STUDIES OF CHLORINE AND SULFUR BEHAVIOR DURING COAL COMBUSTION IN AN AFBC SYSTEM

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INTRODUCTION

The laboratory sized atmospheric bed combustor (AFBC) at Western Kentucky University was designed to serve as a flexible research and development facility to gain operating experience, evaluate combustion performance, and estimate the effects of flue gas emissions. The operating conditions for the AFBC system are similar to those used at the TVA 160-MW AFBC Pilot Plant located near Paducah, Kentucky. Fluidized bed combustion systems are particularly suited to waste fuels because of their ability to burn low grade and variable fuels as well as absorb sulfur oxides through the use of limestone.

It has been demonstrated that the following parameters have an effect on the amount of sulfur retained in the fluidized bed: the molar calcium-to-sulfur ratio, the sorbent particle size, the gas phase residence time, sorbent reactivity, bed temperature, feed mechanisms, and excess air level.[1] The amount of limestone sorbent needed in a fluidized-bed combustor is proportional to the sulfur contained in the fuel and inversely proportional to the amount of calcium contained in the limestone. Calcium in the limestone which can be reacted with sulfur oxides depends on factors specific to the limestone and to the operating conditions in the fluidized-bed combustor.

The chloride content of coal varies from just a few ppm to thousands of ppm. Emissions of chloride from coal-fired plants can range from 50 to several thousand parts per million by volume, depending on the original concentration in the coal, the type of combustor, and any pollution control equipment installed. It has been estimated that 94% of the chloride in coal is volatilized, generally being emitted as gaseous HCl.[2] In an AFBC system limestone may be able to capture the chlorine. Limestone degenerates to CaO, and CaO reacts with HCl to produce $CaCl_2$.[3] In an AFBC system, capture of chloride by limestone in the combustion zone depends upon the temperature of the combustion zone and the ratio of calcium-to-sulfur. A study by Liang and others[4] showed that chloride capture has a large variation with temperature moving from a low of 18% gaseous HCl at 700°C to 99% HCl at 950°C. The resulting product is almost entirely in the form of liquid $CaCl_2$. Munzner and Schilling[5] studied the effect of limestone in a bench-scale AFBC system. The results showed that a greater recapture of chloride occurred with larger excesses of limestone, or when the Ca/S ratio was greater than 2.

To better understand the combustion behavior of sulfur and chlorine during coal combustion in an AFBC system, a comprehensive research project was performed at the Western Kentucky University on different aspects of emission reduction from fluidized beds during coal combustion. Some results of this study are reported in this paper.

EXPERIMENTAL

Two 1,000-hour burns were conducted with the 12-inch laboratory AFBC system at Western Kentucky University. Operating conditions similar to those at the 160-MW system at the TVA Shawnee Steam Plant located near Paducah, KY were used. A 1,000-hour burn was done with a low-chlorine (0.012% Cl and 3.0% S) western Kentucky # 9 coal (95011), which is the same type of coal as that supplied to the TVA plant during 1993. A second 1000-hour burn was conducted with high-chlorine (0.28% Cl and 2.4% S) Illinois # 6 coal (95031). Six moveable heat exchanger tubes are located within the bed area. Typical operation involves setting the correct coal/lime feeds and air flows and then using the moveable tubes to adjust the bed temperature to the desired setting. The combustor's operating parameters (air/water flow, coal/lime feed, bunker weight, temperatures and pressures) were controlled and logged to file with a Zenith 150 MHZ PC utilizing the LABTECH software version 3.0. During the combustion runs any needed changes in the parameters could easily be entered into the computer by accessing the correct control screen and making the necessary corrections on line. During combustion runs the flue gases at the heat exchanger region were analyzed continuously using on-line FTIR, GC, and IC instrumentation.

RESULTS AND DISCUSSION

The major operating parameters for the AFBC system were as follows: excess air level -- approximately 1.3; Ca/S ratio -- approximately 3; bed temperature -- 1144K, CO_2 level -- approximately -- 13%; oxygen in the flue gas -- 5-6%. Figure 1 shows the O_2 and CO_2 concentrations

in the flue gas at various positions above the fuel injection port. The influence of different process parameters on the emissions of SO_2 and HCl will be discussed.

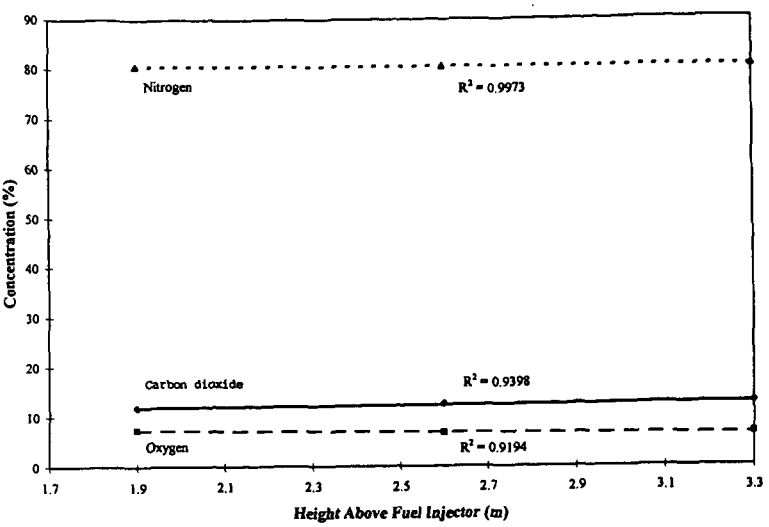

Figure 1. Flue gas composition in the center of the AFBC combustor at different heights above the fuel injection port.

The Effect of Bed Temperature. Figure 2 shows that the SO_2 emission increases as the bed temperature is increased. The optimal sulfur retention is obtained around 1120K. The sulfur retention reaches around 96% at this temperature. At higher temperatures (>1120K), the active internal surface of the limestone particles is decreased, which may be due to the effect of sintering of limestone particles. The thermal decomposition of the $CaSO_4$ under reducing conditions (such as in the presence of CO, hydrogen, or carbon) at the higher temperature may also contribute to the emission of SO_2. The effect of temperature on the emission of chloride is shown on the Figure 3. More HCl is observed when the temperature was raised to the higher temperature. The capture of HCl by limestone is more difficult than the capture of SO_2. Also, the reaction between HCl and CaO is more favorable at the lower temperature.[4]

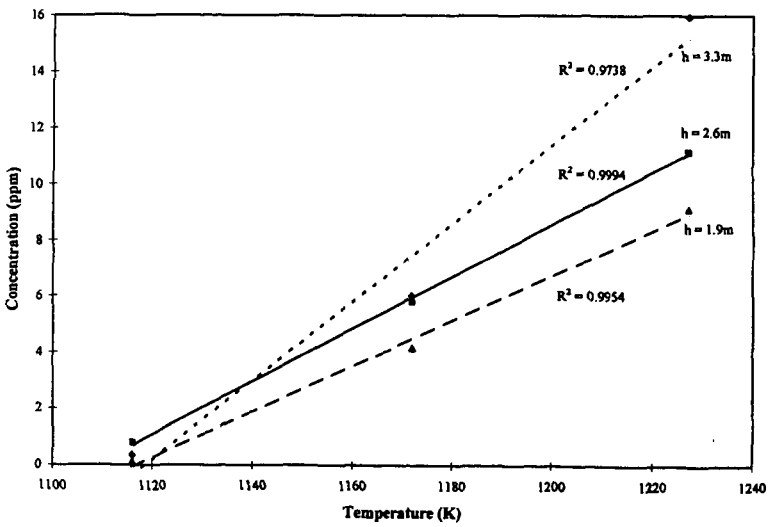

Figure 2. The effect of temperature on the emission of sulfur dioxide at different heights above the fuel injection port.

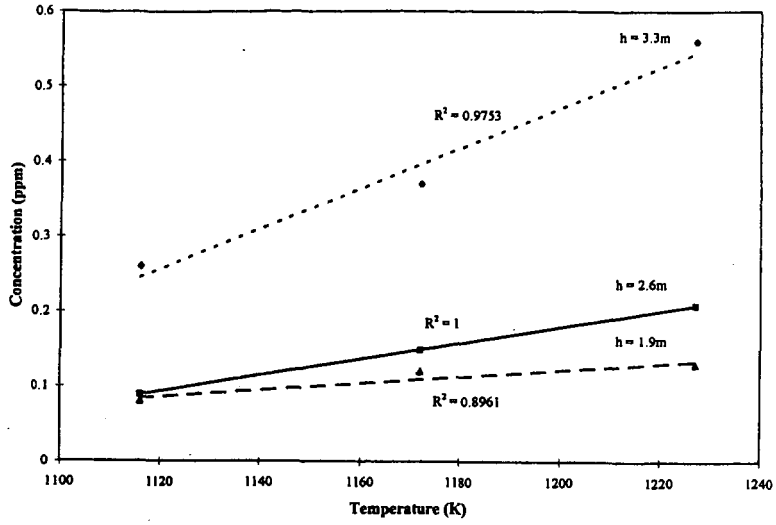

Figure 3. The effect of temperature on the emission of hydrogen chloride at different heights above the fuel injection port.

The Effect of Coal Type. Figure 4 shows the results of sulfur dioxide emission from tests with two different coals (95011 and 95031). It is clear that good sulfur capture is obtained between 1120K and 1170K for both coals. The higher sulfur oxide emission for coal 95011 observed at the higher temperature may be due to the effect of temperature and the higher sulfur content (3%). There is good agreement between the HCl emission and chloride content in the coal, as is illustrated in Figure 5. No chloride containing species were identified in a cold trap solution (methylene chloride with phenol).

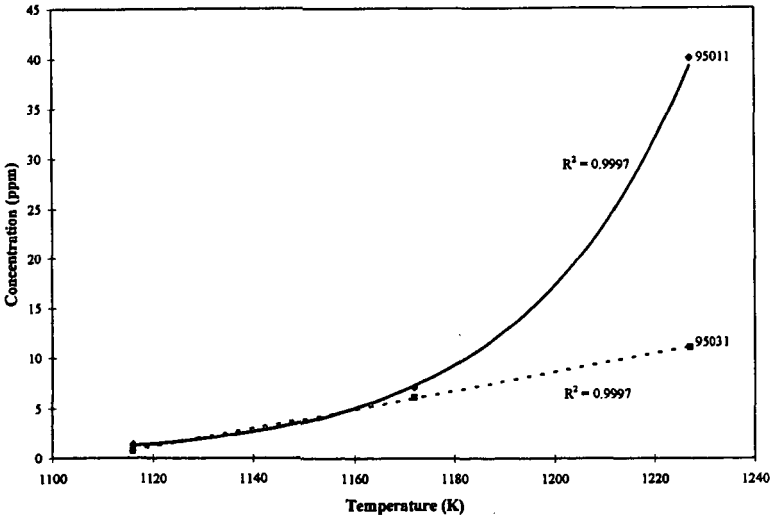

Figure 4. The effect of coal type on the emission of sulfur dioxide at different temperatures in the AFBC system.

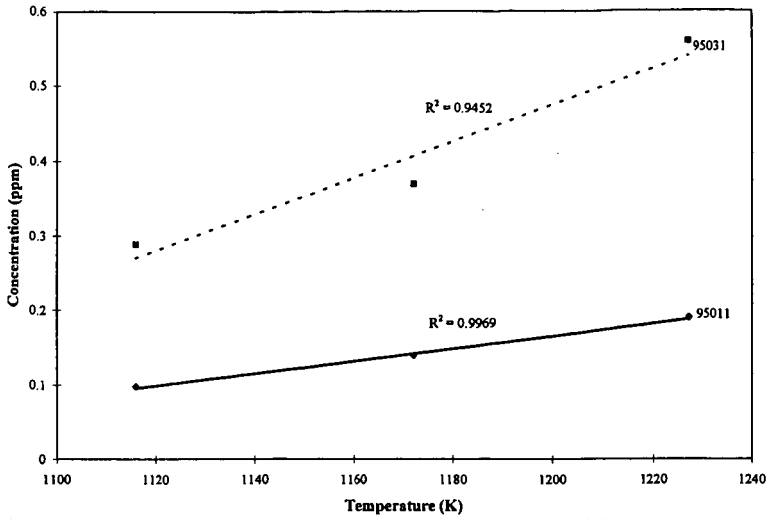

Figure 5. The effect of coal type on the emission of hydrogen chloride at different temperatures in the AFBC system.

The Effect of the Ca/S Ratio. In Figure 6 the measured SO_2 in the flue gas is plotted versus the calcium-to-sulfur molar ratio. The results indicate there is a significant improvement with the sulfur capture with the higher Ca/S ratio in the temperature between 1172 and 1227K. However, there is no effect at the optimal temperature (1116K). In the case of HCl emission, there is no significant difference on the emission of HCl between different Ca/S ratios, as is illustrated in Figure 7.

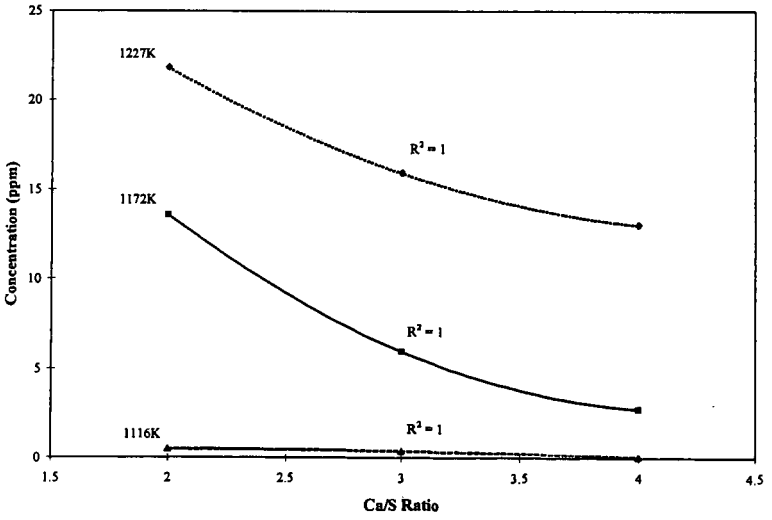

Figure 6. The effect of the Ca/S ratio on the emission of SO_2 different temperatures in the AFBC system.

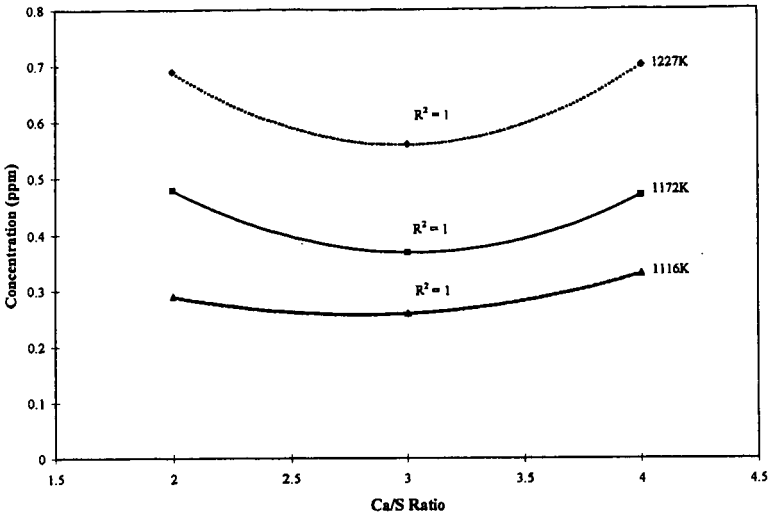

Figure 7. The effect of the Ca/S ratio on the emission of HCl at different temperatures in the AFBC system.

CONCLUSIONS

Based on the information presented in this paper summary statements that can be made include:

- The optimal sulfur retention is obtained around 1120K under our experimental conditions.
- The capture of HCl by limestone is more difficult than the capture of SO_2.
- Molecular chlorine was not identified in any of the flue gases from the AFBC system.
- There is no significant change in the emission of HCl when the Ca/S ratio is varied.

ACKNOWLEDGMENTS

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