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Control of Trace Metal Emissions During Coal Combustion

Quarterly Report
July 1 - September 30, 1997

By
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TECHNICAL PROGRESS REPORT

(July 1, 1997 through September 30, 1997)

Prepared

for the Project

CONTROL OF TRACE METAL EMISSIONS DURING COAL COMBUSTION

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October 1997

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Project Title: **CONTROL OF TRACE METAL EMISSIONS DURING COAL COMBUSTION**
DOE Grant Number: DE-FG22-94PC94221
Principal Investigator: Thomas C. Ho, Lamar University
DOE Project Officer: Mike Baird, FETC

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.

The project was started on July 1, 1994 and this is the thirteenth quarterly technical progress report. Specifically, the following progress has been made during this performance period from July 1, 1997 through September 30, 1997:

1. **Metal Capture Experiments Continued** - Additional combustion experiments involving seven different coal samples were carried out to obtain more statistically representative results.

2. **Additional Results Obtained** - Additional metal capture results were obtained and were added into the existing database. The metals involved included lead, cadmium, chromium, arsenic, and selenium.

3. **Presentation Accepted** - An abstract, entitled "Effect of Temperature on Mercury Desorption from Sorbents in a Packed Bed Absorber," has been accepted for presentation at the 1997 AIChE Annual Meeting to be held in Los Angeles, CA, November 16-21, 1997.

4. **Presentation Submitted** - An abstract, entitled "Simultaneous Sulfur and Metal Capture by Lime During Fluidized Bed Coal Combustion," has been submitted to the 9th International Conference on Fluidization to be held in Durango, Colorado, May 17-22, 1998 for presentation.

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EXECUTIVE SUMMARY

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.

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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):

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

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

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

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

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 SO_2, the following reaction has been well-recognized:

$$CaO(s) + SO_2(g) + 1/2\ O_2(g) \text{ ----> } CaSO_4(s) \quad (E)$$

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 concentration of sulfur, chlorine, and the target metals in coal samples and calcined limestone (lime) is 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-SiO_2 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 SiO_2) - 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 $CaSO_4(s)$ between 730^{o}C and 900^{o}C and the formation of $PbSO_4(s)$ below 730^{o}C. No chemical reactions between lead and CaO, however, are identified. For comparison purpose, the results shown in Figure 4 for the Pb-S-SiO_2 system indicate that, without the existence of CaO, lead will predominately be in the form of $PbSO_4(s)$ up to about 950^{o}C. It then will either decompose to from PbO(g) or react with $SiO_2(s)$ to form $Pb_2SiO_4(s)$, which strongly implies the metal capture reaction of PbO(g) by $SiO_2(s)$.

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^{o}C experiments and around 19 g and 8 g for 900^{o}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^{o}C, the overall sulfur capture efficiency is high and the majority of the capture is by the bed lime. However, at 900^{o}C, the overall sulfur capture efficiency is lower and the capture by the cyclone lime is more significant as compared to those at 750^{o}C. This observation is further detailed by the results shown in Figs. 7 and 8 where it is seen that, at 750^{o}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^{o}C, the trend is reversed. The observation is believed to be due to the equilibrium effect, i.e., the formation of $CaSO_4$(s) is not thermodynamically dominating at a high bed temperature around 900^{o}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

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^{o}C, 900^{o}C
Lime Bed U_{mf} (750^{o}C, 900^{o}C)	4.9, 4.5 cm/sec
Combustion Duration	4.5 hrs (60 g coal)

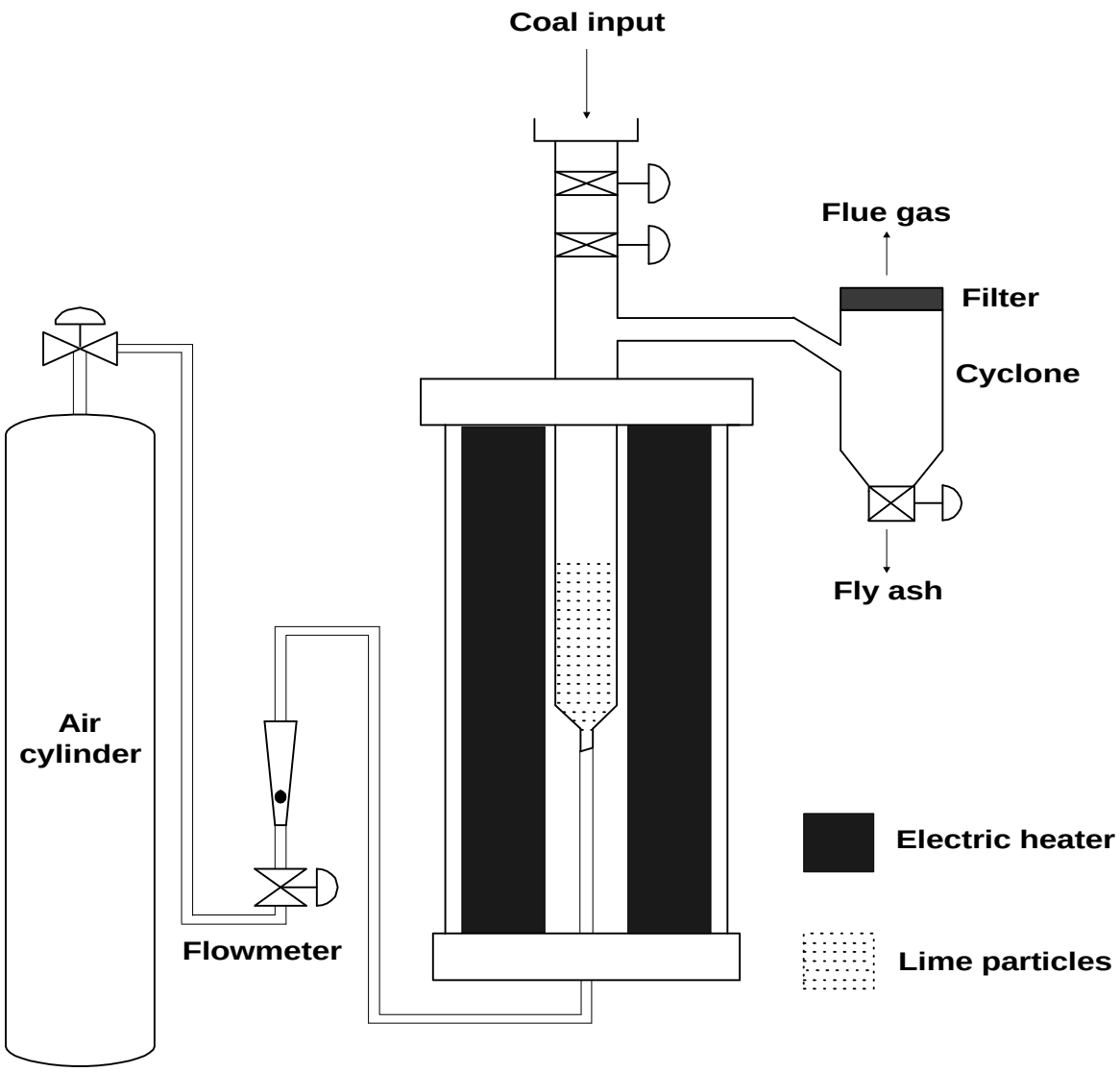

Fig.1. Fluidized bed coal combustion system.

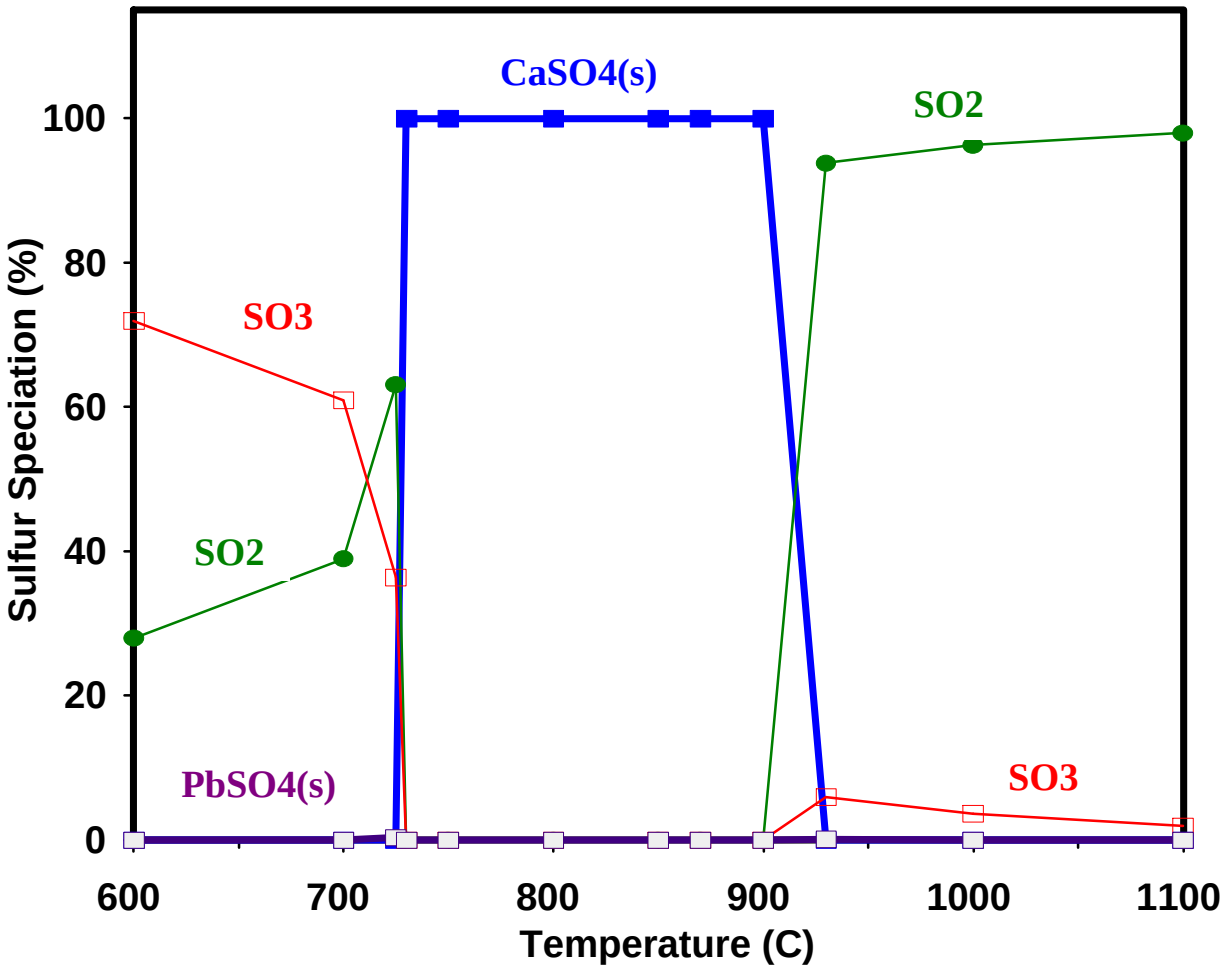

Fig.2. Equilibrium sulfur speciation in a Pb-S-CaO system.

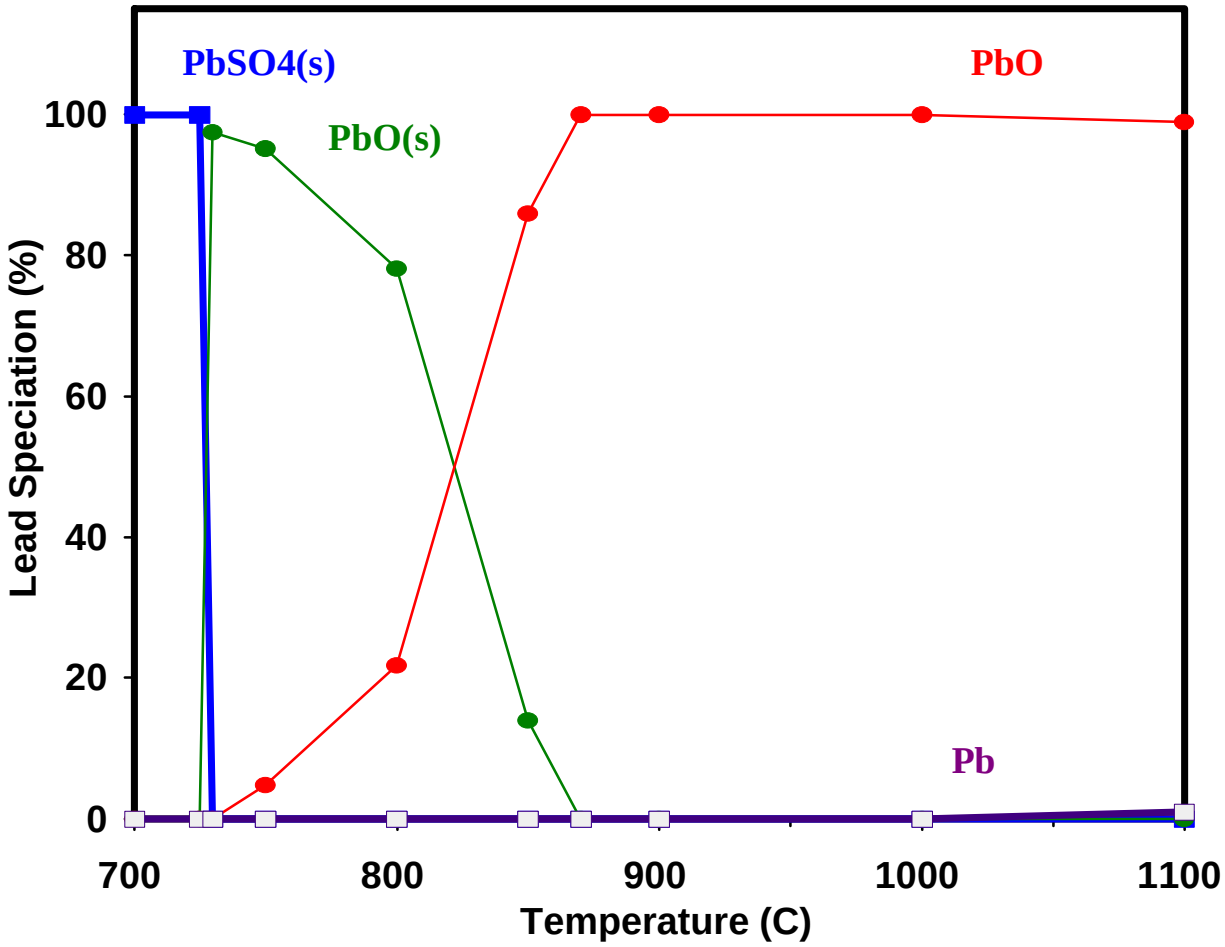

Fig.3. Equilibrium lead speciation in a Pb-S-CaO system.

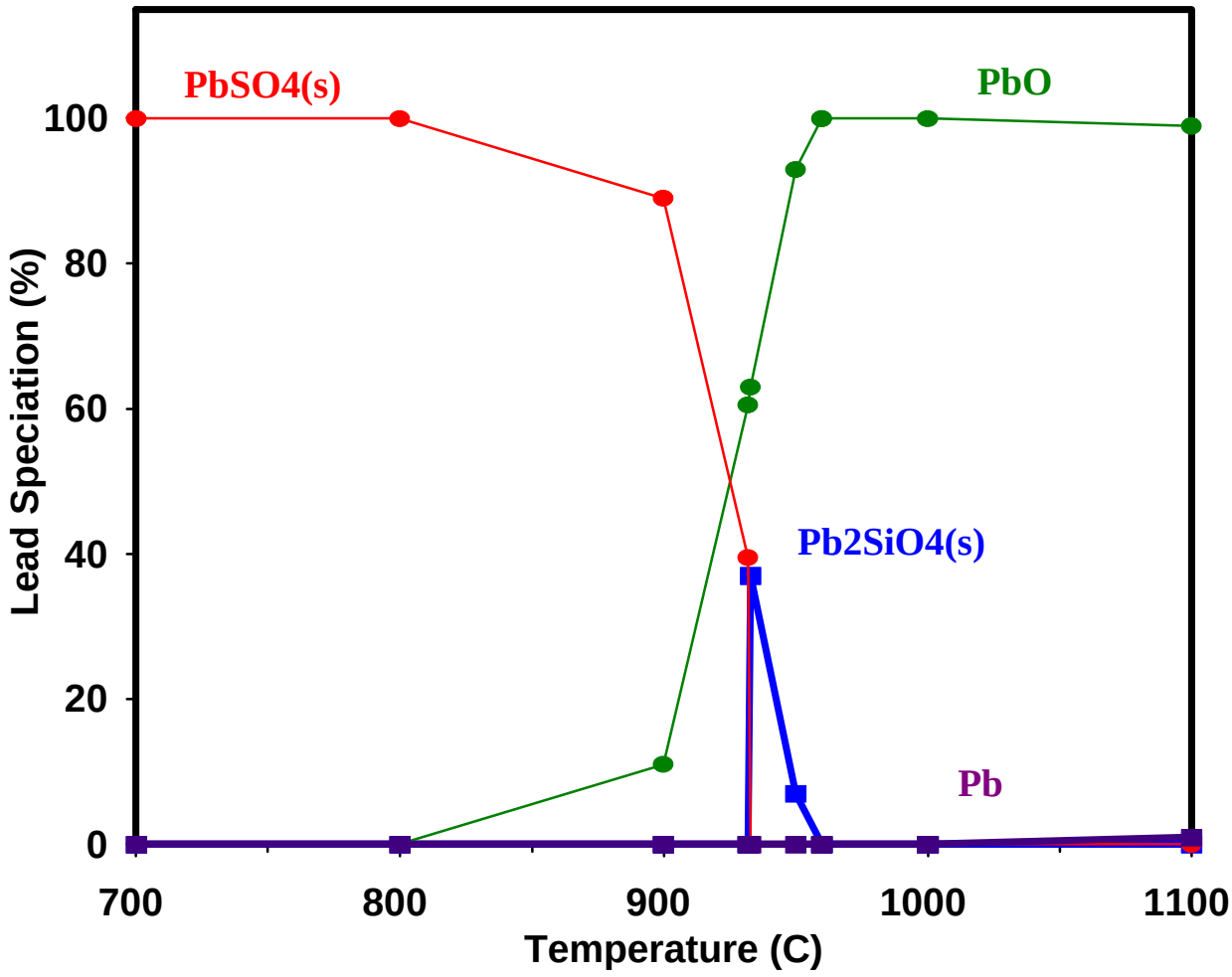

Fig.4. Equilibrium lead speciation in a Pb-S-SiO_2 system.

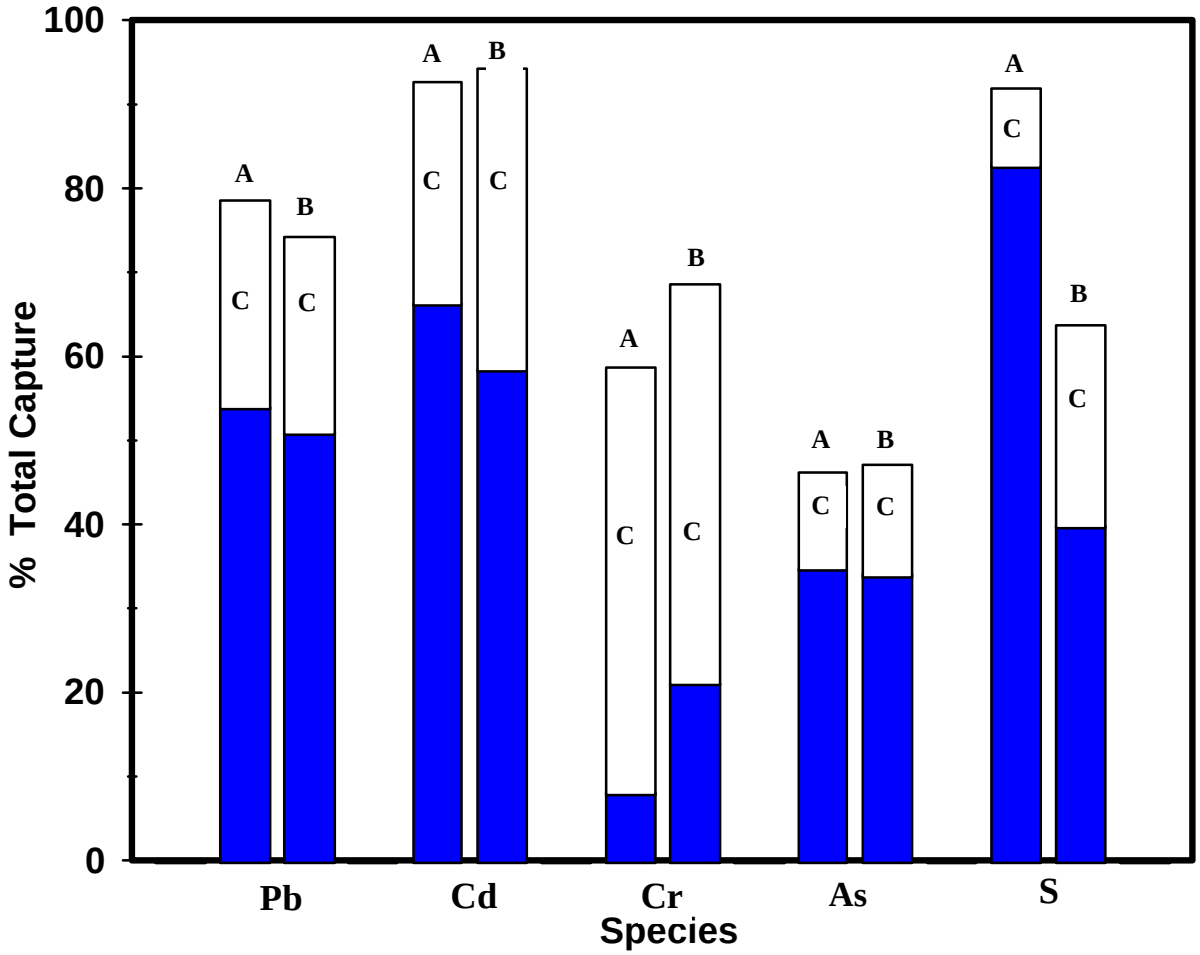

Fig.5. Average capture efficiency by bed and cyclone residue (A:750^{o}C, B:900^{o}C, C:Cyclone Capture, Dark Area: Bed Capture).

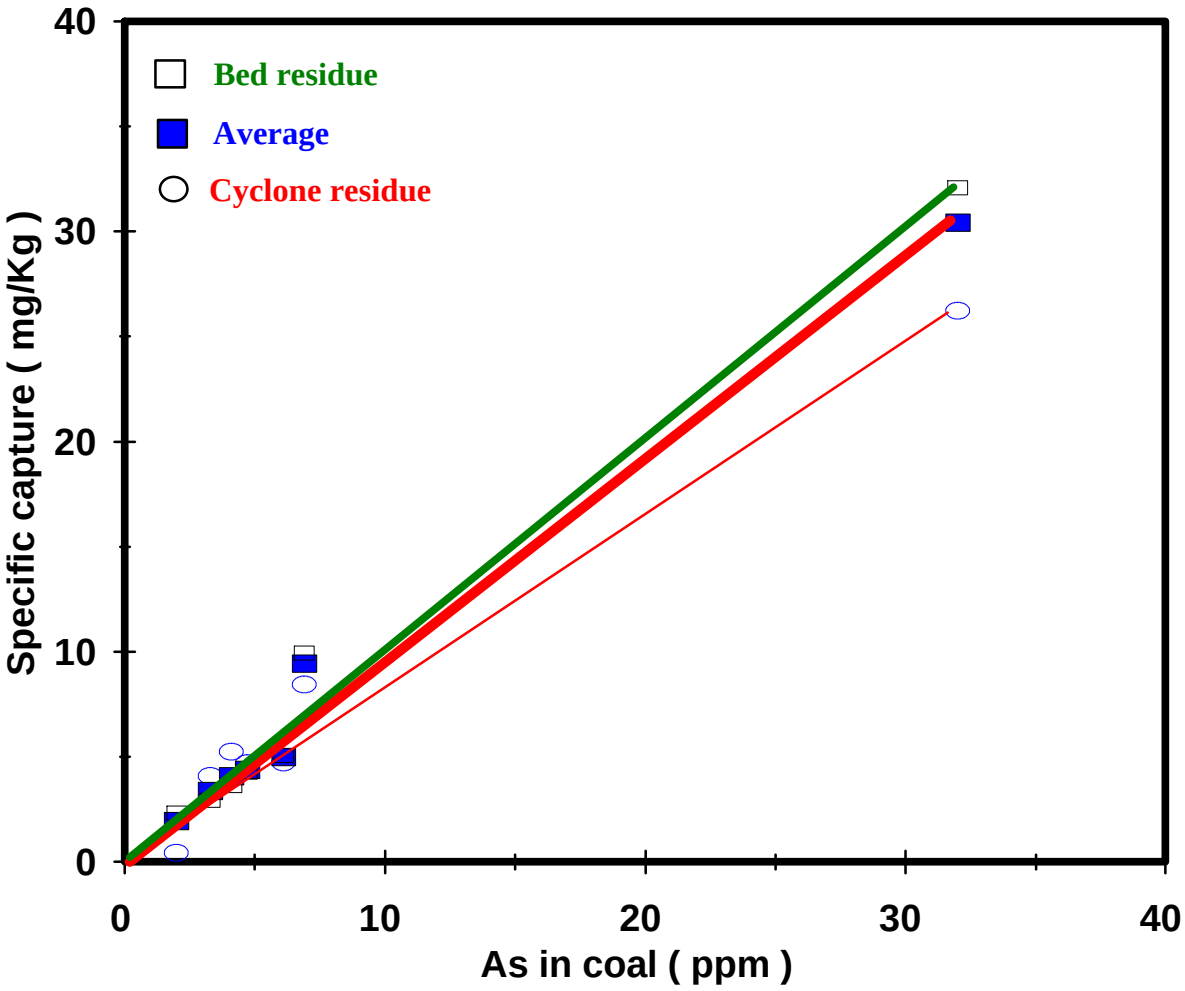

Fig.6. Arsenic capture by bed and cyclone residue at 900^{o}C.

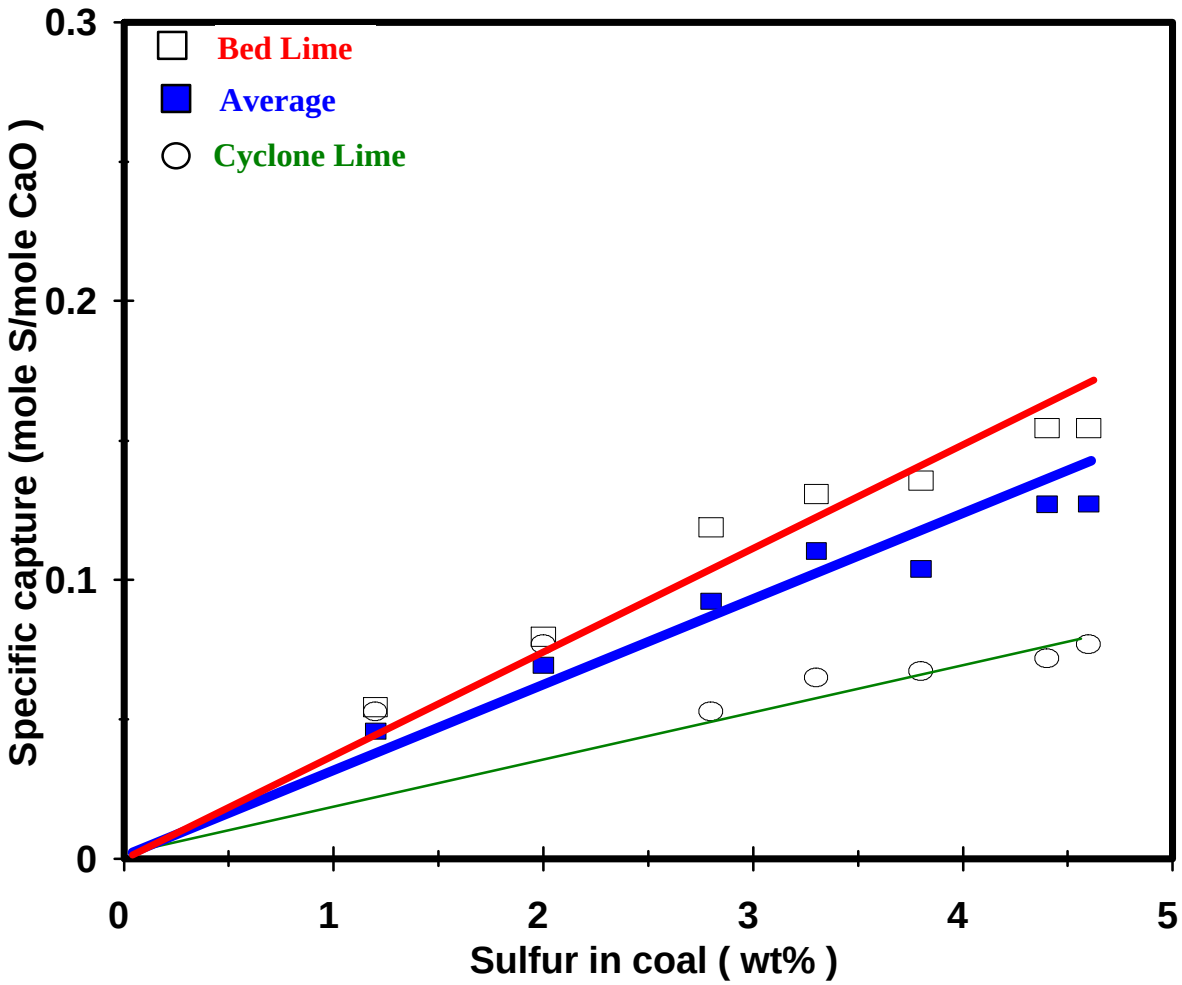

Fig.7. Sulfur capture by bed and cyclone lime at 750°C.

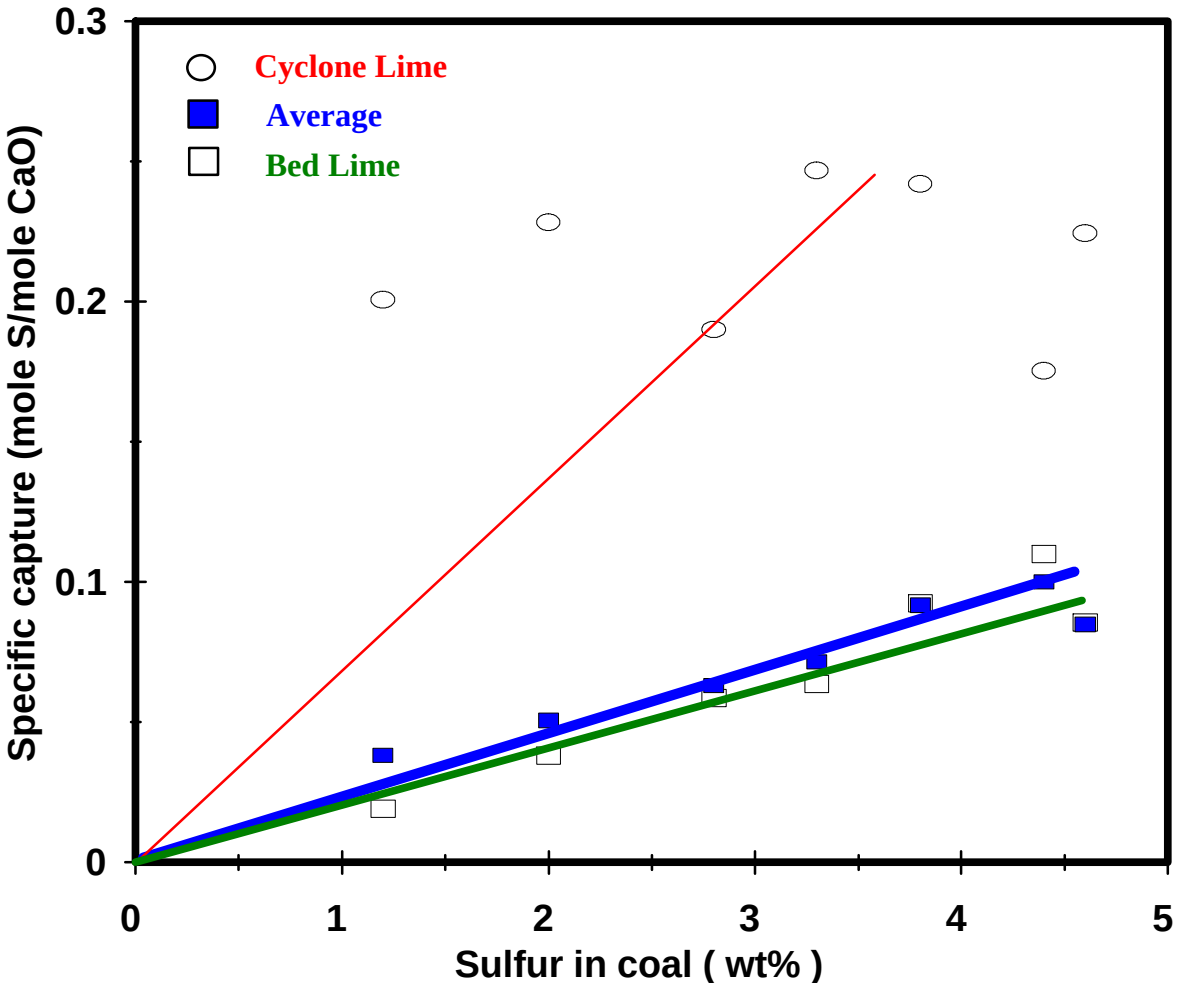

Fig.8. Sulfur capture by bed and cyclone lime at 900^{o}C.