FINAL TECHNICAL REPORT
September 1, 1997, through August 31, 1998

Project Title: **A STUDY OF CHLORINE IN HIGH TEMPERATURE CORROSION OF ALLOYS IN AN AFBC SYSTEM**

ICCI Project Number: 97-1/2.2A-1
Principal Investigator: Wei-Ping Pan, Western Kentucky University
Other Investigators: John T. Riley, Western Kentucky University
                          Ian G. Wright, Oak Ridge National Laboratory
Project Managers: Ken K. Ho, ICCI and Arun K. Mehta, EPRI

ABSTRACT

The possibility of corrosion of power plant boiler components and ash deposits on heat transfer surfaces are always major concerns when high sulfur and high chlorine coals are used. For this reason the chlorine content in some Illinois coals is a concern for potential end users of these coals. The major advantage of fluidized bed combustion (FBC) of fossil fuels is its ability to absorb sulfur oxides by limestone in the combustor. Limestone can also capture hydrogen chloride to form liquid or solid phase calcium chloride under relatively low temperatures in the freeboard area of an AFBC system, which can suppress the corrosion of boiler components caused by chloride compounds. The major purposes of this research project is to help the coal industry solve the corrosion and ash deposit problems that may be associated with the utilization of high chlorine coals, and to provide technical support for the operation of the 160 MWe atmospheric fluidized bed combustion (AFBC) boiler at TVA's Shawnee Steam Plant near Paducah, KY.

During the past year, the 0.1 MW_{th} AFBC facility at WKU was modified extensively, including the combustor, electrical system, gas and solid sampling systems, and the cooling system. The coal (15 tons) and limestone needed for the first 1000-hour test burn, which will begin the first week of September, 1998, were acquired and prepared. Samples of cooled tubes and uncooled-boiler tubes (210-C) were designed, constructed, and suspended in the AFBC system, as well as in an electrical furnace, to test the corrosion rates caused by chloride in the AFBC system and metal wastage caused by oxidation. Forty-two test coupons (14 each of 304SS, 309SS and 347SS alloys) were acquired and analyzed (composition, thickness, etc.). for tests in the AFBC system. Nineteen ash deposits (from previous test runs) were collected from different regions of the AFBC system and were analyzed for the elements and specific compounds present. A comprehensive study was carried out in a TGA and a small scale AFBC to better understand the interaction between chlorine and sulfur during combustion processes in AFBC systems. The results showed desulfurization efficiency can be improved significantly with the existence of HCl in the flue gas. Also, the retention of chlorine by limestone is increased when SO_x is in the flue gas.

EXECUTIVE SUMMARY

At least half the known economically minable coal reserves in Illinois have a chlorine content around 0.3%, which has been a concern for potential end users of these coals. Between 1992 and 1993, TVA's Shawnee Plant observed that the boiler tubes in the primary superheater region of the atmospheric fluidized bed combustion (AFBC) system had wastage/corrosion problems. The system had been firing some Illinois coal and in 1993 TVA declined to renew an Illinois Basin coal (0.4% Cl) contract for approximately 4 million tons per year. The decision was made solely on the chlorine content of the coal. This concern is reflected in the suggested coal chlorine limits used by boiler manufacturers and in the application of coal chlorine content limitations in coal contracts.

It is known that AFBC systems can absorb sulfur oxides with limestone in the combustor with high sulfur retention efficiency. Limestone can also capture hydrogen chloride at relatively low temperatures in the freeboard region of the AFBC system. The scope of this project is to study the behavior of chlorine during coal combustion in an AFBC system. The results from this research project could help reduce the fuel costs for the 160 MWe AFBC unit at the Shawnee Steam Plant near Paducah, KY, if raising the specification limit for chlorine content is possible after completion of the study. A successful project demonstrating the utilization of high chlorine coals may open new markets for Illinois high chlorine coals. It will also reduce the risk of serious damage to commercial units using high chlorine coal, if power plant operators know the limits for utilization of such coals.

In order to honor the requests of TVA for corrosion tests under conditions simulating those of the 160 MWe AFBC system at the Paducah Shawnee Plant, the 0.1 MW_{th} AFBC facility at WKU was extensively modified by replacing the refractory layer using a much harder and stronger inner section, installing a new cooling system, upgrading the control system and installing two sets of secondary air nozzles. With these modifications, the oxygen concentration in the flue gas, the temperature, and the residence time of fine particles in the combustor can be adjusted by changing the primary/secondary air ratios.

Coal and limestone for the first 1,000-hour test burn was acquired, air dried, crushed to -4 mesh, and stored. The coal (15 tons) is a blend of two coals in order to achieve the chlorine (0.2%), sulfur (3%), and ash (10%) contents needed for the study. Analytical data from the two source coals and the blend showed that the alkali contents in all three were nearly the same, and the analytical values for the source coals are very close to those of the blend. The first 1,000-hour test burn will begin the first week of September, 1998.

In order to achieve both high capture efficiencies for SO_x and HCl in the three scheduled 1,000-hour test burns with the AFBC system, a study of limestone decomposition was carried out in a drop-tube furnace using a fast heating rate. It is known that the optimum temperature for capturing hydrogen chloride by limestone in an FBC combustor is less than $600^\circ C$, whereas the optimum temperature for capturing SO_x is around $850^\circ C$. Thus, the decomposition and use of limestone should be looked at in two stages: large particles which stay in the fluidized bed zone capture SO_x at relatively high temperatures, while middle-sized and fine particles that stay in the fluidized bed zone a very short time for decomposition

escape from the bed and enter the freeboard area to react with HCl, thus reducing the HCl concentration in the flue gas. This consequently inhibits corrosion and lowers ash deposits. In this study the effect of particle size, residence time, temperature, and different types of limestone on the decomposition rate were studied. The results indicated two factors that may affect SO_x and HCl capture efficiencies. First, the decomposition temperature shifted to higher value with an increase in particle size of limestone. A higher conversion rate from limestone to calcium oxide is obtained with the smaller particles and longer residence time. Second, the decomposition of limestone is very sensitive to temperature. The higher the temperature, the faster it decomposes. The conversion rate for limestone at 830°C is much faster (almost double) that at 800°C within the first minute.

It was determined in a study of 19 ash deposits, resulting from previous test runs and collected from various sections of the WKU AFBC system, that the temperature in an AFBC system plays a key role in the retention of sulfur and chloride in the ash. While most of the SO_x was captured in the fluidized bed zone at high temperatures around 850°C, the chloride content in the ash deposits increased along the entire height of the combustor, even with small alkali metal contents. This indicates that the reaction between HCl and CaO occurs under relatively low temperatures (<650°C). This information also will be useful for choosing the kind of limestone and particle size to get high absorbance efficiency of SO_x and HCl in the AFBC system.

A study of the interaction between HCl and SO_x captured by a sorbent in an AFBC system was carried out in a TGA system and a lab-scale FBC, which has a 0.05 meter I.D and 1.0 meter height. The major tasks for this investigation were to (1) study the mechanism of the effect of HCl on SO_x emissions from an FBC system, and (2) find the optimum sorbent and conditions for the capture of HCl and SO_x. A goal of the study was to determine whether or not HCl promotes the conversion reaction between SO_2 and SO_3, and whether or not HCl improves the absorbing surface area of sorbent. In this study, limestone (or calcium oxide) was continuously fed into the top of the combustor using an auger feeder, while reaction gases, including HCl, SO_x and oxygen supplied by cylinders, were injected through a distributor at the bottom of the combustor. Nitrogen was chosen as an adjustable reagent. The concentration of each reaction gas was controlled by a calibrated flowmeter. The test results indicated that HCl can influence SO_x emission remarkably. The desulfurization efficiency increases sharply with an increase in HCl concentration in the reaction gases.

Forty-two test coupons (14 each of 304SS, 309SS and 347SS alloys) were acquired and prepared for the three 1,000-hour test burns. Each circular coupon has a 5.08 cm outside diameter, a 1.587 cm hole in the center, and is 0.3175 cm thick. A layer of corrosion-resistant metal (25% Cr, 75% Fe) was coated around one-side rim of each specimen.

Measurement to a high degree of precision of the final surface relative to the original surface protected by the resistant layer can now be made using an optical microscope. The procedures for assessing changes in the coupons requires that specimens be removed after each 250 hours of a test burn. Complete testing of the metal coupons requires destructive examination. However, only eight coupons can be installed in each run. In order to obtain as much corrosion data as possible for every 250 hours of exposure, a special procedure was

adapted. The coupons will be removed in a fixed sequence after each 250 hours, so that coupons of each alloy will be exposed for 250, 500, 750, and 1,000 hours during each test burn. In order to get reference data for future tests, two coupons of each alloy with three random points for each were examined by SEM-EDS. The SEM analysis was performed with a JEOL JSM-5400 SEM with a KEVEX Sigma 1 EDX System with a Quantum detector for elemental analysis down to carbon. A small piece, the analysis sample, was cut from each coupon, mounted, ground, polished and coated by carbon. The analytical results indicate that the profile of each element is very uniform. Also, four points were chosen and marked to provide the same point to measure after every 250-hour test period. The initial thicknesses of all alloy specimens were carefully measured.

A 1000-hour oxidation test with a 304SS metal coupon was carried out in an air atmosphere in an electrically heated furnace. The results will be used as basic reference data to determine what type of metal alloys are helpful in suppressing corrosion. Similar tests with flue gas conditions similar to those in three 1,000-hour runs will be conducted.

For the second year of the project, completion of the first 1,000-hour burn with the 0.20% chlorine coal will be followed by two 1,000 hour burns using coals with higher chlorine contents. Coals with 0.35% and 0.45% chlorine contents containing about 3% sulfur and 10% ash will be used in these tests. Negotiations for the acquisition of these two test coals are underway. Extensive analysis of the test coupons, the exposed boiler tubes, and deposits from the AFBC system will follow the test burns. Comparison of the test results from each test burn, along with results from previous test burns, should provide adequate information about the role coal chlorine may play in the corrosion of boiler components.

OBJECTIVES

The major purposes of this research project are to help the coal industry solve corrosion problems associated with the utilization of high chlorine coal and to provide technical support for the operation of the 160 MWe atmospheric fluidized bed combustion (AFBC) system at TVA's Shawnee Steam Plant near Paducah, KY. A successful project demonstrating the utilization of high chlorine coals may open new markets for some Illinois coals. It will also reduce the risk of serious damage to commercial units using high chlorine coal, if power plant operators know the limits for utilization of such coals. Three coals with different chlorine contents (0.2%, 0.35%, and 0.45%), similar sulfur contents around 3%, and ash contents around 10% will be burned in three 1,000-hour experimental runs. The scope of this project is to study the behavior of chlorine during coal combustion in an AFBC system. The project will include three major tasks for burning three coals with different chlorine contents and similar alkali metal contents, which are:

1. Studies of chloride and sulfur emissions during coal combustion in an AFBC system;
2. Studies of fly ash and ash deposits from different regions in an AFBC system;
3. Studies of the effects of coal chloride and sulfur contents on corrosion of steel alloy coupons and heat exchange tubes at high temperatures in an AFBC system.

INTRODUCTION AND BACKGROUND

For the next century coal is likely to remain the most important fuel for electricity generation in many countries, especially in the USA, UK, Germany and China.[1] With the development of combustion technologies for fossil fuels, the load capacity and thermal efficiency of single units has been increased remarkably during the past several decades, for example, from a 6 MWe unit with low operational parameters to a supercritical parameter 600 MWe unit. The thermal efficiency of systems has also increased from 20% to 47%. However, there are many boiler operational problems associated with the mineral impurities in coals. The more notable among these are corrosion and erosion of boiler heat exchange tubes, and fireside deposits on tubes in high temperature regions, including vaporization tubes and superheater tubes. The fireside problem has been estimated to collectively cost the electrical generating industry 4 billion dollars per year.[2]

It is generally accepted that sulfur, chlorine and molten alkali chlorides in coal may play roles in this corrosion and in the formation of ash deposits. Some studies have indicated that the corrosion rate of boiler tubes increased proportionally with increasing chloride concentration in the flue gases. Based on these studies, many United States boiler manufacturers set their recommended chloride levels at less than 0.3% for burning U.S. coals. Such limitations apparently are rooted in the history of problems presented by the Central Electricity Generating Board in Great Britain and have been extrapolated to the probable corrosion behavior of U.S. coals.[3] However, in a recent survey conducted through a joint effort of the Electric Power Research Institute and the Illinois Clean Coal Institute, as well as a study by the Kerr-McGee Coal Corporation,[4] it was reported that many

Midwestern United States utilities have decades of experience burning high-chlorine Illinois coal in a large variety of boilers with no reported chlorine-related fireside corrosion problem. This suggests that the effect of chlorine in coal on corrosion of boiler components is not only directly related to the content in the coal, but to how and in which form it occurs during combustion. Now the majority view is that, at least for superheater boiler tube corrosion, the alkali content of the coal plays a more significant role in the corrosion, and that the chloride acts on corrosion indirectly by facilitating the release of alkali metals.

The chloride content in Illinois coals has been a concern for potential end users of these coals. This concern, regardless of whether or not chlorine in coal causes corrosion, has had a great impact on the coal market. In 1993, TVA declined to renew an Illinois Basin coal (with 0.4% Cl) contract (approximately 4 million tons per year) for its AFBC unit, due to unexplained wastage/corrosion problems in the primary superheater region between 1992 and 1993. A need to open new markets, or recover previous markets, for Illinois coals is a challenge faced by the Illinois Department of Commerce and Community Affairs/Office of Coal Development and Marketing (DCCA/OCDM).

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 a few to several hundreds ppm 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 volatile, and during combustion processes it generally is emitted as gaseous HCl in the 300-600°C temperature range.[5] Some of the HCl reacts with gaseous alkali metal atoms and ions to form alkali chlorides, while the combustion particle temperatures increase in the combustor.

In a simulated flue gas environment (PC system) containing up to 2 vol% hydrogen chloride, the influence of hydrogen chloride on the corrosion behavior of tubes were investigated in detail by Mayer[6] at metal temperatures of 540, 700, 1000 and 1060°C. Three distinct layers were identified for each specimen using SEM techniques: an inner wustite layer, an intermediate magnetite layer and an outer hematite layer. Chloride was found to accumulate in the outer part of scales, while sulfur accumulated in the magnetite and wustite at the metal-oxide interface in the form of FeS. Nevertheless, the calculations of the wastage ratio is approximately equal to that reported for oxidation of iron in air at similar temperatures. The combined effect of CO and HCl on corrosion was studied using a simulated flue gas by Brooks and Meadowcroft.[7] The flue gas contained 10% CO, 10% H_2O, 0.5% SO_2, and 400 ppm HCl in nitrogen. The results showed that the corrosion rates of mild steel were linear with time. In conditions without HCl in the flue gas, a parabolic rate curve was obtained, which leveled off at the maximum metal loss of only 27 μm. Increasing the HCl concentration in the flue gas to 2000 ppm almost doubled the linear corrosion rate. The data from Cutler[8] also showed that the corrosion rate is increased by the addition of 500 vppm of HCl to the combustion gas. Wright[11] suggested the effects of chlorine on superheater and

water wall corrosion in PC boilers are not directly related to the chlorine itself, but to its

effectiveness in releasing the alkali metals, sodium and potassium, from the coal and its ash.

It is well known that the FBC technique can absorb sulfur oxides with high sulfur retention efficiency when limestone is used as the bed material in the combustor. The addition of limestone may also help reduce chloride emissions, since it is possible that limestone degenerates to CaO, and CaO reacts with HCl to produce $CaCl_2$. A study by Liang and others[9] showed that the capture efficiency of chloride by limestone in the combustor depends upon the surrounding temperature and the ratio of calcium-to-sulfur. Their data indicated that chloride capture shows a large variation with temperature, moving from a low of 18% gaseous HCl at 700ºC to 99% HCl at 950ºC. The resulting product is almost entirely in the form of liquid $CaCl_2$. Munzner and Schilling[10] 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. Matsukata and coworkers[11] reported that the sulfurization of all size particles was markedly accelerated in the presence of HCl. The level of conversion of CaO to $CaSO_4$ and $CaCl_2$ always approached 100% upon the simultaneous absorption of HCl and SO_2. It was proposed that this absorption efficiency was the result of both the formation of a mobile chloride ion-containing phase and the formation of voids playing a role in the diffusion of HCl and SO_2 toward the interior of a limestone particle. Deguchi and coworkers[12] tested HCl retention and the simultaneous retention of HCl and SO_2 in a bubbling fluidized bed at 850ºC. The results showed that HCl was effectively retained by limestone and the desulfurization efficiency was increased in the presence of HCl. Pan and co-workers[13] used a tube furnace to study the behavior of HCl at high temperatures using oxygen-rich conditions while investigating the effect of chloride on SO_x emissions under simulated FBC conditions. It is possible that chloride might also affect the detailed chemistry of sulfur capture in AFBC systems.

In the past two decades, calcium-based sulfur sorbents (limestone, CaO, etc.) have been used more often in flue gas desulfurization systems of coal-fired boilers, especially with the development of fluidized bed combustion technology.[14] Unfortunately, more ash deposits are formed when sorbents are used. This formation can be a result of a sintering process in which the CaO reacts with components in the flue gas after adhering to a heat exchange surface. The heaviest sintering has been measured when CO is present in the flue gas.[15] Also, it is known that the optimum temperature for limestone capture of SO_2 in an FBC system is around 850°C in the fluidized bed itself. However, the favored temperature for HCl retention is relatively lower, and normally less then 650°C. HCl retention by calcium oxide also depends on the concentration of HCl in the flue gases.[16] In order to obtain both high retention efficiency of HCl and SO_2 in an FBC system, the decomposition of limestone should be controlled separately. Large particles should stay in the dense fluidized bed zone capturing SO_2 at relatively high temperatures, while middle-sized and fine particles escape from the bed and enter the freeboard area to react with HCl and reduce the HCl concentration in the flue gas. A study of the decomposition characteristics and reactions of limestone at a very fast heating rate can yield information about the optimum conditions and optimum particle size range for HCl capture during combustion. Besides, low sorbent

4

utilization of the calcium (normally around 30~40% by weight) in limestone also offers an opportunity for significant improvement of the process.

One of the main goals of this project is to evaluate the critical point of coal chlorine content which may cause initial corrosion. The chlorine content of most coals burned in U.S. coal-fired boilers has generally been limited to less than about 0.3% by weight to avoid aggravation of the potential for fireside corrosion. However, no formal report has been published to prove it, although there have been several examinations conducted in the United Kingdom which indicated that aggressive fireside corrosion can be correlated with the use of high-chlorine British coals.[17]

This study is being conducted at Western Kentucky University in order to predict the performance of high chlorine coals in various combustion systems, to better understand the combustion behavior of chlorine during coal combustion in an AFBC system, and to evaluate the critical point of coal chlorine content which may cause initial corrosion. The project will focus on the effect of coal chlorine content on HCl emission reduction, on the effect of chloride on the absorption of SO_x, on the effect of operating parameters on the distribution of chloride in the fly ash and bed ash, and on the high temperature corrosion of different metals in fluidized bed combustors during coal combustion.

EXPERIMENTAL PROCEDURES

The laboratory-sized 0.1 MW_{th} atmospheric fluidized bed combustor (AFBC) at Western Kentucky University (WKU), with a 0.3 m I.D. and 3.5 m height, 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 AFBC system has been configured to simulate the operating and combustion conditions of the 160-MWe AFBC system at TVA's Shawnee Power Plant.

In order to honor the request of TVA for corrosion testing of the surrounding components in the AFBC system and to attain the goals of this project, the 0.1MW_{th} AFBC facility at WKU was extensively modified including the combustor, the electrical system, the gas and solid sampling systems and the cooling system. The schematic diagram of the modified system is shown in Figure 1.

Modification of the AFBC System.

The AFBC combustor was modified by replacing the refractory layer using a much harder and stronger inner section, installing two sets of secondary air nozzles, and a new secondary air forced draft fan. The goal of this modification was to utilize staged combustion

Figure 1

technology, which can improve combustion and reduce pollutant emissions. The first set of secondary air ports, fitted with two nozzles, is 1.6 m above the setter plate and the second set is 0.6 m above the first one, as is illustrated in Figure 2. Forced air, at a calculated ratio, from the high pressure blower is injected tangentially at an angle of 30 degrees into the freeboard through secondary air nozzles. This air forms a strong vortex flow above the nozzles. Under this tangential flow, particles escaping from the fluidized bed are separated from the flow. The large particles fall back into the bed along the wall, while the small particles form a suspended layer to prolong their residence time in the combustor. Thus, the oxygen concentration in the flue gas, temperature, and the utilization coefficient for fine particles in the combustor can be adjusted by changing the primary/secondary air ratio.

Two fuel feeding methods are available on the WKU AFBC system; one is an above-bed feeder and the other is an under-bed feeder. The main purposes of changing feeding positions are to investigate the combustion behavior of coal within the different residence times in the bed, especially the function of releasing HCl, and study the HCl retention performance using limestone after different reaction periods between limestone and SO_x.

A 210-C cooled tube to be used for corrosion testing was placed at 1.45 meter above the air distributor. This position is about 0.3 meter above the fluidized bed surface and 0.2 meter below the first set of secondary air nozzles. The effect of erosion from bed material and from secondary air flow can be minimized in this position. TVA has suggested that the temperature at the surface of the cooled heat exchange tube (210-C) should be kept near 650-700°F and the surrounding flue gas temperature around 1500°F. Thus, a comparison was made between air cooling and water cooling to maintain the desired surface temperature.[18] The air-cooling method was adopted for this study.

The cooling system for the AFBC system was modified in order to reduce the amount of water consumed during combustion runs. The system was changed from an open circuit to a closed circuit recirculating unit.

The safety protect electrical equipment was upgraded. A new power supply plate for the secondary air forced draft fan and the water pump for gas and solid sampling was installed.

A small cyclone with high separation efficiency and two kinds of filters was designed and constructed for solid and gas sampling. Tests to determine the burnout factor of coal, the alkali chloride content in the fly ash, and the concentration of chloride in the flue gas along the height of combustor will be conducted. A water pump within the circuit water system was designed and constructed for vacuum to operate the system. A schematic diagram of the sampling system is shown in Figure 3.

A total of 30,000 lbs of coal and 3,000 lbs of Kentucky limestone was bought, transferred, air dried, crushed to -4 mesh, analyzed, and stored in a trailer for the first 1,000-hour burn. A 50:50 blend of the two coals was prepared to obtain a coal with the appropriate chloride
Figure 2

Figure 3

percentage near 0.2%. The analytical data for the two source coals and the blend are given in Table 1. The averages of the analytical values for coals A and B are very close to the analytical values determined for the A+B blend. The mineral analysis and ash fusion temperatures for the two coals and the blend are given in Tables 2 and 3, respectively. One can see from these values that the mineral matter content, especially the alkalis, was very similar in each of the coals. The thermal properties of the limestone that is being used as a sorbent for SO_x and HCl in first 1000-hour test was analyzed with a TA Instruments Model TA 2950 thermogravimetric analyzer (TGA). The curve in Figure 4 shows the onset and end-point temperature of this limestone is very high (745ºC and 891ºC, respectively) although a little (about 3% by weight) decomposed around 420ºC. This behavior suggests that the operating temperature of an AFBC system should be more than 850ºC in order to achieve high utilization efficiency of limestone.

Table 1. Analytical Values[A] for the Coals Procured for the Study

	Coal 97024	Coal 97025	Blend
Proximate Analysis			
Moisture	3.22	6.52	4.56
Ash	10.75	10.47	10.97
Volatile Matter	36.04	36.71	36.25
Fixed Carbon	53.22	52.83	52.78
Ultimate Analysis			
Ash	10.75	10.47	10.97
Carbon	75.21	74.02	74.69
Hydrogen	4.91	4.74	4.95
Nitrogen	1.60	1.61	1.63
Sulfur	2.48	3.72	3.06
Oxygen	4.73	5.32	4.50
Miscellaneous Analysis			
Chlorine (ppm)	3080	1190	2070
Calorific Value (BTU/lb)	13,294	13,196	13,152

[A] Moisture is as-received, all other values are reported on a dry basis. Unless otherwise noted, all values are given in percent by weight.

A layer of corrosion-resistant metal (25% Cr, 75% Fe) was coated around one-side rim of the specimen to protect the interface and avoid corrosion so that a baseline for corrosion measurements would be available. Measurement of the final surface, relative to the original surface protected by a resistant layer, can then be very accurately made to a high degree of precision using an optical microscope. The application of such procedures requires that test specimens be removed every 250 hours for destructive examination. However, only eight

Figure 4

Table 2. Analytical Values[A] for Ashes Prepared from the Coals Used in the Study

Metal Oxides	97024	97025	Blend
SiO_2	41.42	33.89	58.51
P_2O_5	1.37	0.48	0.79
CaO	1.40	6.36	3.75
K_2O	1.69	1.17	1.48
TiO_2	1.25	0.86	1.00
Fe_2O_3	20.34	36.14	26.98
Na_2O	0.42	0.30	0.41
MgO	1.05	0.85	0.92
Al_2O_3	26.98	13.48	19.52
MnO_2	0.01	0.01	0.01

[A]All values are in percent by weight.

Table 3. Ash Fusion Temperatures for Coals Used in the Study

Temperatures, (°F)	Reducing	Oxidizing	Reducing	Oxidizing	Reducing	Oxidizing
Initial deform. (IT)	2220	2569	1928	2346	1981	2408
Softening (ST)	2469	2645	1950	2460	2012	2469
Hemispherical (HT)	2556	2691	1996	2540	2055	2503
Fluid (FT)	2773	2729	2085	2550	2084	2514

coupons can be installed in each run period. In order to obtain more corrosion data for every 250 exposure hours, the following set-up procedure was used in the first 1,000-hour-test:

Step 1	0 hour	Original arrangement of eight coupons: two 304SS, two 347SS, and four 309SS.
Step 2	250 hrs	Cut and analyze 309_{-1} and 304_{-1} to obtain 250 hrs corrosion point; then install new 304_{-1-1} and 347_{-1-1} to test.
Step 3	500 hrs	Cut and analyze 309_{-2} and 347_{-1} for the 500 hrs point; then fix new 304_{-2-1} and 347_{-2-1} to test.
Step 4	750 hrs	Remove and cut 309_{-3} for 750 hrs point, and 347_{-2-1} for 250 hrs point.
Step 5	1000 hrs	Pick up 309_{-4}, 347_{-2} and 304_{-2} for 1000 hrs point; 304_{-1-1} and 347_{-1-1} for 750 hrs point, 304_{-2-1} for 500 hrs point to cut and examine.

This procedure will help keep one sample (the sample can be cut and analyzed later) for each metal at a different exposure time.

In order to get reference data for future tests, two coupons of each alloy with three random

points on each were examined by SEM-EDS. The analytical results listed in Table 4 indicate that the profile of each element is very uniform. Also, four points were chosen and marked to provide the same point of measurement for elemental analysis of ash deposits on the coupon surface after each 250-hour test period. Since ultrasonic velocity in a material is a function of composition, the velocity should change when materials are first heated to a high temperature and cooled. In order to obtain real information on corrosion reactions on coupons and the cooled tube, duplicate velocity measurements were made. The first measurement was made on original coupons and the tube, and the second was made after the sample was heated for 20 hours at 750°C in an air atmosphere. The examination results are listed in Appendix I (given as an example for one series). Significant changes in measurement data before and after heat treatment were found. These data will be used as a reference for the first 1,000-hour corrosion test.

A cooled-tube and an uncooled-tube (210-C steel) were designed and constructed, and are being tested in the AFBC system to determine the corrosion rates due to chloride in flue gases. The tubes are also being tested in an electric furnace to determine metal oxidation and wastage under different temperatures and gas conditions (15% CO_2 and 5% O_2 in nitrogen) but without HCl and CO gases. The difference between the metal wastage of the 210-C tube in the AFBC and that in the electric furnace can be obtained. The difference will only be due to erosion or due to corrosion caused by alkali, chloride, or sulfur compounds. In order to obtain more corrosion information, thickness measurements on three longitudinal cross-sections of the tubes and one end cover with four-point measurements made on each section. In each section, two thermocouples were installed to measure the local corrosion temperature. The thickness reference data of 16 points marked on the cooled-tube are given in Appendix I as an example.

RESULTS AND DISCUSSION

Coal Analysis

The thermal behavior of the two source coals and the blend was determined using a TA Instruments model 951 Thermogravimetric Analyzer interfaced with a VG Thermolab Mass Spectrometer (TG/MS). The general observations of the thermal degradation of the coals is given in Table 5.

Simultaneous thermal analysis and mass spectrometric techniques have been used in studies of the thermal behavior of coal. In this study, the thermal characteristics of coal were obtained with a TGA by heating the coal in air from 20 to 900°C. When coal is heated in an oxygen-rich atmosphere, it will first undergo pyrolysis, then ignition and combustion of volatile matter, followed by char combustion. During the pyrolysis stage, volatile matter is evolved, including water, CO, CO_2, SO_2, H_2, aliphatic fragments, and aromatic fragments. There are two temperature regions where mass losses take place. In the first temperature

Table 4 here

13

Table 5. Characterization of the Thermal Behavior of the Coal Blend

Thermal Processes	Coal Blend (97024 and 97025)
Thermal mass loss determined by TG after heating to 900ºC	89.0% by weight
Release of water determined by MS (m/z = 18) in three steps	First maximum 100ºC Second maximum 342ºC Third maximum 450ºC
Release of carbon dioxide determined by MS (m/z = 44) in one step	Maximum 500ºC
Release of sulfur dioxide determined by MS (m/z = 64) in two steps	First maximum 417ºC Second maximum, 440ºC
Release of aliphatic fragments determined by MS (m/z = 55) in two steps	First maximum 290ºC Second maximum 430ºC
Release of COS determined by MS (m/z = 60) in one step	Maximum 440ºC
Release of dienes determined by MS (m/z = 68) in one step	Maximum 435ºC
Release of aromatic fragments determined by MS (m/z = 91) in two steps	First maximum 300ºC Second maximum 435ºC

range from 20-100ºC, the mass loss is due to the release of physically bound moisture. In the second temperature range from 300-600ºC, the pyrolysis of coal takes place, followed by the combustion of volatile matter and char.

The pyrolysis and combustion products released from coal samples during heating of the coal in air were measured using a mass spectrometer. The release of water takes place in the temperature range from room temperature to 100ºC and corresponds to the release of physically adsorbed water. The release of water in the temperature range from 400-500ºC corresponds to the release of chemically bound water and water from combustion reactions. The MS spectrum shows good agreement between the release of CO_2 and the consumption of O_2. The release of volatile matter in the temperature range from 350-500ºC during coal pyrolysis, followed by the combustion of volatile matter and char is indicated by the production of CO_2 from 350 to 600ºC. During this stage the oxygen content of the flue gas decreases. The release of SO_2, resulting from the combustion of aliphatic, pyritic, and

aromatic sulfur, takes place in the temperature range from 380-550ºC. The release of organic molecules with the m/z = 55 (aliphatic fragments) and m/z = 91 (aromatic fragments) takes place around 430ºC.

Ash Deposits

Nineteen ash deposits were collected from different regions of the 0.1 MW$_{th}$ AFBC system and analyzed by ICP-AES spectroscopy, ion chromatography, and XRD spectroscopy. These ash deposits were generated during the co-firing of coal with refuse fuels, including wood wastes and plastics. The major purpose of these analyses was to find the optimum conditions and position for HCl capture by limestone in the AFBC combustor. The effect of temperature on the chloride retention in ash deposits is illustrated in Figure 5. Higher chloride contents were observed in the lower temperature regions. The capture of HCl by limestone is more difficult than the capture of SO_2, especially at high temperatures in the fluidized bed of the combustor. However, the reaction between HCl and CaO is more favorable at the lower temperatures in the freeboard area. This information on the distribution of sulfur and chloride in ash deposits will be useful in efforts to minimize corrosion of heat exchange tubes.

In addition to elemental analysis, x-ray diffraction analysis was used to determine the possible forms of these elements as they exist in the ash deposits. The analytical data are listed in Table 6. It can be seen that alkali chlorides (KCl or NaCl) only exist in ash deposits on the moveable heat exchange tube surfaces, where the flue gas temperature is around 850ºC and the metal surface temperature is about 90ºC. The amount of alkali chloride de-decreased with an increase in height from the air distributor (lower temperature). Comparing the ash deposit data between the above-bed heat exchange tubes and in-bed heat exchange tubes, the higher temperature of the metal surface is more favorable for the reaction between alkali chloride in ash deposits and SO_2 in the flue gas to form alkali sulfates.

Limestone Decomposition

The reactivity of sorbent is closely related to the general characteristics of the CaO formed from the decomposition of limestone and to certain properties of the raw sorbent such as chemical composition of the parent stone, particle size, and surface area. The conditions under which calcination is carried out can greatly influence the physical structure and the reactivity of the CaO formed. In this study a quartz tube in an electrically-heated furnace was used to achieve a rapid heating rate to better simulate FBC conditions. More attention was paid to the initial time of the test, or the first 2 minutes. The sample, 10-200 mg, was placed in a ceramic pan and loaded into the tube furnace, where the heating rate was about 40ºC/second.

Figures 5 and 6

Table 6. Relative Amounts of Alkali Chloride Compared to CaCO$_3$ in AFBC Ash Deposits, as Determined by X-Ray Diffraction Spectroscopy

.

Deposit position	Relative Ratio KCl/CaCO$_3$	CaSO4	Comments NaCl	Color
	3.5	minor	none	tan
	4.9	minor	none	tan
Convective region	1.5	minor	none	gray
	5.7	minor	none	dark gray
	10.8	minor	none	dark gray

	9.9	minor plus	none	dark gray
Transition region	9.0	minor plus	none	dark gray
	8.2	minor plus	none	dark gray

Top	12.1	minor	none	dark gray
	13.5	near major	none	dark gray
Moveable heat	68.5	major	possible	white/gray
exchange tube	75.1	minor	possible	white/gray
	61.5	major	possible	mixture
Bottom	120.0	minor plus	possible	white/gray

In TGA studies it was determined that the limestone decomposition temperature shifted to higher temperatures with an increase in the particle size of limestone. This is especially true for the large particle size (0.85-2.36 mm) fraction. In the tube furnace study, the decomposition temperature also shifted to higher temperatures with an increase in the particle size of limestone. Higher conversion of limestone to calcium oxide was also obtained with the smaller particle size limestone using a longer residence time, as is illustrated in Figure 6. For the short residence time (within 60 seconds), there is no significant difference for the conversion rates among the different particle sizes. This may be due to the specific amount of energy that is required for the calcination reaction and the total amount of energy available in the reactor at that temperature. Thus, the conversion rate difference for different particles is minimal at short (< 60 sec) residence times. The higher conversion rate is obtained with the smaller particles after one minute. This is likely due to the effect of surface area.

The decomposition of limestone is very sensitive to the temperature. The higher the temperature, the faster it decomposes. Figure 7 shows that the conversion rate for limestone at 830°C is much faster (almost double) than that at 800°C within the first minute. The major

Figure 7 and 8

energy sources for the decomposition of limestone is from radiation heat. The radiation energy is a function of T^4. Therefore a small incremental change in temperature will make a big difference in the conversion rate. A greater surface area for limestone will be produced at the fast heating rate, which is due to the explosion and fragmentation of the larger particles. More radiation energy will be absorbed by more surface area. Also, both the resistance of heat being conducted from the surface to the inside of particle, and the diffusion of mass from inside to the outside of the particle was reduced. Thus, the surface area, temperature, and heating rate play very important roles in the conversion rate of the limestone. This information should be very helpful in choosing combustion temperatures in order to obtain a high utilization efficiency for limestone.

The Interaction Between HCl and SO_x

A study of the interaction between HCl and SO_x captured by a sorbent in an AFBC system was carried out in a TGA facility and also in a lab-scale FBC system, which has a 0.05 meter I.D and 1.0 meter height. The major purposes of this investigation were to (1) study the effect of HCl on SO_x emission from an FBC system and (2) find the optimum sorbent and conditions for capturing HCl and SO_x efficiently. Specific questions to be answered are whether or not HCl promotes the conversion of SO_2 to SO_3, and whether or not HCl improves the absorbing surface area of the sorbent. In this study limestone (or calcium oxide) was continuously fed into the top of the combustor using an auger feeder, while reaction gases including HCl, SO_2 and O_2, supplied by cylinders, were injected through a distributor at the bottom of the combustor. Nitrogen was chosen as the adjustable reagent. The concentration of each reaction compound was controlled by a calibrated flowmeter.

Figure 8 shows the amount of SO_2 remaining in the flue gas with and without HCl, using limestone as a sorbent. For this test, limestone at a Ca/S mole ratio of 3.0 was fed into the reactor with the reactant gases. However, the addition of limestone to the reaction mixture was stopped when the amount of SO_2 in the flue gas reached a constant value for a certain period. It was determined that a stable desulfurization process continued for a shorter time in the presence of HCl than desulfurization without HCl in the reactant gases. The effect of HCl in the reactant gases on SO_2 capture is presented in Figure 9. In this test, limestone was continuously fed into the reactor during the entire test period. The test results indicate that HCl can influence SO_x emissions. The desulfurization efficiency increases with an increase in the HCl concentration in the reaction gases.

Limestone was heated at a 50°C/min heating rate on a DuPont 951 TGA in a N_2 atmosphere until the limestone completely decomposed into CaO. Isothermal runs at 500, 600, 700, 800, and 900°C with mixed gases (5% O_2, 1000 ppm HCl, and 3000 ppm SO_2) flowing through the system were conducted. The results from this study are illustrated in Figure 10. The data indicate that the temperature is an important parameter to control SO_x and HCl capture. The weight gain increases with an increase in temperature. However, there is no

Figures 9 and 10

significant difference in the weight change during the initial 10 minutes period for the five temperatures.

In order to determine the effect of chloride on SO_x emissions using FBC conditions, the effect of HCl concentration on the rate of conversion of SO_2 to SO_3 at different temperatures without limestone was investigated. The results of this study is illustrated in Figure 11. These results indicate that the conversion rate was enhanced by an increase in the concentration of HCl. The curve rises slowly when the HCl concentration is increased from 0 to 500 ppm, then increases very fast and reaches a maximum at 1000 ppm. After reaching a maximum at 1000 ppm HCl, the conversion rate decreases very fast as the HCl concentration is increased. The curves for the 700°C and 800°C tests are very similar to that obtained at 600°C. The maximum peak for the conversion rate (optimum HCl concentration) was shifted to higher than 1000 ppm. This information can be very helpful for the operation of an AFBC system. At the beginning of the combustion, the concentration of HCl and the bed temperature (above 800°C) are both higher in the bed area than in the freeboard area where the temperature is around 600°C. In this zone, the effect of HCl on the conversion rate is significant. As the temperature decreases from the bed to the freeboard area, as a result of heat exchanges, the reaction between CaO and HCl becomes more significant, forming liquid and/or solid phase calcium chloride. The HCl concentration in the flue gas is reduced gradually as it rises in the combustor. In the freeboard area, the low concentration of HCl can accelerate the conversion of SO_2 to SO_3, as was found in this study. However, the conversion rate from SO_2 to SO_3 is below 6% for all test conditions. These results indicate that HCl promoting the conversion reaction between SO_2 and SO_3 is not a major pathway influencing SO_x emission reduction in the presence of HCl.

It is known that since the molar volume of $CaSO_4$ is much greater than that of CaO, sulfation of SO_2 with calcium oxide causes pore closure in limestone, resulting in the deterioration of the sulfation activity. This is the reason that the utilization of calcium in limestone is only 30-40%. One explanation of the increased capture of SOx by limestone in the presence of HCl is that chlorine trapped on the surface of limestone is transported from the surface to inside the particle by the diffusion of chloride ion in the solid and/or the migration of the $CaCl_2$ liquid phase in an AFBC system. This transient formation of a mobile halide ion-containing phases can modify the surface of the partially sulfated sorbent particles to form more voids on the surface, which provide diffusion paths for HCl and SO_x toward the interior of a limestone particle, leading to increased SO_2 capture. Also, with the progression of sulfation of limestone, the $CaSO_4$ layer outside the limestone particle becomes thicker, and the diffusion into the particle becomes more difficult, stopping the reaction. So this layer can suppress the escape of chloride vapor under a combustion temperature of 850°C which is higher than the melting point of $CaCl_2$ in the system.

Figure 11

Oxidation Tests for Coupons

A 1000-hour oxidation test for a 304 metal coupon was carried out in an air atmosphere in an electrically heated furnace at 800ºC. The purposes of this study were to (1) investigate the function of the coating material around the center of the coupon during oxidation, and (2) to study the profile of the metals in the coupon by SEM-EDS. The results will be used as basic reference data to determine which kind of metals are helpful in suppressing corrosion using flue gas conditions similar to those in the three 1,000-hour runs. In order to check the function of the coating layer, different thicknesses of nickel layers were tested at the same time. The results indicated that spallation easily occurred for thick layers and thin layers were easily destroyed. The optimum thickness of a layer is around 15 μm, which was chosen as the value of coating layer thickness in all three alloys coupons (total 42) for the three corrosion test burns. SEM-EDS analysis was performed on a small piece, the analysis sample, which was cut from the coupon, mounted, ground, polished and coated by carbon. The data obtained from the analysis is listed in Table 7. There are two layers in the corrosion boundary before the original metal is reached. The outer scale was primarily hematite with high Cr, Mn and low Ni content. The inner layer contains high nickel oxide and low chromium concentrations. The chromium migrates from the inner layer to the outer layer and protect the alloy toward oxidation. Nickel in the alloys seems to provide no help in preventing corrosion, and was consumed very fast in the outer layer of the three alloys.

Table 7. Analytical Data for Oxidized Alloy Coupons

Dmm	O	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Co	Ni	Cu
0.005	4.62	0	0	0	0	0	0	0.11	0	0	2.16	5.88	8.64	0.57	76.9	1.17
0.025	8.89	0	0	0	0.50	0	0	0	0.10	0.06	51.41	3.07	21.78	0.35	13.3	0.54
0.031	0	0	0	0	0.89	0	0	0	0	0	12.50	0.15	57.44	0.80	27.1	1.09
0.440	0	0	0	0	0.16	0	0	0	0	0	18.34	2.02	69.58	0.91	8.08	0.85

surface with nickel layer

Dmm	O	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Co	Ni	Cu
0.005	11.2	0	0	0	0.57	0	0	0.08	0	0.07	75.03	8.54	3.47	0	0.47	0.54
0.008	4.35	0	0	0	4.41	0	0.15	0.23	0.16	0	32.79	5.48	46.26	0.58	4.72	0.86
0.015	0.13	0	0	0	0.13	0.07	0	0	0	0	13.29	1.00	74.71	0.85	8.99	0.83
0.165	0	0	0	0	0	0	0	0	0	0	18.35	2.03	69.86	0.83	8.16	0.77

surface without nickel layer

Future Work

For the second year of the project, completion of the first 1,000-hour burn with the 0.20% chlorine coal will be followed by two 1,000 hour burns using coals with higher chlorine contents. Coals with 0.35% and 0.45% chlorine contents containing about 3% sulfur and 10% ash will be used in these tests. Negotiations for the acquisition of these two test coals are underway. Extensive analysis of the test coupons, the exposed boiler tubes, and deposits from the AFBC system will follow the test burns. Comparison of the test results from each

test burn, along with results from previous test burns, should provide adequate information about the role coal chlorine may play in the corrosion of boiler components. Extensive efforts have been made during the first year of the project to prepare the combustor and associated equipment so that the very best results can be obtained from these test burns.

CONCLUSIONS AND RECOMMENDATIONS

1. The temperature and particle size are the most important factors to control in the thermal decomposition of limestone.

2. HCl can promote SO_x capture by limestone. The transient formation of a mobile halide ion-containing phases can modify the surface of the partially sulfated sorbent particles to form more voids in the surface, which provides diffusion paths for HCl and SO_x toward the interior of a limestone particle, leading to increased SO_2 capture.

3. A layer of corrosion-resistant metal (25% Cr, 75% Fe) was coated around the inner rim of steel specimens to protect the interface and avoid corrosion so as to provide a baseline for corrosion measurements. This method can improve corrosion measurements to high degree of precision by comparing the final surface thickness relative to the original surface thickness using an optical microscope or SEM system.

4. Although the favored temperatures for retention of SO_x and HCl by limestone in an AFBC system are very different (850°C for SO_x and lower than 600°C for HCl), high absorption efficiencies of both components can still be gained by choosing a limestone with optimum absorption properties and particle sizes.

5. A 1000-hour oxidation test indicated the chromium migrates from inner layers to the outer layer to protect the alloy against oxidation. Nickel in the alloys seems to provide no corrosion protection. It is consumed in the outer layer of the three alloys very rapidly.

6. Three 1,000-hour burns with three different coals for corrosion testing of steel coupons will be performed during the next six months.

REFERENCES

1.   Vogel, C. 1998. <u>Prepr. Pap.--Amer. Chem. Soc., Div. Fuel Chem.</u>, 43(3):403.

2.   Minchener, A.J., Lloyd, D. M., and J. Stringer. 1983. <u>Corrosion Resistant Materials for Coal Conversion Systems</u>, ed. D.B. Meadowcroft and M.I. Manning, Chap. 15, Applied Science Publishers, New York, p. 299.

3.   Wright, I.G., Mehta, A.K., and K.K. Ho. 1994. Proceedings of the 11th Annual International Pittsburgh Coal Conference, Pittsburgh, PA, Volume 1, p. 358.

4.   Abbott, M.F., Corder, W.C., Campbell, J.A., and E.P. Doane. 1994. "Chlorine in Coal:Utility Power for the Ninety's Conference," Arlington, VA, May 11-13.

5.   Shao, T. 1992. M.S. Thesis, Western Kentucky University.

6.   Mayer, P., Manolescu, A.V., and S.J. Thorpe. 1983. <u>Corrosion Resistant Materials for Coal Conversion Systems</u>, ed. D.B. Meadowcroft and M.I. Manning, Chap 5, Applied Science Publishers, New York, p. 87.

7.   Brooks, S. and D.B. Meadowcroft. 1983. <u>Corrosion Resistant Materials for Coal Conversion Systems</u>, ed. D.B. Meadowcroft and M.I. Manning, Chap 6, Applied Science Publishers, New York, p. 105 .

8.   Cutler, A.J.B., Grant, C.J., Laxton, J.W., Price, D.D., and C.G. Stevents. 1983. <u>Corrosion in Coal Conversion Systems</u>. ed. D.B. Meadowcroft and M.I. Manning, hap 13, Applied Science Publishers, New York, p. 212.

9.   Liang, D.T., Anthony, E.J., Leowen, B.K., and D.J. Yates. 1991. Proceedings of the 11th International Conference on FBC, Montreal, Canada, April 21-24, Volume 2, p. 917.

10.   Munzner, H., and D.H. Schilling. 1985. Proceedings of the 8th International Conference on FBC, Volume III, Houston, March 18-21, p. 1219.

11.   Matsukata, M., Tacked, K., Miyatani, T., and K. Ueyama. 1996. <u>Chemical Engineering Science</u>, 11:2529.

12.   Deguchi, A.Y., Kochiyama, Y., Hosoda, H., Miura, M., Hirama, T., Nishzaki, H., and M. Horio. 1982. <u>J. Jpn Inst. Energy</u>, 61:1109.

13.   Pan, W.-P. and J.T. Riley. 1997. "Co-Firing High Sulfur Coal with Refuse Derived Fuels," Final Report, DE-FG-94PC94211, November 30, 73p.

14.   Vernon, J.L. and H.N. Soud. 1990. "FGD Installations on Coal-Fired Plants,",

IEACR/22 (IEA Coal Research), April.

15. Skrifvars, B.J., Hupa, M. and P. Hyoty. 1991. " Superheater Fouling Due to Limestone Injection in Coal-fired Boilers," Journal of the Institute of Energy, 64, December, p. 196.

16. Bramer, E. A. 1995. "Flue Gas Emission from FBC," in Coal Science and Technology 22, Elsevier, p. 51.

17. Bettelheim, J., Halstead, W.D., Les, D.J. and D. Mortimer. 1980. "Combustion Problems Associated with High Chlorine Coals: Erdol and Kohle-Erdgas," Petrochemie, 33:436.

18. Pan, W.-P. and J.T. Riley. 1998. "A Study of Chlorine in High Temperature Corrosion of Alloys in An AFBC System", Mid-Year Report, ICCI 97-06, April.

DISCLAIMER STATEMENT