THE EFFECT OF CHLORIDE ON EMISSIONS FROM ATMOSPHERIC FLUIDIZED BED COMBUSTORS

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ABSTRACT
The ability to capture SO_2 is one of the most important advantages of fluidized bed combustion. Also the capture of halogen species by limestone may help in the use of high chlorine coals. In order to clarify the affects of chlorine in the absorption of SO_2 and other emissions, experiments involving PVC addition have been carried out using the 12-inch laboratory AFBC system at Western Kentucky University. From the emission studies, the experimental results showed that SO_2 concentration in flue gases is dramatically reduced when PVC is fed into the combustor at a rate of 1% by weight of the fuel, and then leveled off when PVC feeding is 3.3%. These results are explained in terms of the interaction between SO_2 and HCl. Meanwhile, the addition of PVC resulted in decreases of CO_2 and increases in the O_2 level in the flue gas. This indicated that HCl, as a flame inhibitor inhibits CO oxidation. A mechanism involving the interaction between HCl and SO_2 in AFBC systems is proposed.

INTRODUCTION
It is well known that the emission of SO_2 from coal-fired power plants is one of the main reasons for acid rain, and SO_2 together with hydrogen chloride emitted from coal combustion may play roles in the corrosion of boiler components. Collectively, such emissions cause some operational and economic concerns.[1] In situ sulfur and halogen capture by limestone is a major advantage of fluidized bed combustion (FBC). Experimental work on the retention of sulfur and halogen species has been studied for decades. It has been found that sulfur and halogen capture by sorbents are interrelated.[2,3]

Incineration is an important waste-to-energy technology used for the disposal of municipal solid waste (MSW). However, it is necessary to reduce the possibility of the forming volatile organic compounds (VOCS) during combustion before incineration can reach its full potential. In previous work, the proposed mechanism for the formation of chlorinated organics and possibly polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDF) has been proposed as follows:[4]

PVC $\rightarrow$ HCl (undergoes thermal decomposition)	(1)
$4HCl + O_2 \rightarrow 2H_2O + 2Cl_2$ (Deacon Reaction)	(2)
$C_6H_5OH + Cl_2 \rightarrow$ chlorophenols	(3)
Condensation of chlorophenols $\rightarrow$ PCDDs and PCDFs	(4)

Chlorine gas is a key intermediate in the formation of chlorinated compounds. It is generally thought that it is molecular chlorine, but not HCl, that reacts with aromatic compounds such as phenols, to produce chlorinated aromatic compounds, such as chlorophenols and polychlorophenols, which are precursors to PCDDs and PCDFs. On the other hand, it is also believed that molecular chlorine, instead of HCl, that attacks metal in coal-fired combustion systems causing corrosion.

In previous studies, it was found that SO_2 emission decreases with an increase in the chlorine content of coal used for combustion in an AFBC system. Also, the sulfur content in ash (both fly ash and bed ash) increases in the same time. It was reported that the presence of halide species may help SO_2 capture.[2]

The main objectives of the study reported in this paper are to study the chlorine-sulfur interactions during coal combustion and to investigate new ways for using AFBC systems with high sulfur/high chlorine coal co-fired with MSW to minimize SO_2 emission and the emission of chlorinated aromatic compounds (such as PCDDs and PCDFs).

EXPERIMENTAL
All experimental work was conducted with the 0.3-meter (12-inch) laboratory AFBC system at Western Kentucky University. A full description of the AFBC system has been previously reported,[5] so only a brief description is given in this paper. In this project, an under-bed continuous feed

fuel/limestone system was installed in the AFBC system. This modification improved combustion efficiency to around 95%. Six movable bed heat exchangers in the bed area were added to the AFBC system. Typical operation involves setting the correct coal/limestone feed and air flows and then using the movable tubes to adjust the bed temperature to the desired setting. Another sixty-six gas heat exchanger tubes are in fixed position located approximately one meter from the top of the combustor. The hot gases from the combustor are allowed to enter a wet cyclone where they are met with a wall of water (which keeps the cyclone cool), which subsequently takes almost all solids to the bottom of the cyclone into a holding tank. The combustor's operating parameters (air/water flow, coal/limestone feed, fuel bunker weight, temperatures, and pressure) are controlled and logged to file with a Zenith 150 MHz computer utilizing the LABTECH software version 3.0. During the combustion runs any needed changes in the parameters can easily be entered into the computer, by accessing the correct control screen and making the necessary corrections on line.

Two coals were used in this study, an Illinois # 6 coal (0.28% Cl and 2.4% S) and an eastern Ky coal (95010). Analytical data for the two coals and the limestone used in the study are presented in Table 1. The limestone came from Kentucky Stone in Princeton, KY. The coal and limestone both were air dried before being crushed to -4 mesh (4.75 mm). The limestone also was used as the bed material in the AFBC system. The PVC was mixed with coal as a 0.1% by weight and 0.33% by weight. During combustion runs, limestone also was fed into the system at a constant rate dependent upon the fuel used.

A full description of the flue gas sampling system and procedure, as well as the fly ash and bed ash sampling procedures, has been presented elsewhere.[5-7] During combustion runs the flue gases at the gas heat exchanger region were analyzed continuously using on-line FTIR spectroscopy and gas chromatography.

The major operating parameters for the experiments were as follows: excess air level -- around 1.3; Ca/S ratio -- approximately 3; bed temperature was controlled between 1140 K and 1160 K.

RESULTS AND DISCUSSION

One of the objectives of this study was to illustrate that SO_2 emission decreases as the amount of chloride in the fuel mixture used in the AFBC system increased. PVC is the principal source of chloride in the fuels used in the study. Figure 1 shows that SO_2 emission decreases as the amount of PVC used in the fuel mixture increases. It can be clearly seen that the SO_2 emission decreases dramatically when a mixture of 1% by weight of PVC with coal is fed into the combustor, and then leveled off when the PVC content in the fuel mixture increases from 1% to 3.3%. The sulfur contents in the fly ash and bed ash increase with an increase in the amount of PVC used in the fuel. Figure 2 illustrates that the sulfur content in the fly ash increases as the PVC/fuel ratio increases. Likewise, Figure 3 shows that the sulfur content of the bed ash increases with an increase in the PVC/fuel ratio. One explanation of the increased capture of SO_2 by the limestone is that the transient formation of liquid calcium halide phases can modify the surface of the partially sulfated sorbent particles, leading to increased SO_2 capture.[2] However, a more complex mechanism includes the possibility that the SO_2 from fuel sulfur combustion would undergo reaction with Cl_2 to form HCl and SO_3. Molecular chlorine is a key organic chlorinating agent and is replaced by HCl, which is less likely to cause any chlorination of organic species. In the case of HCl emissions, both HCl concentration in the flue gas and the chlorine contents in fly ash and bed ash increase with the increase of amount of PVC in the fuel.

The results of the effect of limestone on the capture both SO_2 and HCl are shown in Tables 2 and 3. With the presence of limestone, there is a significant improvement in the sulfur capture from the flue gas. Likewise, the sulfur contents in both fly ash and bed ash increase. In contrast, there is no significant difference in the emission of HCl regardless of the amount of limestone used. These results are in agreement with previous studies in our lab,[8] as well as Liang's work,[9] in which it was reported that chlorine is not effectively captured by limestone sorbent in both bubbling and circulating fluidized bed combustors.

A possible mechanism for the interaction between SO_2 and HCl can be proposed from the combination of results from previous reports[9] and those given in this paper. Thermodynamic data[10] shows the Deacon reaction (Reaction 2, as previously given)

$$4HCl + O_2 \rightarrow 2H_2O + 2Cl_2 \text{ (Deacon Reaction)} \qquad (2)$$

is favored over the range of temperatures from 300 K to 1500 K and is exothermic at 25°C (ΔH = -114 KJ/mol, ΔG = -76 KJ/mol). An increase in temperature will cause the equilibrium to move toward the reactants, which will lower the conversion of HCl to Cl_2. Before the equilibrium is reached, however, the reaction is predominantly kinetically-controlled. A rise in temperature will lead to more products. Yang[11] reported that in the case where the reaction takes place in a steady moving gas flow and no catalysts are present, the reaction is far from equilibrium. Consequently, a higher temperature will lead to a higher reaction rate, meaning more Cl_2 will be produced. Also it should be noted that the Le Chatelier principle indicates that the addition of oxygen to the system to enhance the combustion process would tend to form more Cl_2.

When SO_2 is present from coal sulfur combustion, a most interesting and important reaction is that SO_2 may be attacked by Cl_2 to form SO_3 and HCl:

$$Cl_2 + SO_2 + H_2O \leftrightarrow 2HCl + SO_3 \quad (5)$$

During atmospheric fluidized bed combustion, SO_3 will be absorbed by limestone, according to the reactions represented by the following equations:

$$CaCO_3 \rightarrow CaO + CO_2 \text{ (calcination)} \quad (6)$$

$$CaO + SO_3 \rightarrow CaSO_4 \text{ (sulfation)} \quad (7)$$

The use of limestone as the bed material and feeding coal and limestone mixtures in fluidized bed combustion will keep excess CaO in the combustor. It is believed that it is SO_3, not SO_2, that reacts with CaO to form $CaSO_4$. Reaction 7, therefore, will be favored. Consequently, this will promote SO_2 reacting with Cl_2 (reaction 5) to produce SO_3 and HCl to minimize both SO_2 and molecular chlorine emissions.

It has been well established that halogenated species are good flame inhibitors.[12] According to Bulewicz,[13] there is a phenomenon of halogen inhibition of oxidation of CO and other species in an AFBC system. Thus, it might be expected that the concentration of SO_2 may increase due to its incomplete combustion to SO_3 in the presence of chloride. Reaction 7, however, can promote the oxidation of SO_2 to SO_3 in the different ways through the Deacon Reaction in the presence of chloride and oxygen-rich conditions. These two effects compete with each other during coal combustion. From our experimental results, it is clear that reaction 7 predominates over the presence of chloride as the flame inhibitor.

CONCLUSIONS

From experimental investigations in an atmospheric fluidized bed combustor system of the influence of chlorine on sulfur capture, it was shown that the presence of HCl will promote SO_2 capture. On the other hand, the presence of sulfur will lead to the reduction of the formation of molecular chlorine. As a result, a minimization of the formation of PCDDs and PCDFs results. However, the optimum Cl/S ratio for the mechanisms proposed above can not be decided from this study and further studies are needed.

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Table 1. Analytical Data* for the Coals and Limestone Used in the Study.

	Coal 95010	Coal 95031	KY Limestone
Moisture	2.32	8.32	0.19
Ash	7.22	10.78	57.93
Volatile Matter	39.97	37.21	18.90
Fixed Carbon	52.82	52.02	22.98
Carbon	79.38	72.16	11.18
Hydrogen	5.31	4.82	0.16
Nitrogen	1.63	1.54	0.00
Sulfur	0.67	2.38	0.00
Oxygen	5.69	7.57	30.73
Chlorine (ppm)	1039	3070	36
BTU/pound	14077	12842	-----

* Moisture is as-determined, all other values are reported on a dry basis.

Table 2. The Effect of Limestone on the Distribution of Sulfur.

	Coal 95010 with 3.3% PVC		Coal 95031 with 3.3% PVC	
	with limestone	no limestone	with limestone	no limestone
SO_2 emission in the flue gas (ppm)	0.126	3.125	0.202	28.274
Sulfur content in fly ash (%)	0.739	n/a	1.295	1.271
Sulfur content in bed ash (%)	4.319	n/a	5.162	4.959

Table 3. The Effect of Limestone on the Distribution of Chlorine.

	Coal 95010 with 3.3% PVC		Coal 95031 with 3.3% PVC	
	with limestone	no limestone	with limestone	no limestone
HCl emission in the flue gas (ppm)	168.58	160.39	174.72	169.26
Chloride content in fly ash (%)	0.347	0.343	0.384	0.382
Chloride content in bed ash (%)	not determined	not determined	0.83	1.00

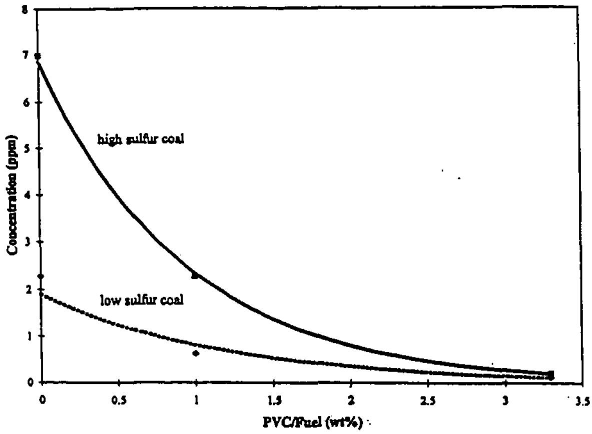

Figure 1. The effect of the PVC/fuel ratio on the emission of sulfur dioxide from the AFBC system.

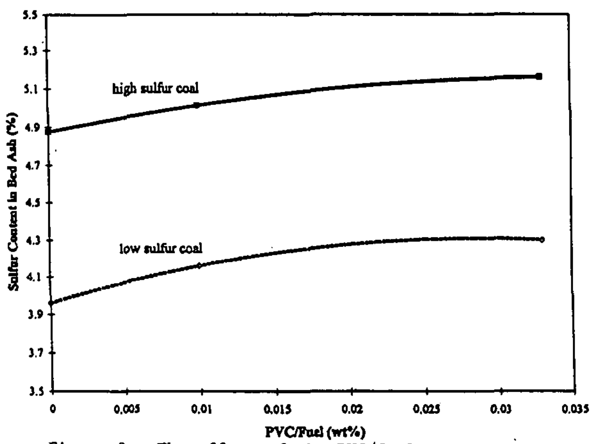

Figure 2. The effect of the PVC/fuel ratio on the concentration of sulfur in the fly ash of the AFBC system.

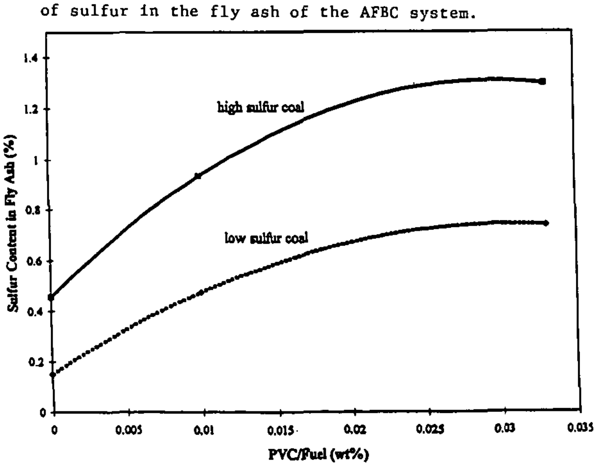

Figure 3. The effect of the PVC/fuel ratio on the concentration of sulfur in the bed ash of the AFBC system.