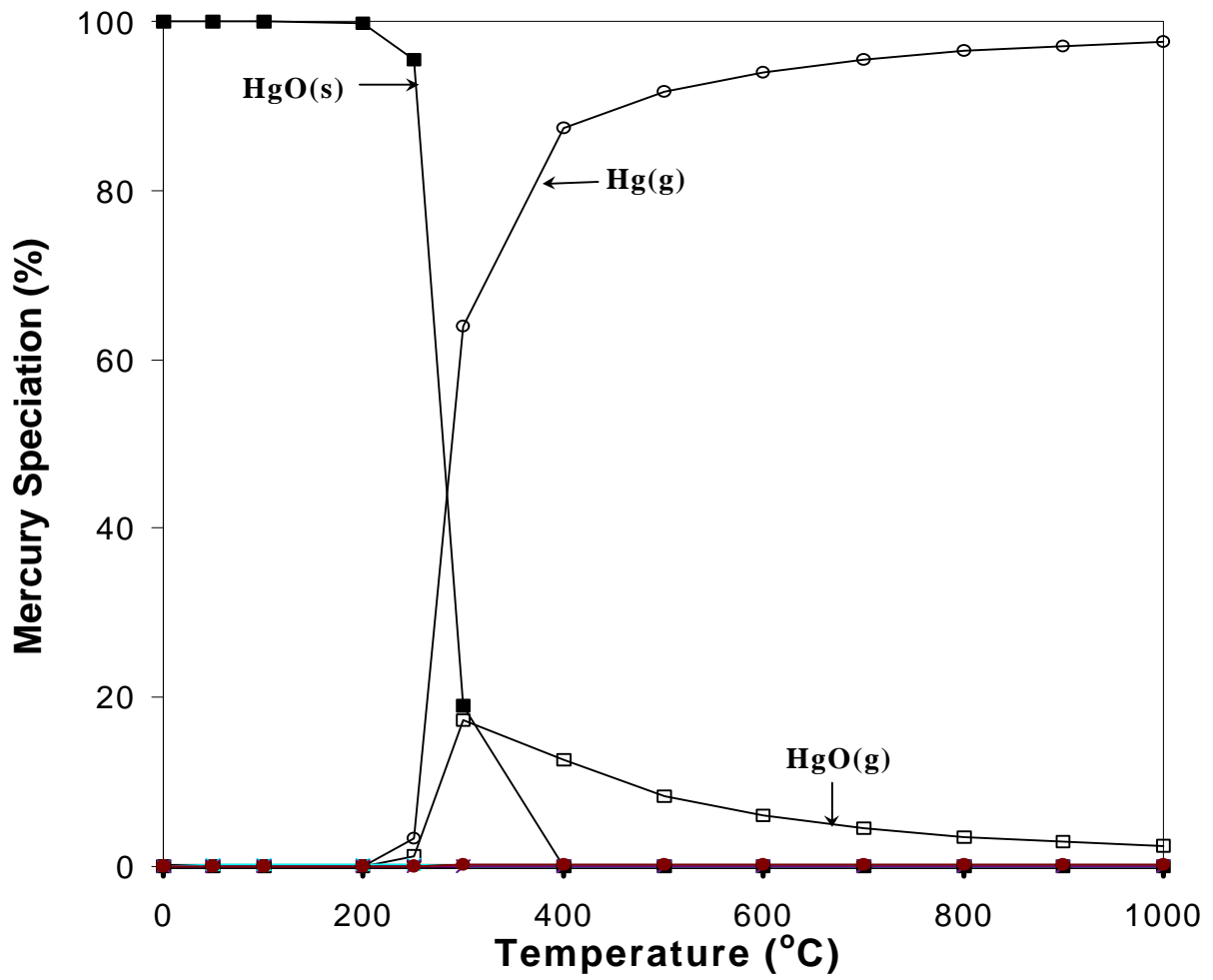


Figure 5. Equilibrium mercury speciation in a Hg° -Air system (Hg° : 1.6 wt%; Air: 98.4 wt%).

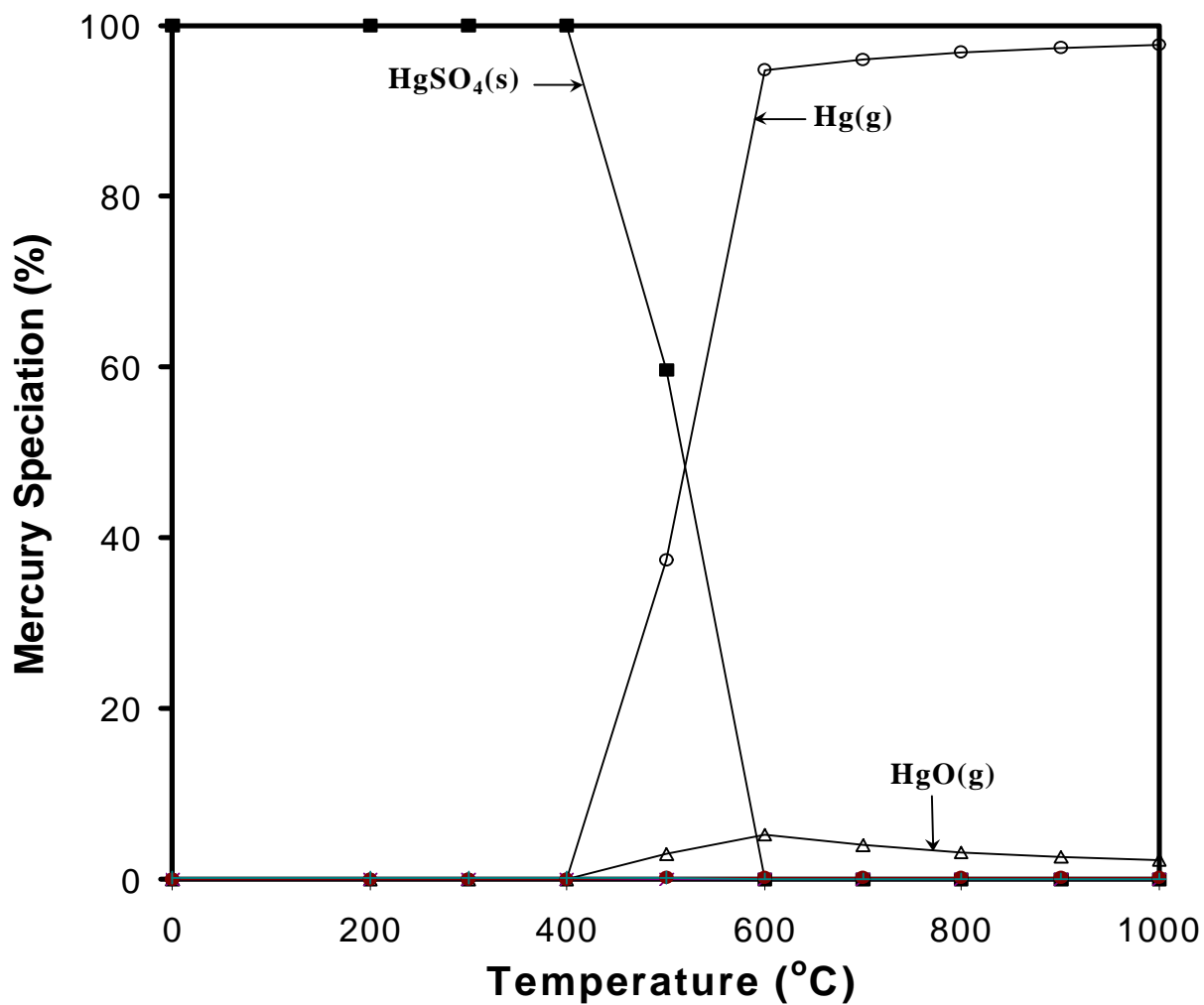


Figure 6. Equilibrium mercury speciation in a Hg⁰-Air-Sulfur system (Hg⁰: 1.5 wt%; Air: 94.5 wt%; Sulfur: 4.0 wt%).

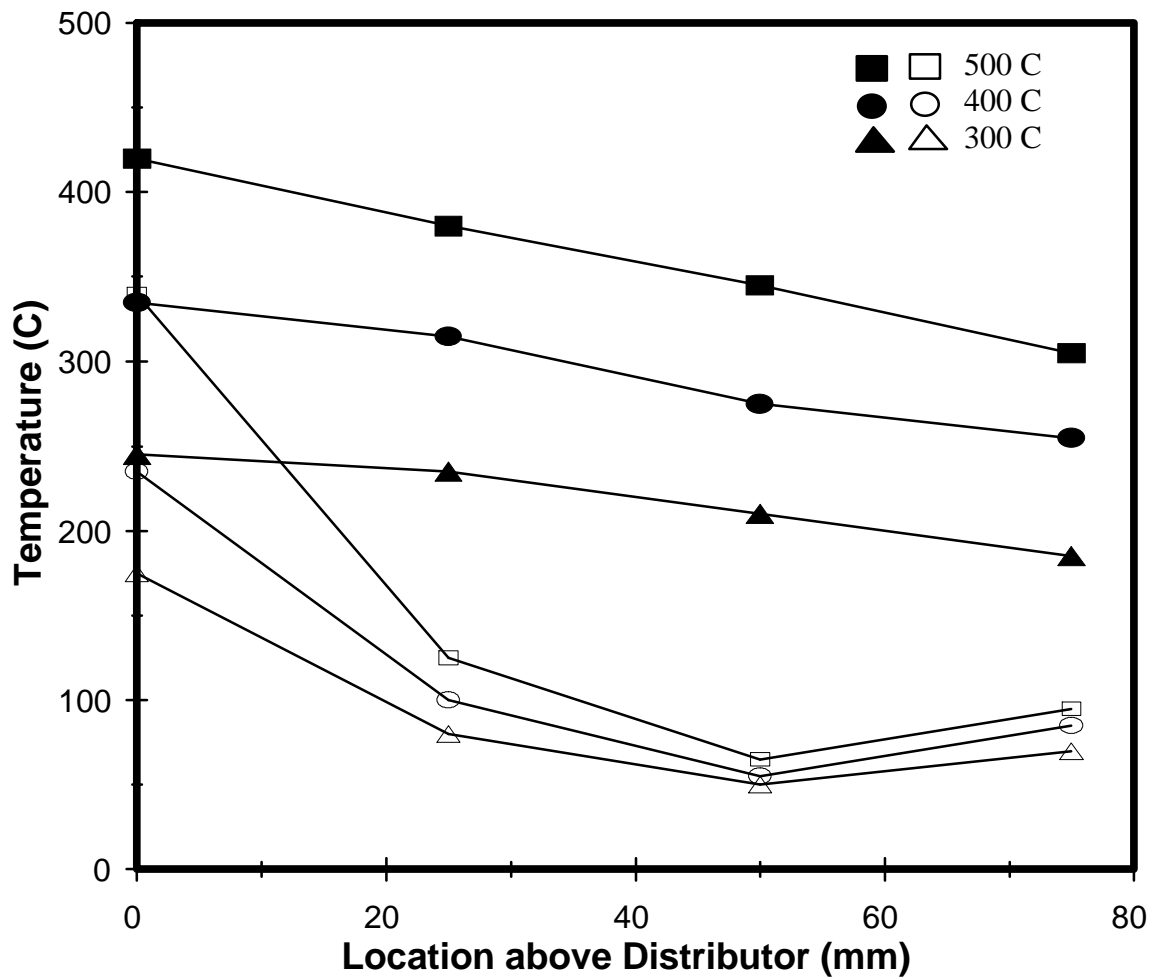


Figure 7. Bed temperature profiles at vaporization temperatures of 500, 400 and 300°C (Solid Symbol: Without Cooling Water; Open Symbol: With Cooling Water).

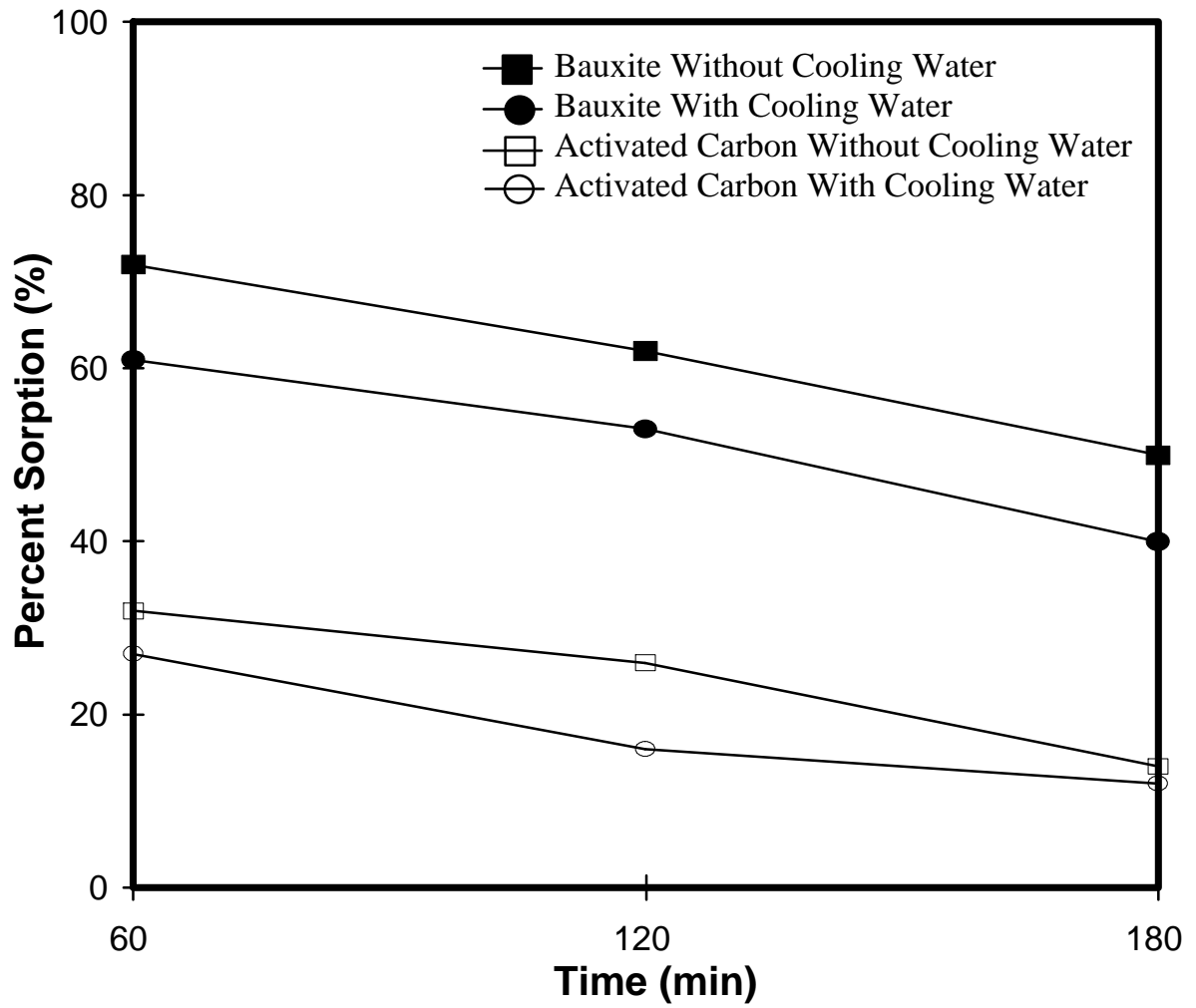


Figure 8. Plot of dynamic mercury sorption on sorbents (Mercury: HgCl_2 ; Vaporization Temperature: 400°C ; Sorbent Bed Height: 100 mm).

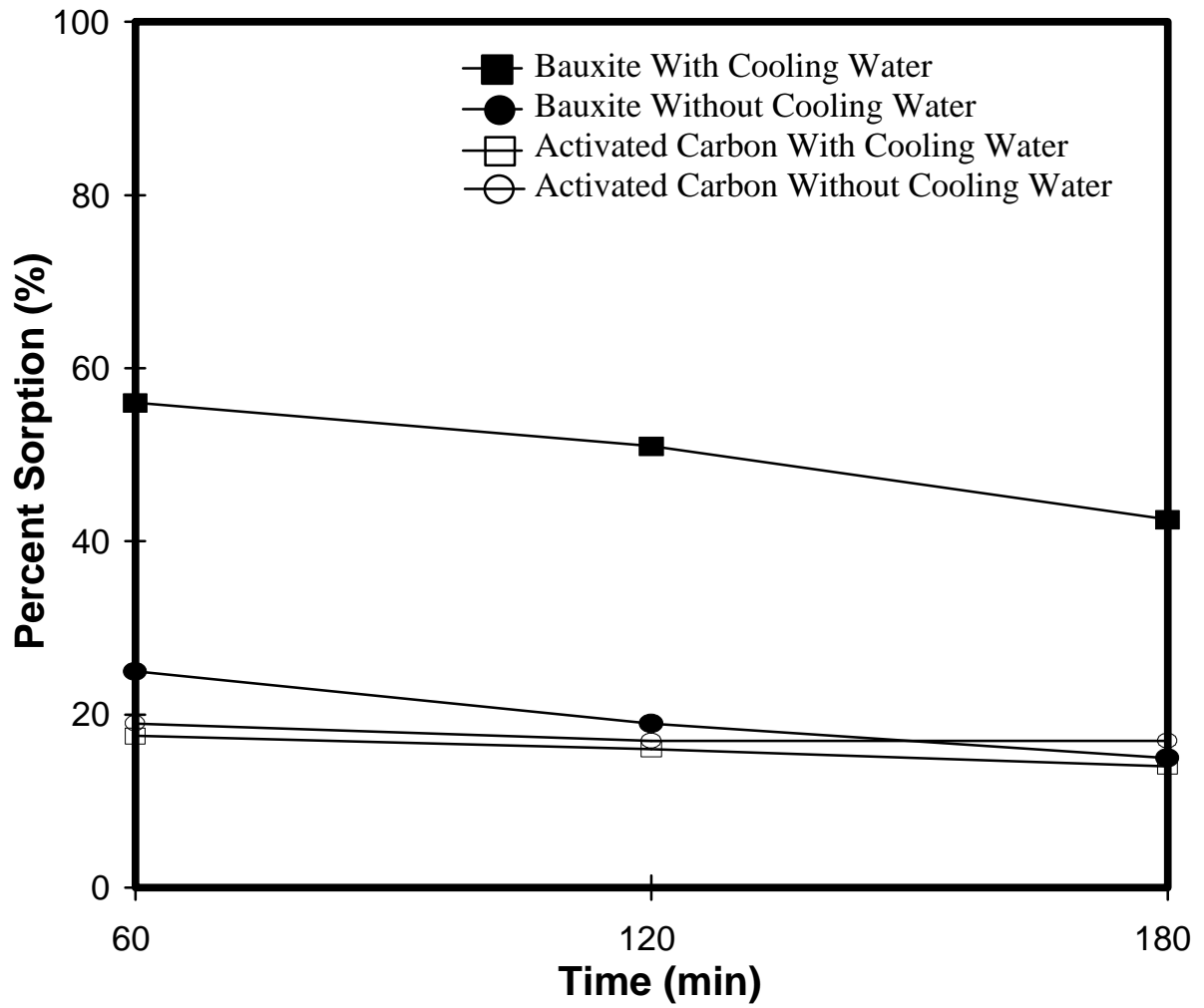


Figure 9. Plot of dynamic mercury sorption on sorbents (Mercury: Hg^0 ; Vaporization Temperature: $400^{\circ}C$; Sorbent Bed Height: 100 mm).

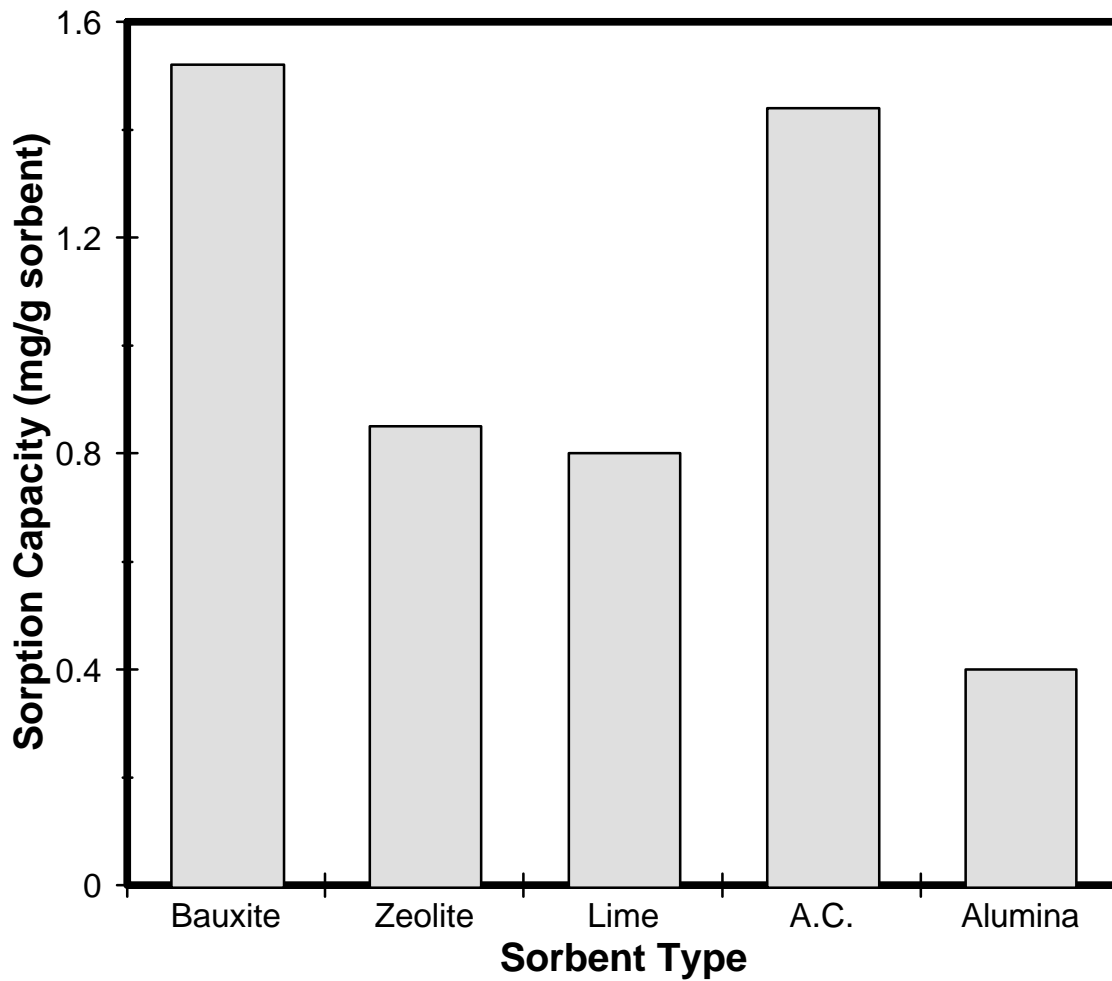


Figure 10. Effect of sorbent type on Mercury sorption (Mercury: HgCl_2 ; Vaporization Temperature: 400°C ; Sorbent Bed Height: 100 mm; Duration: 60 minutes).

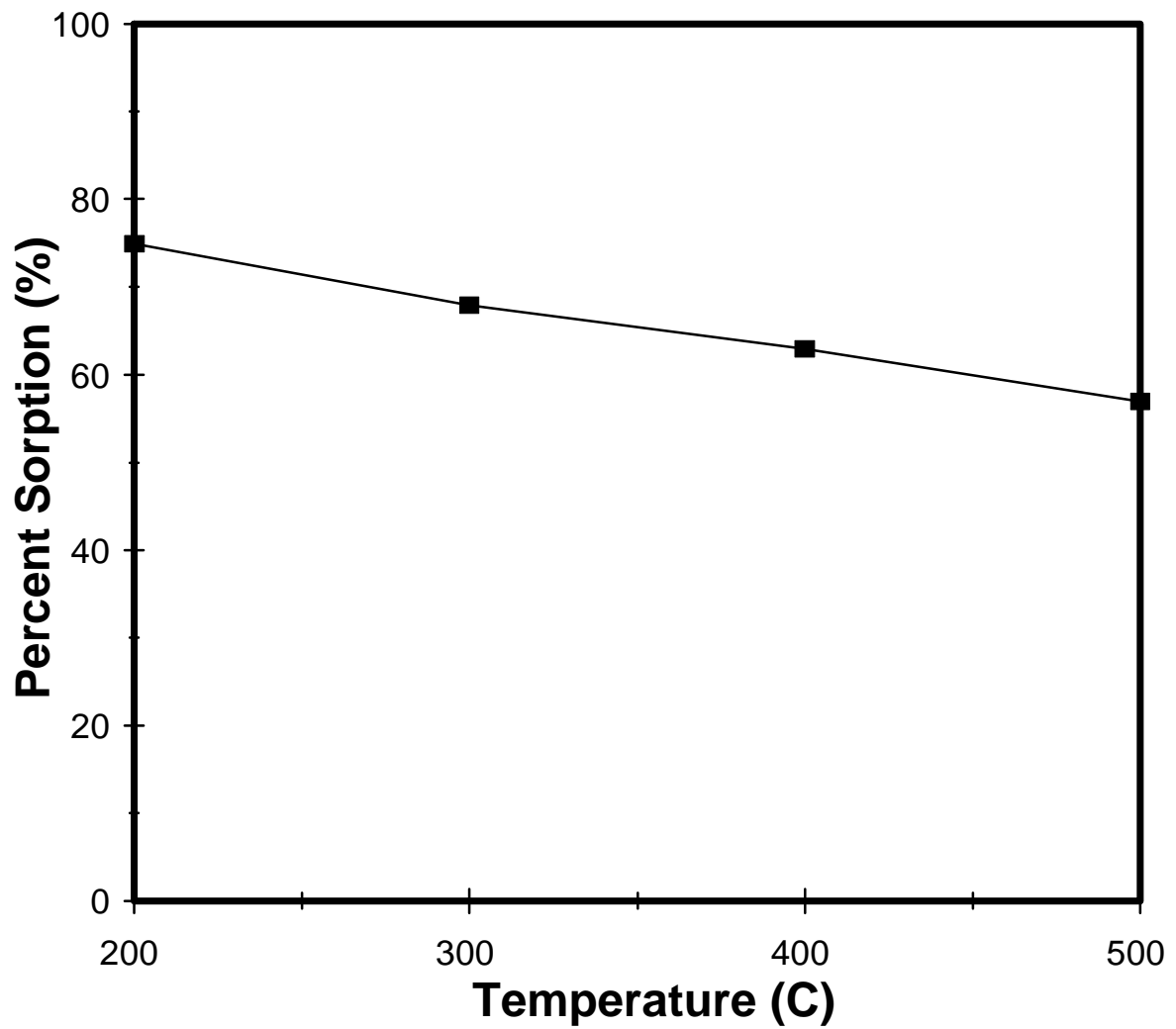


Figure 11. Effect of vaporization temperature on mercury sorption (Mercury: HgCl_2 ; Sorbent: Bauxite; Sorbent Bed Height: 100 mm; Duration: 60 minutes).

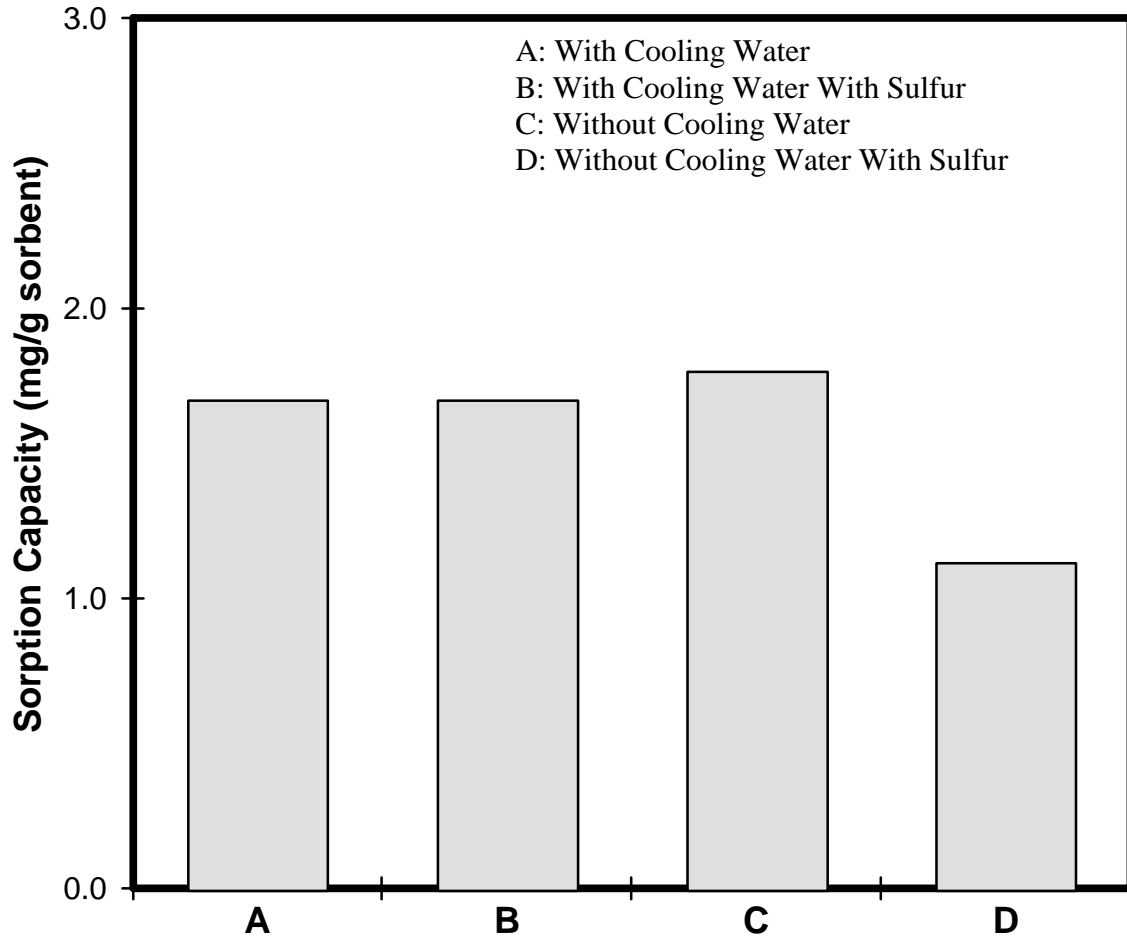


Figure 12. Effect of cooling water and sulfur impregnation on mercury chloride sorption by bauxite (Vaporization Temperature: 500°C; Duration: 60 minutes).

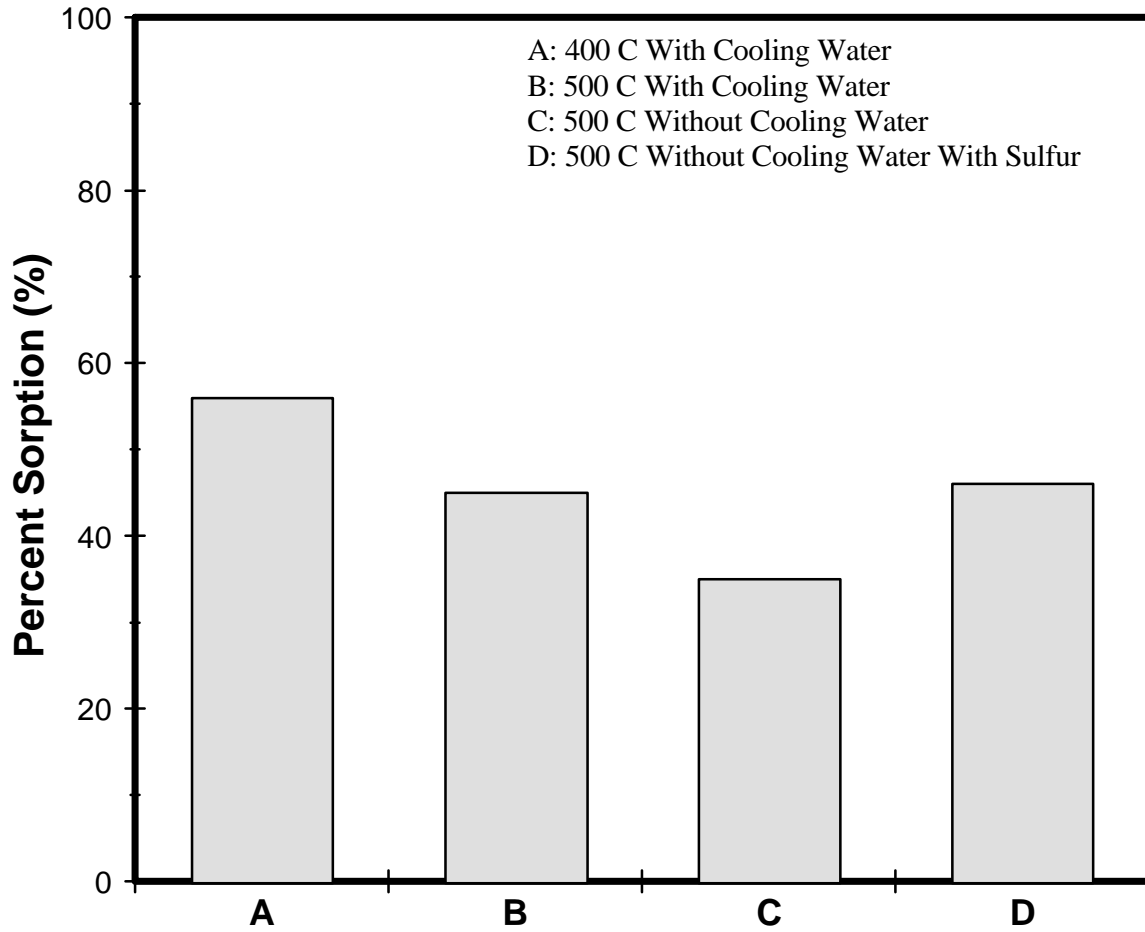


Figure 13. Effect of vaporization temperature on elemental mercury sorption by bauxite at a duration of 60 minutes.

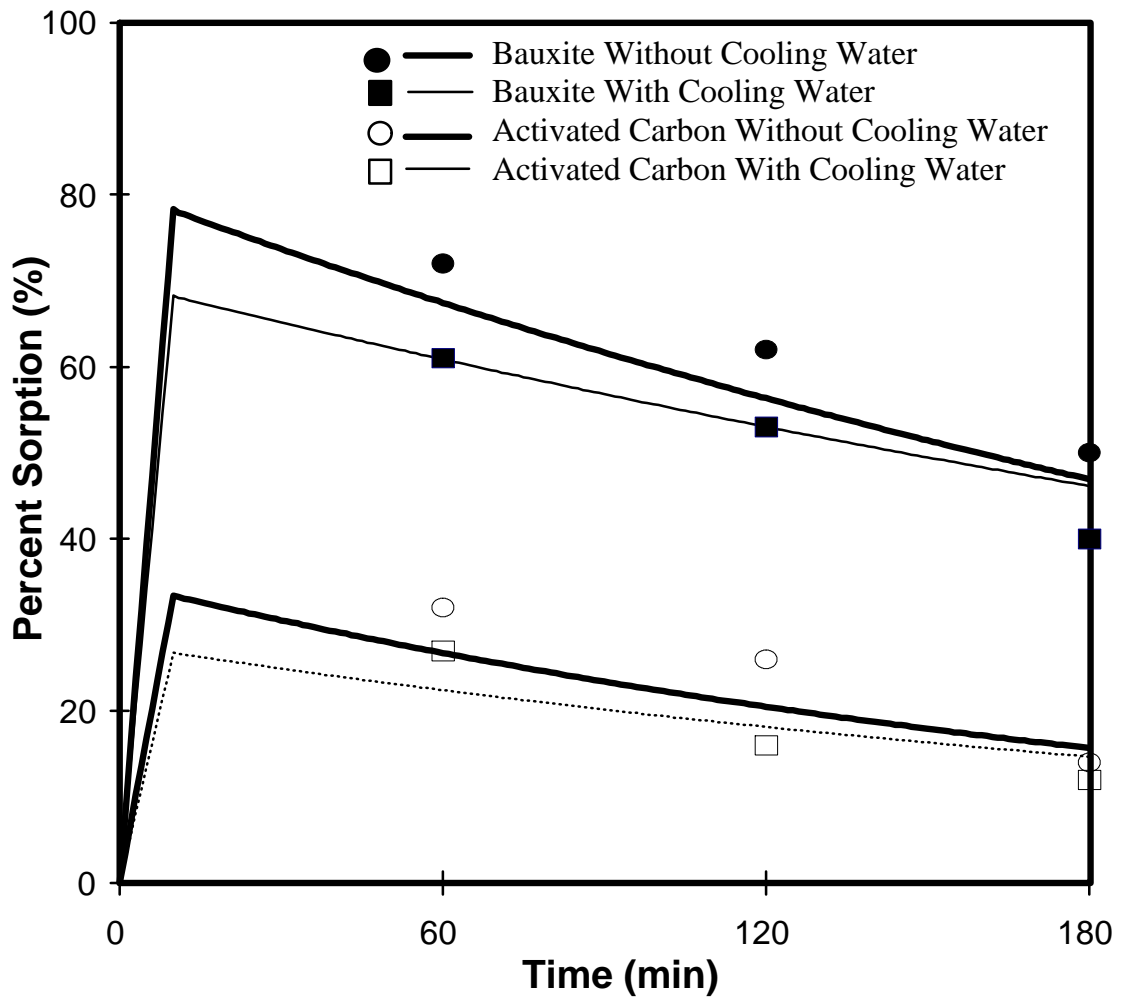


Figure 14. Plot of experimental and simulated results of dynamic mercury sorption by sorbents (Mercury: HgCl_2 ; Vaporization Temperature: 400°C ; Sorbent Bed Height: 100 mm; Air Flow Rate: 4.7×10^{-4} scmm).

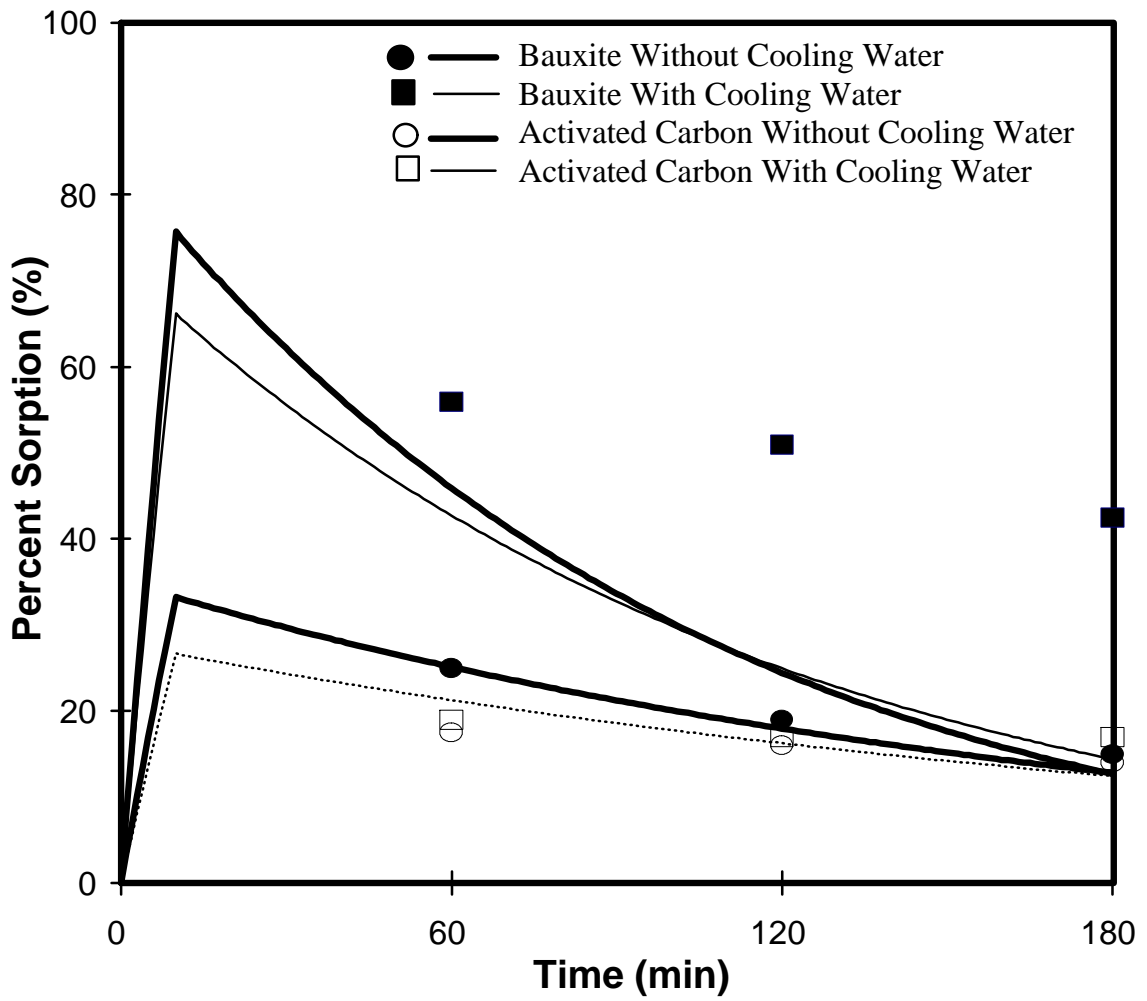


Figure 15. Plot of experimental and simulated results of dynamic mercury sorption by sorbents (Mercury: Hg^0 ; Vaporization Temperature: $400^{\circ}C$; Sorbent Bed Height: 100 mm; Air Flow Rate: 4.7×10^{-4} scmm).

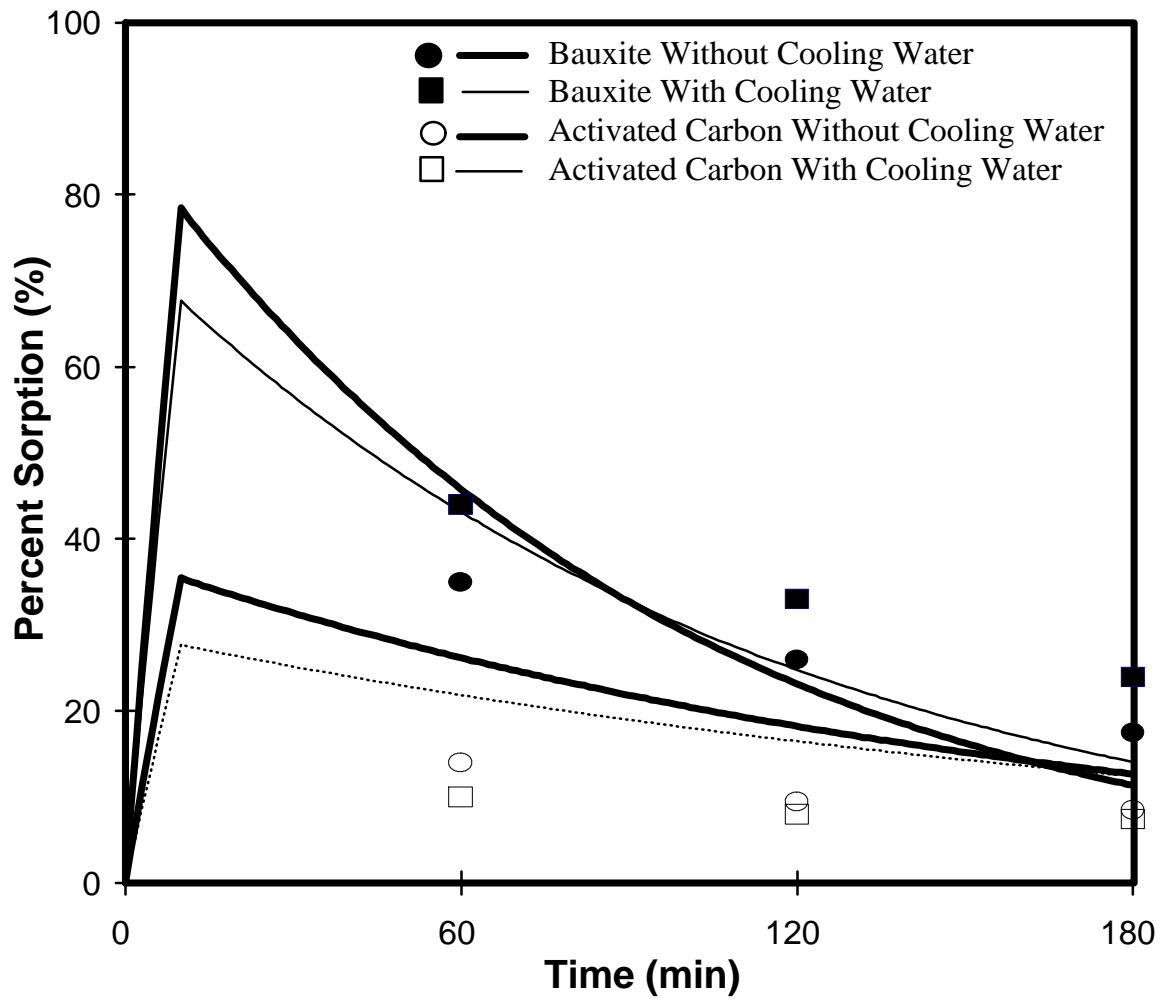


Figure 16. Plot of experimental and simulated results of dynamic mercury sorption by sorbents (Mercury: Hg^0 ; Vaporization Temperature: $500^{\circ}C$; Sorbent Bed Height: 100 mm; Air Flow Rate: 4.7×10^{-4} scmm).

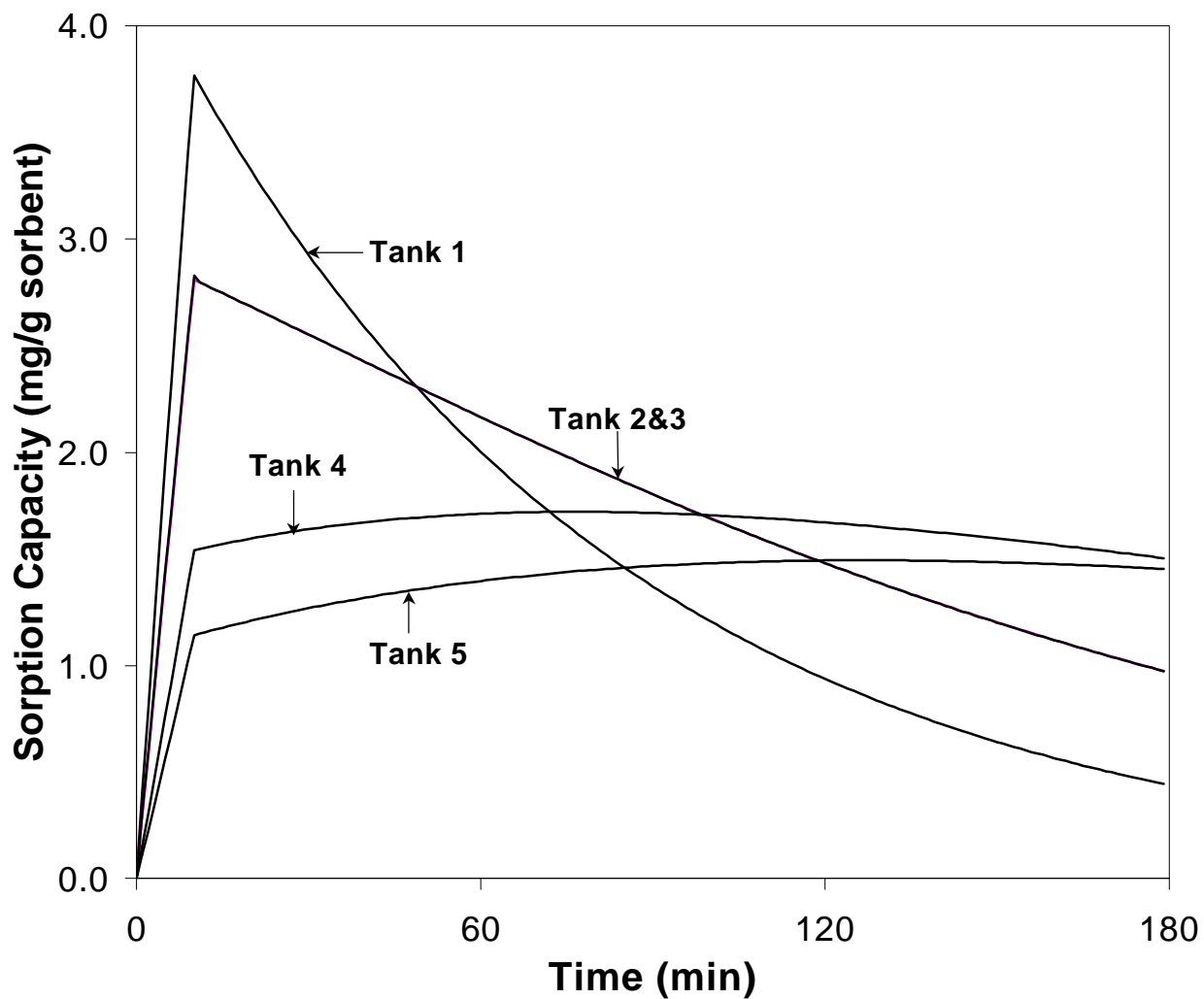


Figure 17. Model simulation of sorption capacity in each tank (Mercury: HgCl_2 ; Vaporization Temperature: 500°C ; Sorbent Bed Height: 100 mm).

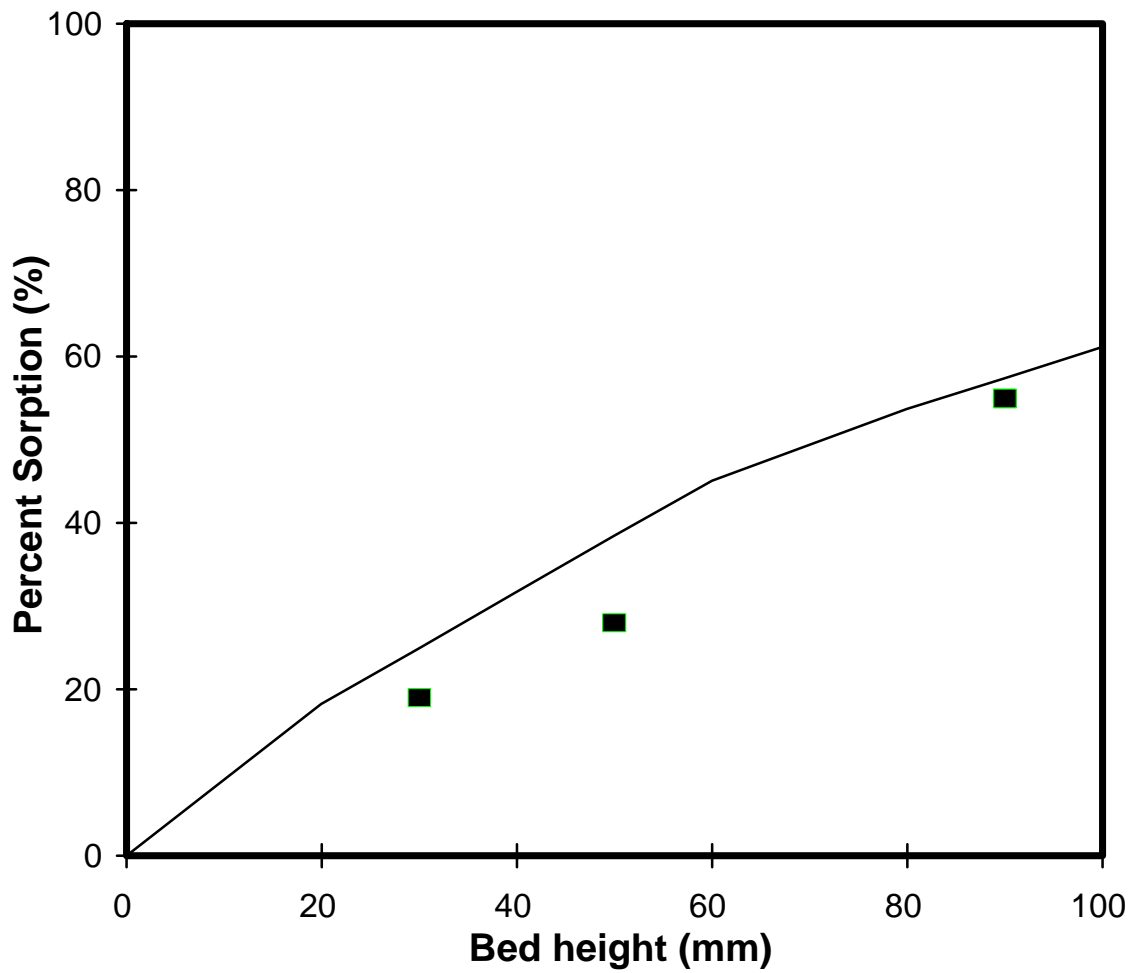


Figure 18. Experimental and simulation results on mercury sorption at various sorbent bed height (Mercury: HgCl_2 ; Vaporization Temperature: 500°C ; Duration: 60 minutes).

CHAPTER 5. PROJECT CONCLUSIONS

Toxic (or potentially toxic) trace metallic elements such as barium, beryllium, boron, cadmium, chromium, lead, mercury, nickel, performed selenium, strontium, vanadium, zinc and zirconium are usually contained in coal in various forms. 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. Most of the emitted metals will be in the form of metal fumes or particulates with diameters less than 1 micron and are potentially hazardous to the environment. 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 metals are listed as potential air pollutants.

Current practice of controlling trace metal emissions during coal combustion employs conventional air pollution control devices (APCDs), e.g., venturi scrubbers, electrostatic precipitators, baghouses etc., to collect fly ash and metal fumes. This type of control is essentially a cold-end control because metals are allowed to vaporize and condense before being controlled. The control may not always be effective on metal fumes due to their extremely fine sizes.

An alternative technology for metal emission control is to minimize the formation of metal fumes at the hot-end of the coal combustion process, i.e., in the combustion chamber. The technology proposed is to prevent the metal fumes from forming during the process, which would effectively eliminate the metal emission problems. Specifically, the technology is to employ suitable sorbents to (1) reduce the amount of metal volatilization during combustion and (2) capture volatilized metal vapors. The objectives of the project are to demonstrate the technology and to characterize the metal capture process during coal combustion in a fluidized bed combustor.

The characteristics of metal capture by various sorbents during fluidized bed coal combustion are reported in Chapter 2. Metal capture experiments were carried out in a 25.4 mm quartz fluidized bed combustor enclosed in an electric furnace. The metals involved were cadmium, lead, chromium, arsenic, and selenium, and the sorbents tested included bauxite, zeolite, and calcined limestone. 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 sorbents can be as high as 88% depending on the metal species and sorbent involved. 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.

The characteristics of simultaneous sulfur and metal capture by calcined limestone during fluidized bed coal combustion are reported in Chapter 3. Experimental results on seven coal samples have indicated that the capture process can be effective. Good fluidization, however, is essential in achieving the optimum capture efficiency which was observed to range from 93% to 15% in the order of cadmium, sulfur, lead, chromium, arsenic, and selenium. Also reported are capture mechanism, effect of metal concentration in coal, and effect of bed temperature.

Mercury concentrations in the spent sorbents and the combusted coal fly ash were also measured during the above metal capture experiments. It was found that neither of them contained any mercury. To further investigate the mercury sorption characteristics, mercury was intentionally diffused into sorbents and the mercury-loaded sorbents was placed in a high temperature furnace to test the reactivity between mercury and the tested sorbents at elevated temperatures. All the mercury was observed to have completely vaporized at about 500°C. The observations indicated that mercury can not be retained by the tested sorbents at the combustion temperatures. The conclusion appears to be supported by equilibrium calculations where $\text{Hg}^{\circ}(\text{g})$ is determined to be the thermodynamically preferred species at high temperatures and no potential reactions can be identified between $\text{Hg}^{\circ}(\text{g})$ and any other species. Although mercury can not be retained by sorbents under combustion conditions, effective mercury emission control can be accomplished at low temperatures during the cooling of combustion flue gas. Two promising methods are sorbent injection and fixed bed adsorption using effective sorbents, such as activated carbon.

The adsorption/desorption characteristics of mercury on various sorbents at relatively low temperatures are reported in Chapter 4. Experiments were carried out in a 25.4 mm (1") ID fixed bed absorber. The mercury compounds involved were mercury chloride and elemental mercury, and the sorbents tested included bauxite, zeolite, lime, alumina and activated carbon. Experimental parameters were air flow rate, vaporization temperature, sorbent bed temperature, sorbent bed height, and sulfur impregnation. The Toxicity Characteristics Leaching Procedure (TCLP) tests were also performed to evaluate the leachability of the retained mercury. The results indicated that different sorbents have different mercury sorption capacity. Bauxite and activated carbon were found to be more effective than other tested sorbents for mercury retention. Besides experimental investigations, potential mercury reactions during the experiments were identified through equilibrium simulations and a model based on the mass transfer control mechanism was proposed to simulate the mercury sorption process. The proposed sorption model appeared to describe reasonably well the experimental results. Additional study, however, is needed for optimum implementing the mercury control technology.

In Summary, toxic trace heavy metals are generally classified into three groups, namely volatile, semi-volatile, and refractory. Among the 11 metals listed in the Clean Air Act Amendments of 1990, i.e., Sb, As, Be, Cd, Cr, Co, Pb, Hg, Mn, Ni, and Se, mercury and selenium are classified as volatile; arsenic, cadmium and lead are semi-volatile; and the rest of the metals are refractory. For coal combustion, the most troublesome metals are mercury and selenium because they tend to stay in gas phase and are less reactive with sorbents at high temperatures as reported in this project. Additional control technologies such as low temperature sorbent injection/carbon adsorption or acid scrubbing are required to effectively control their emissions. The semi-volatile metals, i.e., arsenic, cadmium and lead, also tend to volatilize during combustion and, if not reactively retained by sorbents, will eventually recondense during flue gas cooling to form metal fumes or to deposit on fine particular matter (PM). The efficient collection of fine particular matter, micron and sub-micron in size, is therefore extremely crucial to control the emissions of these metals. These metals, however, are found to be relatively reactive and can be effectively retained by sorbents at high temperatures as demonstrated in the current project. The refractory metals are thermally stable and most of them will stay in bed ash or fly ash without being vaporized. The effective control of fly ash emission therefore controls

the emissions of these metals. In this group of metals, the behavior of chromium during coal combustion often receives more attention because chromium has potential to transform into chromium (+6) which is more volatile and more toxic than chromium (+3).

Overall, the project has generated 18 presentations and/or publications in professional conferences and journals. They are listed below:

1. Ho et al., "Transformation of Chromium from Cr(III) to Cr(VI) in a Simulated Wet Scrubber," Proceedings of the 1995 International Incineration Conference held in Bellevue, Washington, pp. 569-573, May 8-12, 1995.
2. Ho et al., "Lead and Cadmium Capture by Various Sorbents During Fluidized Bed Combustion/Incineration," Proceedings of the 8th International Fluidization Conference held in Tours, France, pp. 899-906, May 14-19, 1995.
3. Ho et al., "Metal Behavior During Fluidized Bed Thermal Treatment of Soil," Waste Management, **15**, 325 (1995).
4. Ho, T.C., "Control of Trace Metal Emissions During Coal Combustion," paper presented at the 1995 DOE Review of Fossil Energy Advanced Research Projects Conference held in Nashville, TN, June 13-15, 1995.
5. Ho et al., "Effect of Chlorine and Sulfur on Metal Capture by Sorbents During Fluidized Bed Incineration," Proceedings of the 1996 International Incineration Conference held in Savannah, Georgia, pp. 415-422, May 6-10, 1996.
6. Ho, T.C., "Control of Trace Metal Emissions During Coal Combustion," paper presented at the 1996 DOE Annual UCR Contractors Review Conference held in Pittsburgh, PA, June 4-5, 1996.
7. Ho et al., "Trace Metal Capture by Various Sorbents During Fluidized Bed Coal Combustion," paper presented at the 212th ACS National Meeting held in Orlando, Florida, August 25-30, 1996.
8. Lee and Ho et al., "Dynamic Volatilization Characteristics of Heavy Metals During the Thermal Treatment of Contaminated Soil," Proceedings of the Fifth Asian Conference on Fluidized-Bed & Three-Phase Reactors held in Hsitou, Taiwan, pp. 200-206, December 16-20, 1996.
9. Ho et al., "Trace Metal Capture by Various Sorbents During Fluidized Bed Coal Combustion," Proceedings of the Fifth Asian Conference on Fluidized-Bed & Three-Phase Reactors held in Hsitou, Taiwan, pp. 207-212, December 16-20, 1996.
10. Ho et al., "Trace Metal Capture by Various Sorbents During Fluidized Bed Coal Combustion," pp. 877-888, Proceedings of the 22nd International Conference on Coal Utilization & Fuel Systems held in Clearwater, FL, March 16-19, 1997.

11. Ho et al., "Metal Vaporization and Metal Binding by Additives or Sorbents During High Temperature Thermal Treatment," pp. 761-768, Proceedings of the 1997 Incineration Conference held in Oakland, CA, May 12-16, 1997.
12. Ho, T.C., "Trace Metal Capture by Various Sorbents During Fluidized Bed Coal Combustion," paper presented at the 1997 DOE Annual UCR Contractors Review Conference held in Pittsburgh, PA, June 3-4, 1997.
13. "Effect of Temperature on Mercury Desorption from Sorbents in a Packed Bed Absorber," paper presented at the 1997 AIChE Los Angeles Annual Meeting, November 16-21, 1997.
14. Ho et al., "Simultaneous Sulfur and Metal Capture by Lime During Fluidized Bed Combustion," paper accepted for publication at the AIChE Symposium Series on Fluidization and Fluid Particle Systems (1998).
15. Ho et al., "Adsorption and Desorption of Mercury on Sorbents at Elevated Temperatures," paper presented at the 5th International Congress on Toxic Combustion By-Products held at the University of Dayton, June 25-27, 1997 and accepted by Combustion Sci. & Tech. for publication (1998).
16. Ho et al., "Multipollutants Air Emission Control During Fluidized Bed Combustion," paper accepted for presentation at the 28th Annual Meeting of the Fine Particle Society to be held in Dallas, TX, April 1-3, 1998.
17. Ho et al., "Characterization of Mercury Desorption from Spent Sorbents During Regeneration at Elevated Temperature," paper accepted for presentation at the 1998 Incineration Conference to be held in Salt Lake City, Utah, May 11-15, 1998.
18. Ho et al., "Simultaneous Sulfur and Metal Capture by Lime During Fluidized Bed Coal Combustion," paper accepted for presentation at the 9th International Fluidization Conference to be held at Durango, CO, May 17-22, 1998.