

**GREENHOUSE GAS EMISSIONS CONTROL  
BY OXYGEN FIRING IN CIRCULATING FLUIDIZED BED BOILERS:  
PHASE 1 – A PRELIMINARY SYSTEMS EVALUATION**

**FINAL REPORT**

**VOLUME I**

**EVALUATION OF ADVANCED COAL COMBUSTION & GASIFICATION  
POWER PLANTS WITH GREENHOUSE GAS EMISSIONS CONTROL**

**VOLUME II**

**BENCH-SCALE FLUIDIZED BED COMBUSTION TESTING**

**SUBMITTED BY**

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(COOPERATIVE AGREEMENT NO. DE-fC26-01NT41146)**

**PHASE I REPORT SUBMITTAL DATE: MAY 15, 2003  
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**PPL REPORT NO. PPL-03-CT-09**

# VOLUME II

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## ACRONYMS AND ABBREVIATIONS

ALSTOM	Alstom Power Inc.
ASTM	American Society for Testing and Materials
atm	Atmosphere
Btu	British Thermal Unit
Ca/S	Calcium/Sulfur Mole Ratio
cc	Cubic centimeter
CFB	Circulating Fluidized Bed
CO	Carbon Monoxide
CO <sub>2</sub>	Carbon Dioxide Gas
DAF, daf	Dry-Ash-Free
DOE/NETL	Department of Energy/National Energy Technology Laboratory
EGR	Enhanced Gas Recovery
EOR	Enhanced Oil Recovery
FBC	Fluidized Bed Combustion
FCE	Fuel Combustion Efficiency
ft	Foot
g	Gram
Hc	Heat Conduction
Hg	Heat Generation
HHV	Higher Heating Value
Hr	Heat Radiation
h <sub>v</sub> C <sub>b</sub>	High volatile C bituminous
IGCC	Integrated Gasification Combined Cycle
l	liter
lb/MMBtu	Pounds per Million Btu
min	Minute
MTF	Multi-use Test Facility
m <sub>v</sub> b	Medium volatile bituminous
N <sub>2</sub>	Nitrogen Gas
O <sub>2</sub>	Oxygen Gas
PPL	Power Plant Laboratories
ppm	Parts per million
sec	second
SO <sub>2</sub>	Sulfur Dioxide
T <sub>g</sub>	Gas Temperature
TGA	Thermo-Gravimetric Analysis
T <sub>s</sub>	Surface Temperature
UBC	Unburned Carbon
vppm	Volumetric parts per million



## EXECUTIVE SUMMARY

### Background

Because fossil fuel fired power plants are among the largest and most concentrated producers of CO<sub>2</sub> emissions, recovery and sequestration of CO<sub>2</sub> from the flue gas of such plants has been identified as one of the primary means for reducing anthropogenic CO<sub>2</sub> emissions. In this study, ALSTOM Power Inc. (ALSTOM) has investigated several coal fired plant configurations designed to capture CO<sub>2</sub> from effluent gas streams for sequestration.

Burning fossil fuels in mixtures of oxygen and recirculated flue gas (consisting principally of CO<sub>2</sub>) essentially eliminates the presence of atmospheric nitrogen in the flue gas. The resulting flue gas is composed primarily of CO<sub>2</sub>, along with some moisture, nitrogen, oxygen, and trace gases like SO<sub>2</sub> and NO<sub>x</sub>. Oxygen firing in utility scale boilers has been shown to be a more economical method for CO<sub>2</sub> capture than amine scrubbing (Bozzuto, et al., 2001). Additionally, oxygen firing in Circulating Fluid Bed Boilers (CFBs) can be more economical than in Pulverized Coal (PC) or Stoker firing, because recirculated gas flow can be reduced significantly. Oxygen-fired PC and Stoker units require large quantities of recirculated flue gas to maintain acceptable furnace temperatures. Oxygen-fired CFB units, on the other hand, can accomplish this by additional cooling of recirculated solids. The reduced recirculated gas flow with CFB units results in significant boiler island cost savings.

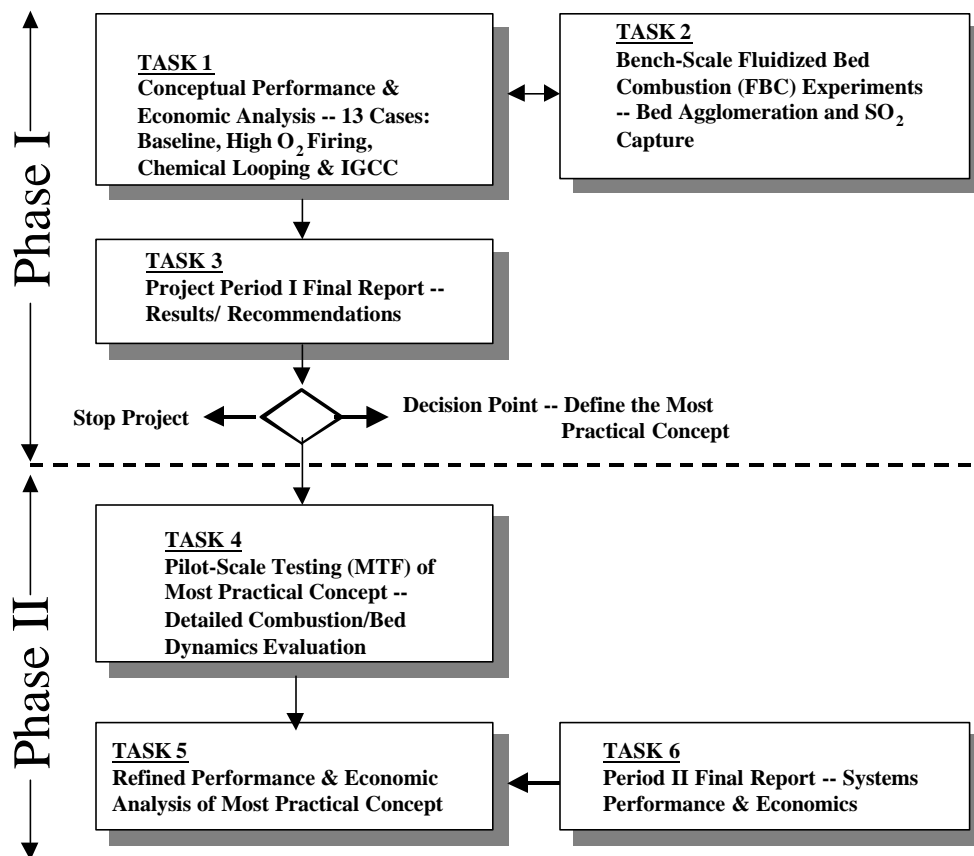
Additionally, ALSTOM has identified several advanced/novel plant configurations, which improve the efficiency and cost of the CO<sub>2</sub> product cleanup and compression process. These advanced/novel concepts require long development efforts. A preliminary economic analysis indicates that the proposed oxygen-firing technology in circulating fluidized boilers (CFB's) could be developed and deployed economically in the near future in enhanced oil recovery (EOR) applications or enhanced gas recovery (EGR), such as coal bed methane recovery.

ALSTOM received a cooperative agreement from the US Department of Energy National Energy Technology Laboratory (DOE) in 2001 to carry out a project entitled "Greenhouse Gas Emissions Control by Oxygen Firing in Circulating Fluidized Bed Boilers." This two-phased project is in effect from September 28, 2001, to October 27, 2004. (U.S. DOE NETL Cooperative Agreement No. DE-FC26-01NT41146).

A comprehensive study evaluating the technical feasibility and economics of alternate CO<sub>2</sub> capture technologies applied to Greenfield US coal-fired electric generation power plants was conducted. Thirteen separate but related cases, representing various levels of technology development, were evaluated as described herein. The first seven cases represent coal combustion cases in CFB type equipment. The next four cases represent traditional Integrated Gasification Combined Cycle (IGCC) systems. The last two cases represent advanced Chemical Looping systems, which were completely paid for by ALSTOM and included for completeness.

The Work breakdown Structure of each Phase in a following flow chart. Phase I is comprised of three tasks, as follows:

- Task 1: Conceptual and Economic Performance Analyses of Thirteen Study Cases
- Task 2: Bench-Scale Fluidized Bed Combustion (FBC) Testing
- Task 3: Phase I Final Report.



Project Flow Chart

## Bench-Scale Fluidized Bed Combustion (FBC) Testing: Technical Summary

### Objectives

The overall objective of this FBC testing is to derive pertinent combustion performance and bed dynamic information under highly controlled operating conditions in a 4-inch fluidized bed test facility. Results from various oxy-fuel firing of three fuels – two coals and one delayed petroleum coke – are to be compared to those obtained from air firing. Key Outputs include:

- ❑ Bed and ash characteristics (e.g., potential bed agglomeration/sintering)
- ❑ Gaseous emissions (NO<sub>x</sub>, SO<sub>2</sub> and CO)
- ❑ Desulfurization potentials
- ❑ NO<sub>x</sub> emissions reductions
- ❑ Unburned carbon (UBC) emissions

### Results and Conclusions

The coal sample obtained from the base case CFB plant (known hereafter as base case CFB coal) was evaluated in ALSTOM's 4-inch FBC test facility along with two other fuels. This coal was tested in air and O<sub>2</sub>/CO<sub>2</sub> mediums containing from 21% to 70%O<sub>2</sub>. The other two fuels – Illinois #6 coal and delayed petroleum coke – were tested in air and limited O<sub>2</sub>/CO<sub>2</sub> mixtures. Additionally, all three fuels were tested in air and 30%O<sub>2</sub>/70%CO<sub>2</sub> in the presence of a Ca/S mole ratio of 3.5. ALSTOM's Thermo-Gravimetric Analysis (TGA) apparatus was also used to evaluate the base case CFB coal in environments simulating combustion in air and in 30%O<sub>2</sub>/70%CO<sub>2</sub> medium. Results from the FBC and TGA can be succinctly summarized as follows:

- Coal combustion in 30%O<sub>2</sub>/70%CO<sub>2</sub> medium does not adversely affect the combustion process kinetics.
- Testing the base case CFB coal in O<sub>2</sub>/CO<sub>2</sub> mediums containing up to 70% O<sub>2</sub> caused bed temperature rises of up to about 250 °F. Nevertheless, it was possible to obviate bed slugging/defluidization problems as long as the bed was well fluidized.
- The added emission benefits offered by oxy-fuel firing over air firing in circulating Fluidized Bed Boilers (CFBs) are:
  - ◆ CO<sub>2</sub> in the flue gas is highly concentrated (~90% vs.~15%), thus making the processing of this stream to achieve the required CO<sub>2</sub> purity for EOR application relatively cheaper.
  - ◆ Typically, low NO<sub>x</sub> emissions in combustion-staged air-fired CFBs are further reduced due primarily to elimination of thermal NO<sub>x</sub>.
  - ◆ SO<sub>2</sub> emissions reductions of up to 90% with sorbent utilization should not be negatively impacted. Furthermore, ALSTOM has a commercial product called, "Flash Drier Absorbent (FDA)," which has been successfully demonstrated in the pilot-scale Multi-use Test Facility (MTF) to reduce SO<sub>2</sub> emissions by as much as 99%.
  - ◆ Burning the three fuels in high O<sub>2</sub> combustion mediums improved overall fuel combustion efficiencies, which, correspondingly, improved carbon losses.
  - ◆ The addition of limestone to the combustion process to control sulfur dioxide emissions did not adversely impact the overall combustion efficiency of each fuel.
- The test conditions used in the FBC facility are much more aggressive than those encountered in commercial CFBs (e.g., furnace outlet O<sub>2</sub> concentrations: 13-51% vs. ~3%; superficial gas velocity: ~2-3 ft/sec. vs. ~18 ft/sec). Hence, it is preliminarily concluded that the choice of 70% O<sub>2</sub>/30% recycled flue gas (principally CO<sub>2</sub>) as a combustion medium for study Case 2 (New Compact O<sub>2</sub>-Fired CFB, see Section 2.2, Volume I) was feasible.

#### **Recommendations for Future Work**

Based on these encouraging test results, on the findings from technical and economic analyses presented in volume I, and on practical considerations, it was recommended and agreed to by the DOE/NETL that Phase II workscope be implemented as recommended in the Revised Statement of Work of December 13, 2002. Pilot-scale testing in Phase II will evaluate this concept, among other things. Based on the pilot-scale testing the concept presented in Case 2 (see Section 2.2, volume I) will be either affirmed for further commercial development or modified beforehand.

## 1.0 BACKGROUND/OBJECTIVES

Burning fossil fuels in mixtures of oxygen and recirculated flue gas (consisting principally of CO<sub>2</sub>), results in a combustion process that essentially eliminates the presence of atmospheric nitrogen in the flue gas. The resulting flue gas is, therefore, composed primarily of CO<sub>2</sub>, along with some moisture, oxygen, and trace gases like SO<sub>2</sub> and NO<sub>x</sub>. Applying this concept to Circulating Fluidized Bed (CFB) boilers greatly enhances their efficiency and cost effectiveness by reducing the quantity of recirculated flue gas and by reducing the potential for atmospheric air in-leakage, both of which are significant cost and performance hurdles with alternate boiler or furnace approaches. Additionally, ALSTOM Power Inc. (ALSTOM) has identified several advanced/novel plant configurations, which improve the efficiency and cost of the CO<sub>2</sub> product cleanup and compression with respect to their commercialization potentials, these advanced/novel concepts require long development efforts. A preliminary economic analysis indicates that the proposed oxygen-firing technology in Circulating Fluidized Bed (CFB) boilers could be developed and deployed economically in the near future in Enhanced Oil Recovery (EOR) application or Enhanced Gas Recovery (EGR), such as coal bed methane recovery.

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- ❑ Bed and ash characteristics (e.g., potential bed agglomeration/sintering)
- ❑ Gaseous emissions (NO<sub>x</sub>, SO<sub>2</sub> and CO)
- ❑ Desulfurization potentials
- ❑ NO<sub>x</sub> emissions reductions
- ❑ Unburned carbon (UBC) emissions

Results obtained from this study are discussed below.

## 2.0 TEST PROGRAM

### 2.1 Test Plan

The test plan was comprised of three key elements:

- Chemical analysis of fuel and limestone samples
- Thermo-Gravimetric Analysis (TGA) to determine fuel and limestone reactivities
- Bench-scale fluidized bed combustion tests.

Chemical analysis of the fuels included standard ASTM proximate and ultimate analyses, heating values, and ash compositions and fusibility temperatures. Limestone composition was also determined.

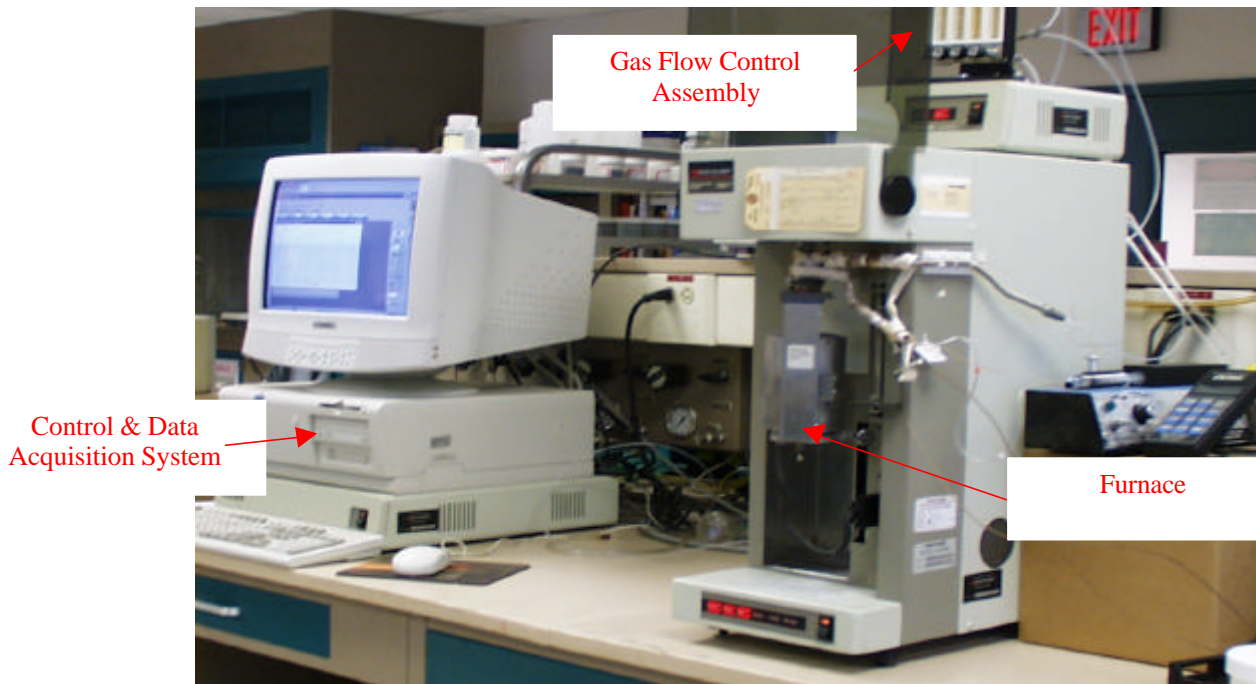
### 2.2 Test Facility Descriptions

A Thermo-Gravimetric Analyzer (TGA) and a four-inch Fluidized Bed Combustor (FBC) were the principal facilities used in the bench-scale test program. These facilities are briefly described below.

#### 2.2.1 TGA Description

ALSTOM uses a Perkin-Elmer TGA Model 7 (Figure 2.2.1) to obtain specific reactivity parameters of fuels and limestones, among other things. The TGA is also used to derive the “micro-proximate” analyses of coals and coal chars, based on a test protocol developed in-house. Testing is conducted as follows. For fuel reactivity determination, about 4-6 mg of sample, normally sized to 200x400 mesh, is placed in the TGA sample pan. The sample amount is such that it is distributed over the bottom of the pan in almost a monolayer, thus minimizing the O<sub>2</sub> mass transfer control phenomenon during combustion. Equal amounts of nitrogen (which serves to protect the balance) and air or a combination of O<sub>2</sub> and CO<sub>2</sub> is allowed to pass through the reaction tube containing the coal sample. The temperature control mechanism is actuated, such that the heating rate is maintained at 10 °C/min from room temperature to the completion of combustion. Both weight loss and rate of weight loss are monitored and recorded throughout the combustion process. The information from this testing is used, as shown in Section 3.2, to derive combustion efficiency (or burn-off) curves and “pseudo” surface reaction kinetic parameters of the test fuels as a function of reaction medium.

In the case of limestone sulfation reactivity tests, a number of measurements are normally done as a function of limestone particle size and temperature. In this abbreviated study, only one particle size (25x35 mesh) and one reaction temperature (850 °C) were utilized. Testing entails the following steps. The sample is first brought to the test temperature (850 °C) in a 15% CO<sub>2</sub>/85% N<sub>2</sub> mixture to effect calcination. After the weight has stabilized, the reacting atmosphere is switched to a mixture of 3000 vppm SO<sub>2</sub>, 5% O<sub>2</sub>, 15% CO<sub>2</sub> with the remainder as N<sub>2</sub>. The limestone sample is then sulfated at 850 °C in this atmosphere for 210 minutes. The resulting weight gain is attributed to the reaction of CaO with SO<sub>2</sub> and O<sub>2</sub> to form CaSO<sub>4</sub>. The weight gain is then used to calculate the percent calcium utilization and plotted against reaction time, as shown in Section 3.2.1



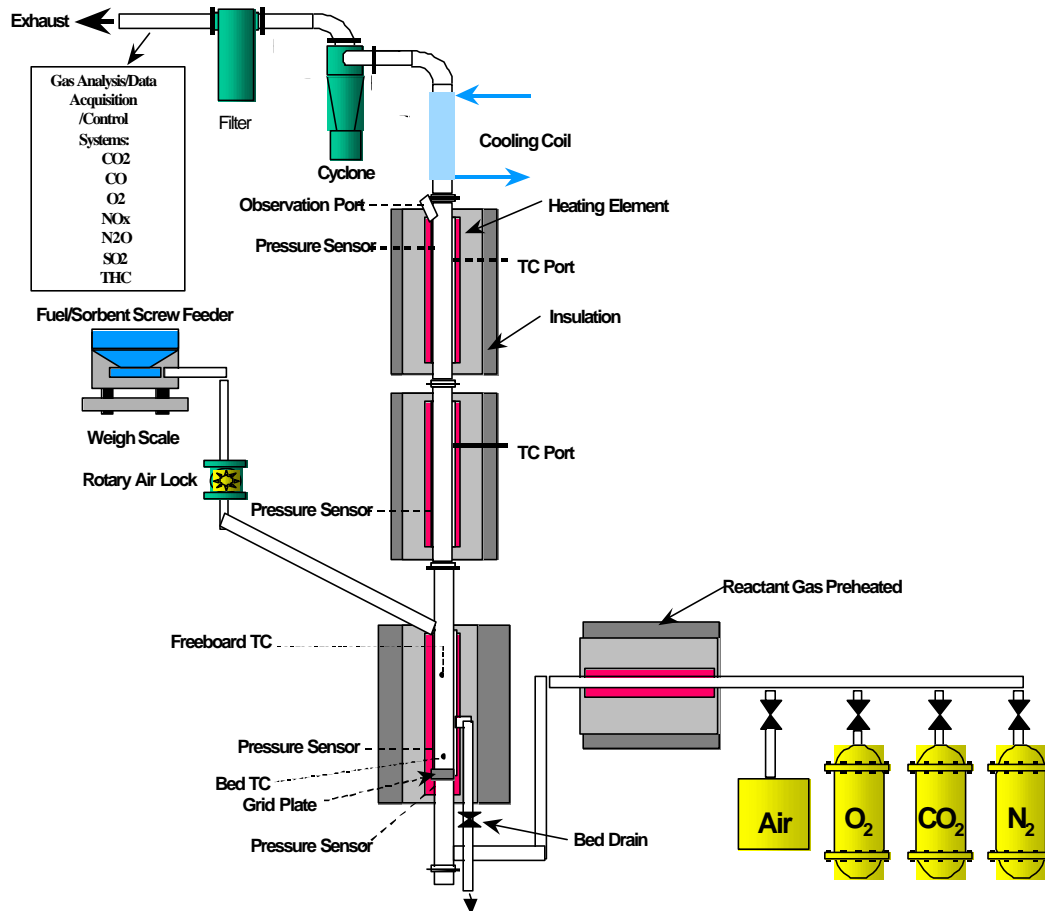
**Figure 2.2. 1: Thermo-Gavimetric Analyzer (TGA)**

## 2.2.2 Bench-Scale Fluidized Bed Combustion Description

The bench-scale Fluidized Bed Combustion (FBC) test facility used in this project is depicted schematically in Figure 2.2.2. The reactor in this electrically heated test facility is four inches in inner diameter and ~6 feet in total length. It is equipped with several thermocouples and pressure sensors for measuring bed and freeboard temperatures as well as static pressures. Size-graded fuel, premixed with a sorbent (if required), is accurately screw fed into the fluidized bed through a rotary airlock for “steady state” combustion tests. If batch tests are needed, a single shot of fuel can be directly fed into the furnace through a funnel system.

The combustion gas (e.g., air, O<sub>2</sub>/N<sub>2</sub>, or O<sub>2</sub>/CO<sub>2</sub>), which is measured with a mass flow meter, is preheated before being admitted into the furnace through a grid plate to fluidize the bed materials. The flue gas leaving the combustion chamber is cooled to approximately 400 °F before entering a cyclone; a filter housing is located further downstream for removal of fine particulate. An aliquot of the effluent gas stream is sent to a pre-calibrated gas analysis system for on-line measurement of carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), oxygen (O<sub>2</sub>), oxides of nitrogen (NO<sub>x</sub>, NO, and NO<sub>2</sub>), and sulfur dioxide (SO<sub>2</sub>) concentrations. A dedicated, proprietary LabView-based data acquisition system is used to: (1) Record gaseous species concentrations in real time as well as other process/operating parameters (gas flow rates, fuel feed rates, temperatures, pressures, etc.), and (2) Control furnace temperatures and gas flow rates to pre-set conditions. The reactor is designed such that bed materials can be drawn out through a bed drain or the whole bed can be dropped completely out of the heated zone and quenched with an inert gas. The facility currently operates within the following parameters:

- ❑ Bed temperature: up to 2000 °F
- ❑ Fluidizing gas: air, or various gas mixtures
- ❑ Bed materials: silica sand, fly ash, limestone, etc.
- ❑ Static bed height: 4-6 inches



**Figure 2.2. 2 Schematic of Bench-Scale Fluid Bed Combustor**

It was necessary to make some modification to the test facility to enable testing in  $O_2/CO_2$  combustion mixtures containing very high oxygen contents (up to 70% by volume). A 1/2-inch copper tubing was used to convey each reactant gas ( $O_2$ ,  $CO_2$ , and  $N_2$ ) from its Dewar bottle to the mixing chamber. A section of the tubing was "coiled" and immersed into a thermostat water bath, which was kept at 70 °C to avoid sample freeze-ups. A relief valve was installed downstream of the water bath. Gas flow rates were measured through mass flow meters, which were located upstream of the mixing chamber. The same 1/2-inch copper tubing used to convey the gas mixture into the 1-1/2-inch carbon steel pipe, which then fed it into the pre-heaters. Special guidelines, specified in the ASTM G-94-92 protocol (1999), were used in connecting various portions of the tubing, and in cleaning them for oxygen service. Additionally,  $N_2$  and  $O_2$  lines were connected such that  $N_2$  could be used to purge the  $O_2$  line before and after each operation.

### 3.0 TEST RESULTS

#### 3.1 Chemical Analyses of Test Fuels and Limestone Samples

The base case CFB coal, Illinois # 6 coal, and delayed petroleum coke were subjected to proximate and ultimate analyses and higher heating value determinations as shown in Table 3.1.1. Additionally, they were subjected to ash analysis and fusibility temperature measurements, as shown in Table 3.1.2. The limestone sample from the base case CFB plant was also subjected to ASTM analysis, as shown in Table 3.1.3.

The base case CFB coal has nitrogen and sulfur contents of 2.4% and 1.7% on a dry-ash-free (DAF) basis, respectively. These values, which are typical of those of Eastern bituminous coals, result in nitrogen and sulfur loadings of 1.2 and 1.6 lb/MMBtu. The Illinois # 6 coal, on the other hand, has corresponding nitrogen and sulfur loadings of 1.0 and 3.5 lb/MMBtu. The pet coke is somewhat unusual with its lower sulfur content (1.3%, DAF basis) than typical; pet cokes generally have sulfur contents ranging from 3% to 5%. By contrast, typical delayed pet cokes have nitrogen contents ranging from 0.5 to 1.0%, whereas the subject pet coke has a nitrogen content of 3.3 % on a DAF basis. These values result in nitrogen and sulfur loadings of 2.1 and 0.8 lb/MMBtu, respectively. These data foreshadow high NO<sub>x</sub> emission potential for the delayed pet coke and high SO<sub>2</sub> emissions potential for the Illinois #6 coal.

The Illinois #6 coal ash is typical of Eastern bituminous coals, with an iron content (as Fe<sub>2</sub>O<sub>3</sub>) greater than the sum of alkali and alkaline earth metals (i.e., CaO+MgO+Na<sub>2</sub>O+K<sub>2</sub>O). The combination of high sulfur content in the coal and ash composition leads to low ash fusibility temperatures, indicating, as is well known, high slagging potential for this coal. The pet coke has an ash content (0.3%, see Table 3.1.2) near the lower end of the typical range for pet cokes. Despite the relatively high concentration of vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) in the ash (19.8%), the very low ash content puts the vanadium pentoxide at about 600 ppm on a fuel-fired basis. This concentration of vanadium pentoxide is well within the range of other pet cokes that have been successfully fired in CFB combustors.

The limestone sample from the base case CFB plant was analyzed to determine its composition. Table 3.1.3 shows the results of this limestone versus relatively high and low reactivity reference limestones used in ALSTOM-supplied CFBs. Compositionally, this limestone contains more "inerts" than reference Limestones 1 and 2. Suffice it to note that this limestone is successfully used at the base case CFB plant.



**Table 3.1.1: Selected Analyses of Test Fuels**

QUANTITY	BASE CASE CFB COAL		ILLINOIS No. 6 COAL		DELAYED PETROLEUM COKE	
	As-Received	Dry-Ash-Free	As-Received	Dry-Ash-Free	As-Received	Dry-Ash-Free
Prox. & Ult. Analyses, Wt. %						
Moisture	3.9	---	16.4	---	9.4	---
Volatile Matter	15.6	20.9	32.7	43.6	10.2	11.3
Fixed Carbon (Diff.)	59.0	79.1	42.3	56.4	80.1	88.7
Ash	21.5	---	8.6	---	0.3	---
Hydrogen	3.3	4.4	4.1	5.5	3.6	4.0
Carbon	65.2	87.4	59.2	78.9	81.6	90.4
Sulfur	1.8	2.4	3.7	4.9	1.1	1.2
Nitrogen	1.3	1.7	1.1	1.5	3.0	3.3
Oxygen (Diff.)	3.0	4.0	6.9	9.2	1.0	1.1
HHV, Btu/lb, daf	11342	15204	10630	12715	14048	15557
O/N Ratio	2.31	---	6.27	---	0.33	---
FC/VM Ratio	3.78	---	1.29	---	7.85	---
N Loading (lb/MMBtu)	1.15	---	1.03	---	2.14	---
Sulfur Loading (lb/MMBtu)	1.59		3.48		0.78	

**Table 3.1.2: Ash Compositions and Fusibility Temperatures of Test Fuels**

QUANTITY	BASE CASE CFB COAL	ILLINOIS #6 COAL	DELAYED PET COKE
<b>Ash Fusibility Temperatures, °F</b>			
I.T.	2440	2070	Not Measured
S.T.	2535	2135	
H.T.	2650	2190	
F.T.	2800	2260	
$\Delta T = F.T.-I.T.$	360	190	
<b>Ash Compositions, Wt.%, Dry</b>			
SiO <sub>2</sub>	56.2	47.7	13.7
Al <sub>2</sub> O <sub>3</sub>	26.6	18.3	7.4
Fe <sub>2</sub> O <sub>3</sub>	9.1	17.2	12.9
CaO	1	4.8	12.3
MgO	0.7	0.8	1.9
Na <sub>2</sub> O	0.5	1.7	4.6
K <sub>2</sub> O	2.7	1.9	0.7
TiO <sub>2</sub>	1.3	0.8	0.8
P <sub>2</sub> O <sub>5</sub>	0.6	0.1	0.4
SO <sub>3</sub>	0.8	5.5	14.1
MnO	0.1	0.1	0.1
V <sub>2</sub> O <sub>5</sub>	---	---	19.8
BaO	0.1	0.1	0.1
SrO	0.1	0.1	0.1
NiO	---	---	10.1
TOTAL	99.8	99.1	99.0

**Table 3.1.3: Limestone Composition**

Item	Reference Limestone-1	Base Case CFB Limestone	Reference Limestone-2
% Moisture	<0.1	0.19	<0.1
Raw Data - Dry basis	wt %	wt %	wt %
Total Ca	37.53	32.26	38.59
Total Mg	0.23	2.28	0.34
CO <sub>2</sub>	41.62	39.86	42.32
Report Basis			
% as CaCO <sub>3</sub>	93.7	80.6	96.4
% as MgCO <sub>3</sub>	0.8	7.9	1.2
% Inerts (difference)	5.5	11.5	2.4

### 3.2 TGA Reactivity Test Results

As noted previously, ALSTOM's TGA apparatus was used to determine fuel and limestone reactivities. In the case of fuel reactivity, the measurement involves determining the time for complete burnout of the combustibles of a given fuel. In the case of limestone the measurement involves the time for sulfation to occur and the percent calcium utilization in sulfur absorption. Results are presented below.

#### 3.2.1 Limestone Reactivity

The base case CFB plant-supplied limestone is compared with two other reference limestones that are used successfully in commercial CFBs built by ALSTOM. The subject limestone is slightly less reactive than Reference Limestone-1 and significantly more reactive than Reference Limestone-2. Limestones vary in porosity, and hence reactive surface areas, when undergoing calcination. Though not measured, it can be surmized that the subject limestone has a relatively greater surface area after calcination than Reference Limestone-2, and a surface area slightly less than Reference Limestone-1. Importantly, the three limestones evaluated here are currently used successfully at their respective CFB power plants.

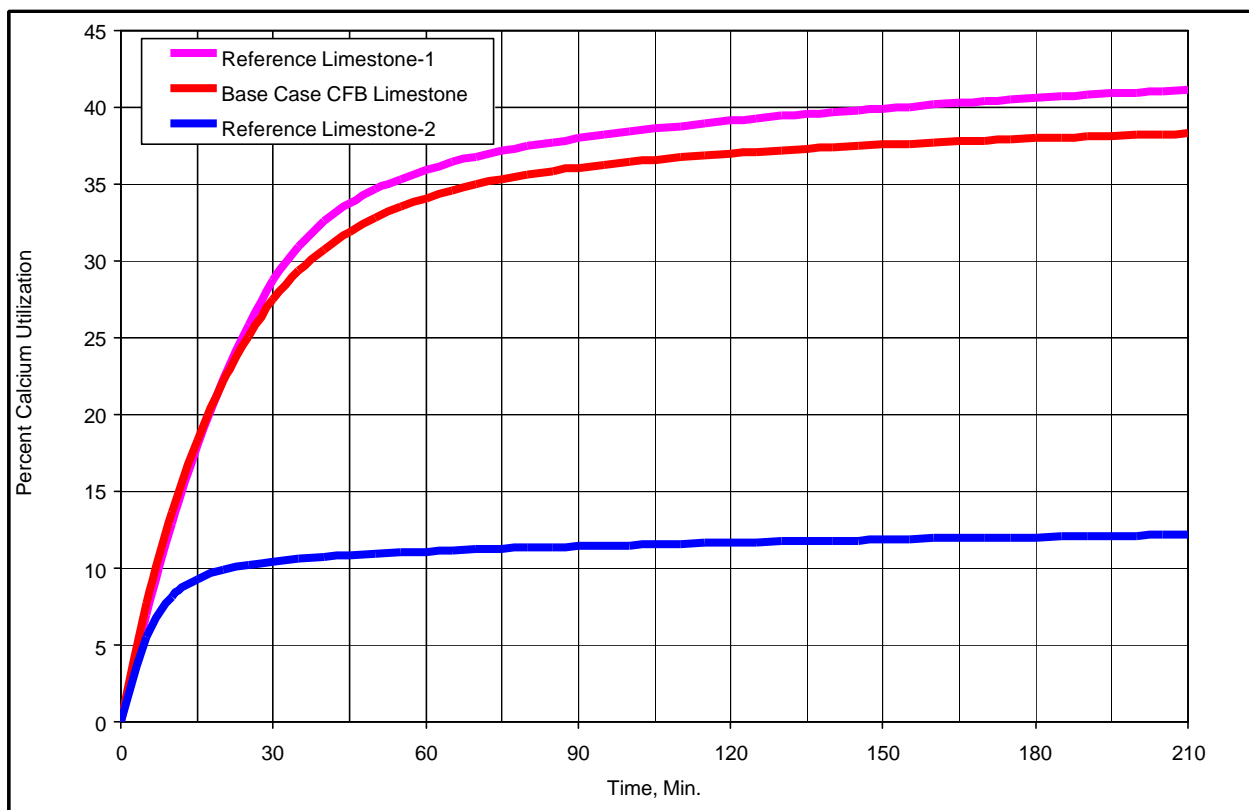


Figure 3.2.1: Sulfation Reactivity of Base Case CFB and Reference Limestones

### 3.2.2 Fuel Reactivity

Each of the three subject fuels was burned in air along with other reference fuels. Additionally, three cases were evaluated for the base case CFB's coal (Table 3.2.1). Fifty (50) cc/min of N<sub>2</sub> gas were admitted into the balance compartment to protect it from over-heating. The first (Reference) case consisted of burning the coal in 50 cc/min of air. The so-called "Constant Mass" case consisted of burning the coal in an O<sub>2</sub>/CO<sub>2</sub> mixture, such that the mass of O<sub>2</sub> used in the Reference case was maintained and the mass of N<sub>2</sub> used in the reference case was replaced with an equal mass of CO<sub>2</sub>. The "Constant Volume" case consisted of burning the coal in O<sub>2</sub>/CO<sub>2</sub> mixture, such that the mass of O<sub>2</sub> used in the Reference case was again maintained and the volume of N<sub>2</sub> used in the reference case was replaced with an equal volume of CO<sub>2</sub>. The two oxy-fuel firing cases are important for the following reasons:

- The "Constant Mass" case simulates a scenario involving a retrofit of an existing air-fired CFB to oxy-fuel firing. It has been shown by ALSTOM (Bozzuto, et al., 2001) that such a case would require only minimal modification to the boiler island.
- The "Constant Volume" case simulates a "Greenfield" oxy-fuel-fired CFB scenario. It should, nevertheless, be borne in mind that ALSTOM has pushed the envelope by proposing a full-scale CFB firing coal in a combustion medium comprising 70% O<sub>2</sub> and 30% recycled flue gas. Test results for oxy-fuel firing with the O<sub>2</sub> concentration in the combustion medium (in CO<sub>2</sub> balance) increased progressively from 21% to 70% are presented in Section 3.3.

**Table 3.2.1: TGA Test Matrix for Base Case CFB Coal**

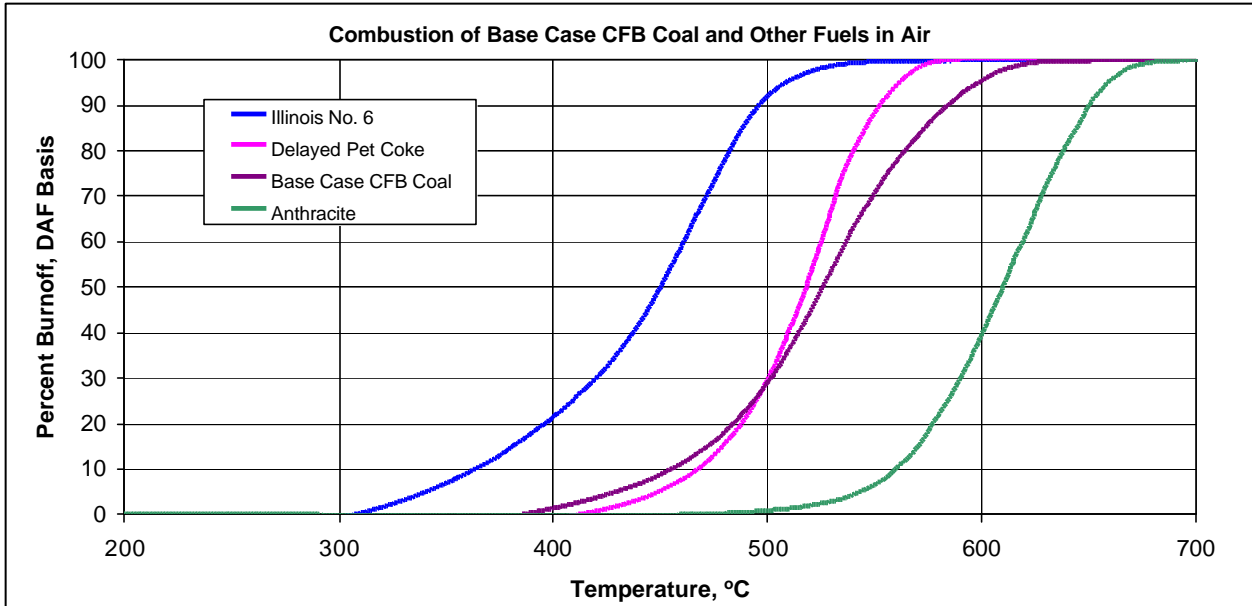
Combustion Medium	Case	Balance		Combustion Air						CO <sub>2</sub>		Grand Total		Comb.Med. Comp.		
		Cooling N <sub>2</sub>		Total Air		O <sub>2</sub>		N <sub>2</sub>						(Vol. %)		
		(cc/min)	(g/min)	(cc/min)	(g/min)	(cc/min)	(g/min)	(cc/min)	(g/min)	(cc/min)	(g/min)	(cc/min)	(g/min)	N <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub>
Air	Baseline	50	0.0573	50	0.0592	10.5	0.01373	39.5	0.04524	0.0	0.0	100.0	0.1162	89.5	---	10.5
O <sub>2</sub> /CO <sub>2</sub> Mixture	Constant Mass	50	0.0573	0.0	0.0	10.5	0.01373	0.0	0.0	25.2	0.0452	85.7	0.1162	58.4	29.4	12.3
O <sub>2</sub> /CO <sub>2</sub> Mixture	Constant Volume	50	0.0573	0.0	0.0	10.5	0.01373	0.0	0.0	39.5	0.071	100.0	0.1420	50.0	39.5	10.5

All flow rates @ 25 °C & 1 atm.

Burn-off curves of the three subject fuels are shown in Figure 3.2.2 along with that of a Pennsylvania anthracite sample. According to these burn-off curves, the base case CFB coal, which is a medium volatile bituminous coal, takes somewhat longer to burn to completion than the pet coke. As expected, both fuels take longer to burn to completion than the Illinois #6 high volatile C bituminous (hvCb) coal. Also, as expected, both fuels burn to completion faster than a reference anthracite sample.

Figure 3.2.3 shows data from the same TGA tests plotted as the rate of weight loss as a function of temperature. These plots are also shown for the three subject fuels with the same anthracite as a reference fuel for comparative purposes. Plotting the data in this manner shows the position of peak combustion intensity, as evidenced by peak rates of weight loss. Relative positions of fuel reactivity are unchanged from the previous figure, but the shapes of the curves denote something about the nature of the combustibles. Generally, the position of the weight loss peak varies inversely with the volatile matter content in the fuel. This is supported by the fact that the volatile matter contents of the Illinois #6 coal, base case CFB coal, and

the anthracite are 44, 21, and 4%, respectively. The corresponding value for the pet coke is 14%. These fuels are similar to those routinely burned in ALSTOM-designed CFBs (e.g., Tanca, 1994).



**Figure 3.2.2: Burn-Off Shown as Weight Loss of Various Fuels in Air as a Function of Temperature**

Figures 3.2.4, 3.2.5, and 3.5.6 show the burn-off, rate of weight loss, and pseudo-combustion kinetics of the base case CFB coal in air and O<sub>2</sub>/CO<sub>2</sub> mixtures under constant mass and constant volume scenarios. The basic message from these plots is that oxy-fuel firing does not negatively impact the overall combustion efficiency of a fuel compared to air firing. These results are consistent with those obtained previously by ALSTOM (Bozzuto, et al., 2001).

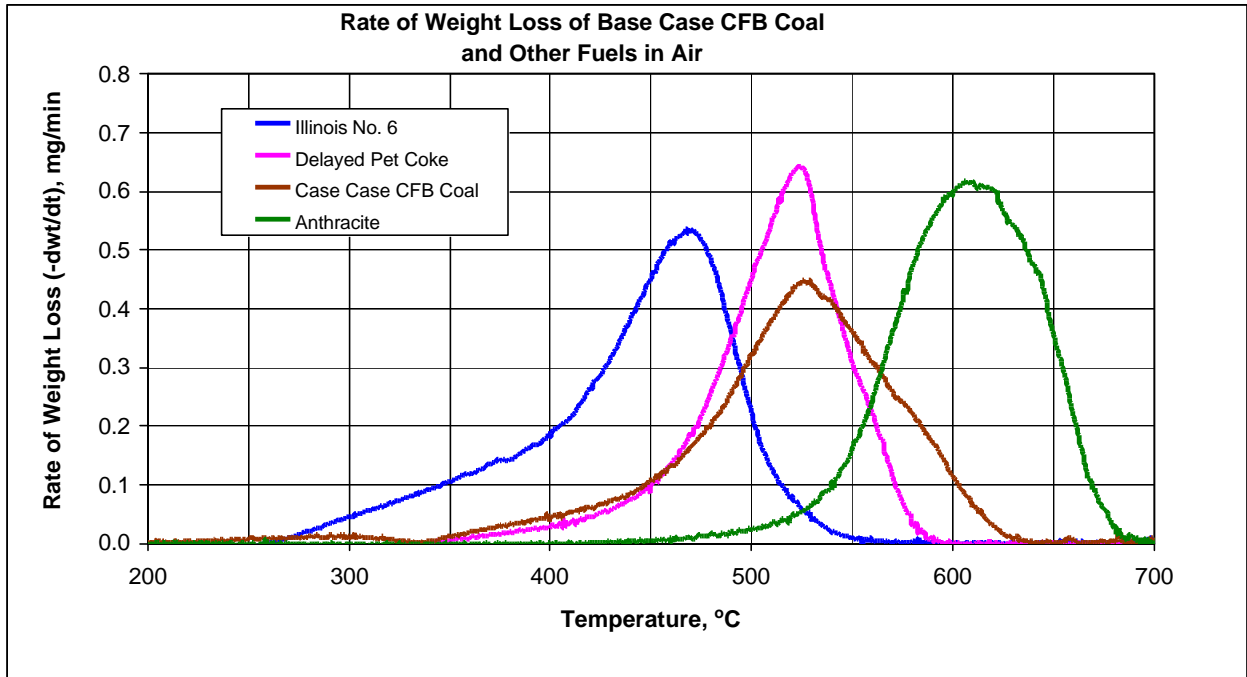


Figure 3.2.3: Rate of Weight Loss of Various Fuels in Air as a Function of Temperature

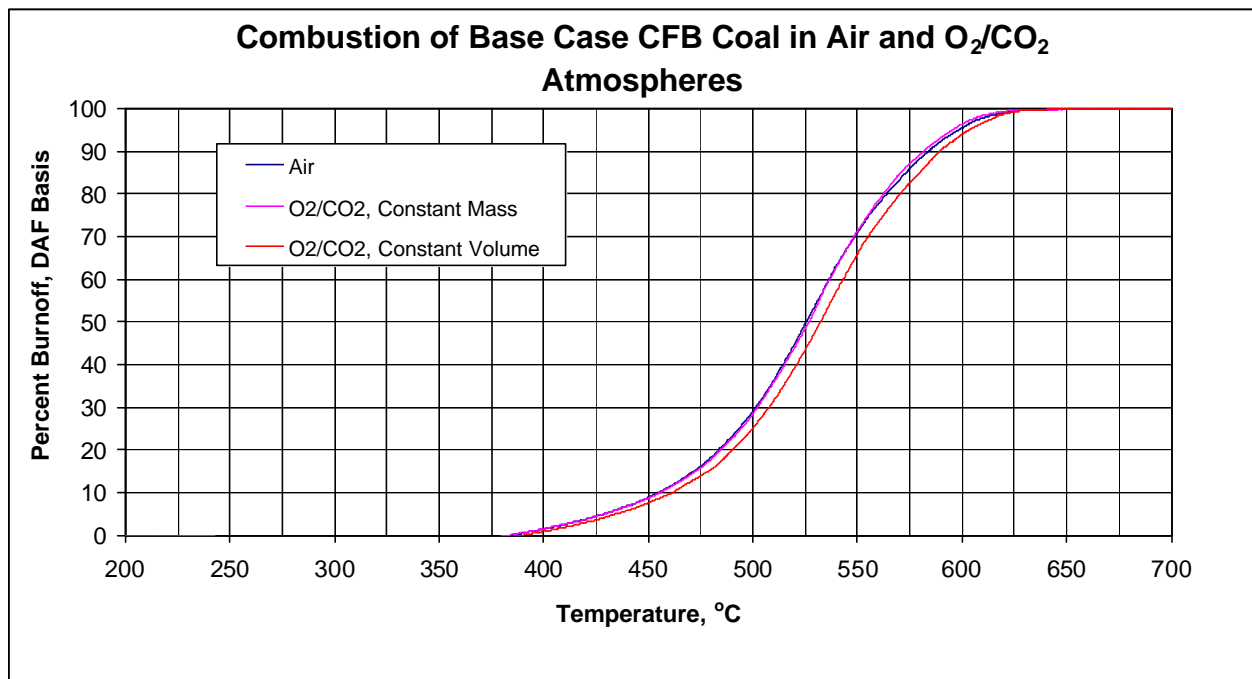


Figure 3.2.4: Burn-Off Shown as Weight Loss of Base Case CFB Coal in Air and O<sub>2</sub>/CO<sub>2</sub> Mixtures as a Function of Temperature

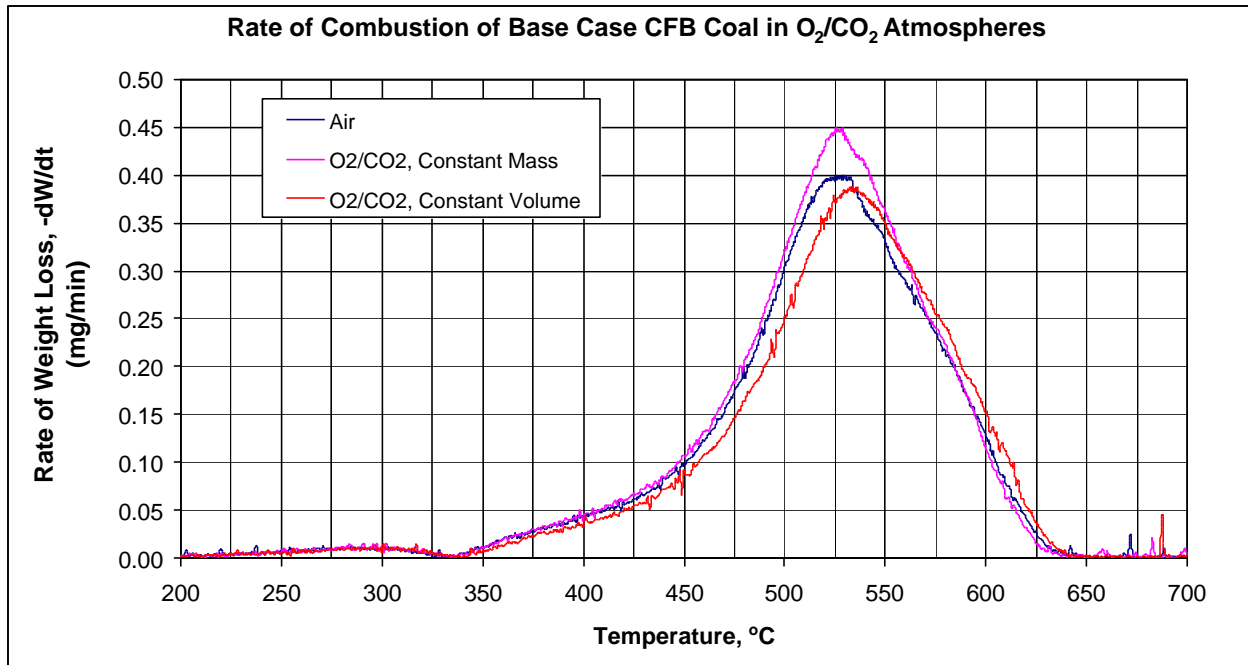


Figure 3.2.5: Rate of Weight Loss of Base Case CFB Coal in air and O<sub>2</sub>/CO<sub>2</sub> Mixtures as a Function of Temperature

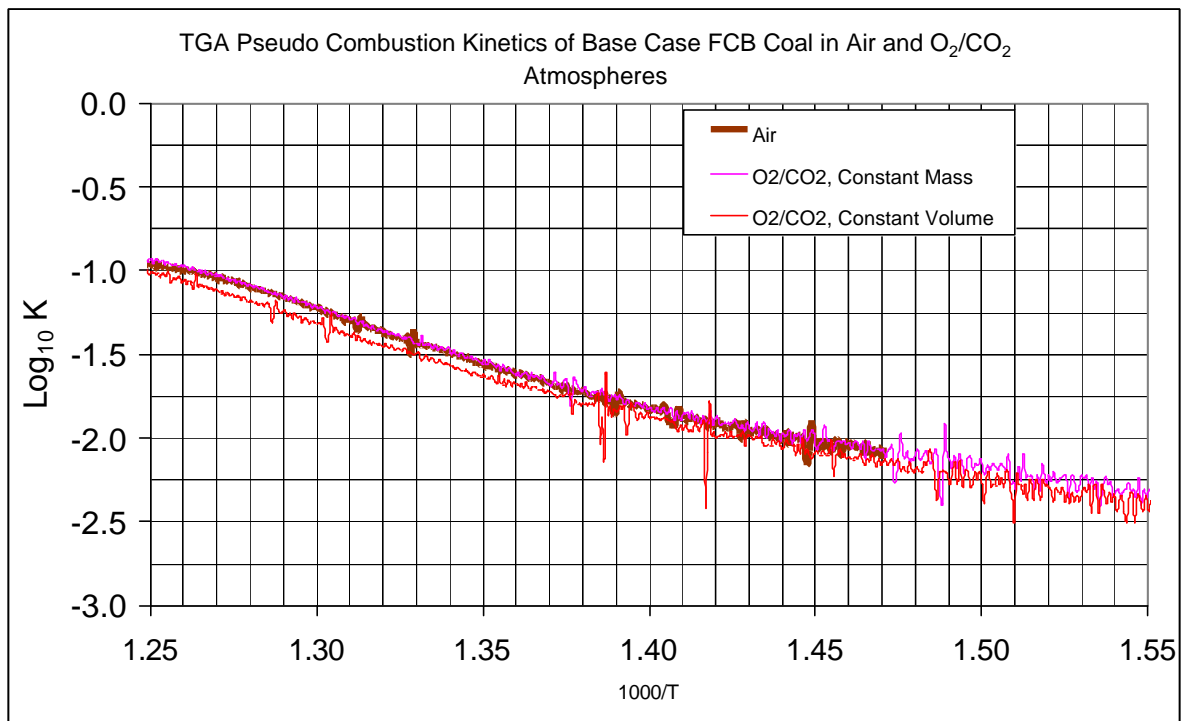


Figure 3.2.6: Pseudo Combustion Kinetics of Base Case CFB Coal in Air and O<sub>2</sub>/CO<sub>2</sub> Mixtures

### 3.3 Bench-Scale Fluidized Bed Combustion (FBC) Tests Results

Table 3.3.1 shows the test matrix followed when performing the combustion testing of the three subject fuels in the four-inch inner diameter Fluidized Bed Combustion (FBC) facility. Three series of tests were carried out on each fuel, with the major emphasis placed on the base case CFB coal. The first series (I) involved burning the fuel in air to provide a frame of reference for comparing the results from the other series. The second series (II) was dedicated to firing each fuel in one or more O<sub>2</sub>/CO<sub>2</sub> mixtures. The third series (III) was for determining the desulfurization potential of each fuel with the limestone sample from the base case CFB plant in air and in 30% O<sub>2</sub>/70% CO<sub>2</sub> (which simulates the constant mass scenario explained in Section 3.2.2). The superficial gas velocity was maintained in a narrow range of 1.8-3.3 ft/sec. The stoichiometry was varies in the 2.0-4.7 range. Under these conditions, the furnace outlet O<sub>2</sub> concentration was in the 13-51% (Dry basis).

The test conditions in Table 3.3.1 were selected on the basis of a balanced consideration of personnel safety, furnace operation, and the nature of the results obtained. A few scoping tests were run up-front to ensure that the widely varying conditions represented in this test matrix could be run without resorting to unreasonable compromises.

**Table 3.3.1: Test Matrix for Bench-Scale Fluidized Bed Combustion**

Fuel	Series	Ca/S Mole Ratio	Combustion Gas Medium	Bed Temperature, °F	Superficial Gas Velocity, ft/sec.	Stoichiometry, λ	Measurements/Observations:
Base Case CFB Coal	I	---	Air	1635-1908	1.8 - 3.3	2.0 - 4.7	<input type="checkbox"/> Ash slagging/sintering potentials as a result of increased oxygen concentrations in the combustion gas, and/or use of a slagging coal  <input type="checkbox"/> Flue gas desulfurization potential by the limestone sample used  <input type="checkbox"/> NOx emissions reduction by use of nitrogen-free O <sub>2</sub> /CO <sub>2</sub> combustion mediums  <input type="checkbox"/> Impact of various combustion mediums on: (1) overall fuel combustion efficiency; (2) unburned carbon emissions; and (3) CO emissions  <input type="checkbox"/> Impact of fuel nature on all the parameters specified above
	II	---	23% O <sub>2</sub> -70% O <sub>2</sub> /in CO <sub>2</sub> Balance				
	III	3.5	Air				
		3.5	30% O <sub>2</sub> /70% CO <sub>2</sub>				
Illinois #6 Coal	I	---	Air				
	II	---	21% O <sub>2</sub> -50% O <sub>2</sub> /in CO <sub>2</sub> Balance				
	III	3.5	Air				
		3.5	30% O <sub>2</sub> /70% CO <sub>2</sub>				
Delayed Petroleum Coke	I	---	Air				
	II	---	30% O <sub>2</sub> /70% CO <sub>2</sub>				
	III	3.50	Air				
		3.50	30% O <sub>2</sub> /70% CO <sub>2</sub>				

The impact of both CO<sub>2</sub> partial pressure and temperature on limestone calcination in the furnace is shown in Figure 3.3.1. This thermodynamic calculation shows, for example, that limestone calcination with a CO<sub>2</sub> partial pressure of 0.7 atm is not a problem, as long as the temperature is greater than 1600 °F. Based on this result, it was decided to carry out all the tests with high CO<sub>2</sub> partial pressures at not less than 1650 °F bed temperature. A Ca/S mole ratio of 3.5 was used in all the desulfurization tests, based on previous experience. It should be understood at the outset that the test matrix in Table 3.3.1 was tailored to provide results on a comparative basis only. No conclusions should be drawn on the actual magnitudes of the data points.



The types of measurements/observations made in this evaluation are specified in Table 3.3.1. The results obtained from this test program are discussed below.

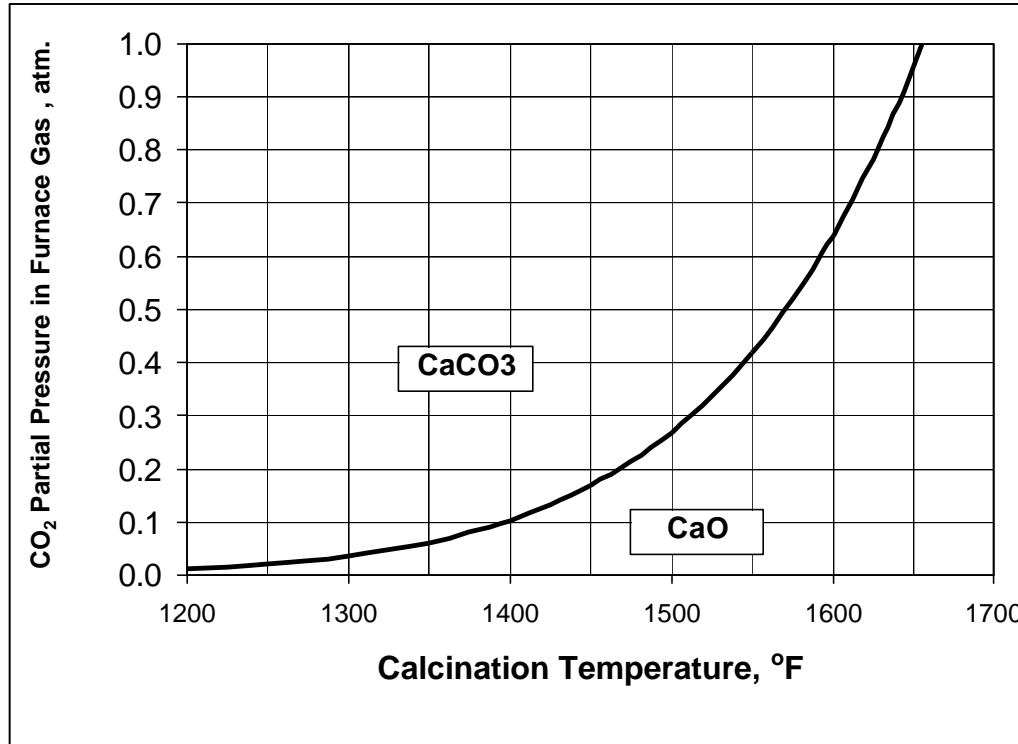


Figure 3.3.1: Limestone Calcination as a Function of Furnace CO<sub>2</sub> Partial Pressure And Temperature

### 3.3.1 Observations on Combustion Behavior/Ash Slagging Potentials

The coal sample obtained from the base case CFB plant was used to evaluate the impacts of superficial gas velocity and O<sub>2</sub> content in the combustion gas on its ash slagging potential. Given that the minimum fluidization velocity of the alumina bed materials used was less than 0.5 ft/sec, it was decided to first determine the minimum superficial gas velocity that could be used during combustion in air without any slagging-related defluidization problems. This value was found to be about 1.7 ft/sec with a bed temperature of about 1650 °F. Testing in 30% O<sub>2</sub>/70% CO<sub>2</sub> medium also presented no defluidization problems at this temperature. Testing in 50% O<sub>2</sub>/50% CO<sub>2</sub> medium, however, caused, at first, a virtually uncontrollable bed temperature rise and subsequent bed defluidization. Consistent with increased bed temperature with increasing O<sub>2</sub> in the combustion medium, it was observed that the flames studied were (1) orange-yellowish in air and 30% O<sub>2</sub>/70% CO<sub>2</sub> combustion; and (2) increasingly bright and whitish in combustion mediums with 40% O<sub>2</sub> or greater. In fact, the 70% O<sub>2</sub>/30% CO<sub>2</sub> flame was exceedingly whitish in nature and hard to look at.

Testing this coal in O<sub>2</sub>/CO<sub>2</sub> mediums containing up to 70% O<sub>2</sub> caused, as expected, a bed temperature rise of up to about 250 °F. Nevertheless, it was possible to obviate bed slagging/defluidization problems as long as the bed was well fluidized. As a frame of reference, the superficial gas velocity had to be maintained at greater than 2.5 ft/sec, whereas for combustion testing in air and O<sub>2</sub>/CO<sub>2</sub> mediums containing equal to or less than 40% O<sub>2</sub>, a superficial gas velocity of ~1.7 ft/sec was sufficient to keep the bed fluidized at all times.

The increase in particle surface temperature (T<sub>s</sub>) with O<sub>2</sub> partial pressure was confirmed through calculations based on heat balance (Field, et al., 1967), i.e.,  $H_g = H_r + H_c$ , where  $H_g$  is the heat generated by the burning particle and  $H_r$  and  $H_c$  are the radiation and conduction heat losses from the particle, respectively. Depending on the particle size and O<sub>2</sub> partial pressure surrounding the particle, its surface temperature (T<sub>s</sub>) could be lower than the bulk gas temperature (T<sub>g</sub>) or higher by several hundred to thousands of degrees Fahrenheit (see illustration of heat balance algorithm in Figure 3.3.2).

A number of lessons were learned through trial and error to successfully burn the subject fuels under the test conditions specified in Table 3.3.1.

- Start fuel feeding while the bed temperature was about 200 °F below the target value. Slowly increase the feed rate as the bed temperature rises steadily, and approaches its target.
- Ensure that the whole bed is fully fluidized at all times. A superficial gas velocity of 2.5 ft/sec or higher was sufficient for obviating bed slagging/defluidization under the conditions prevailing in this study.

Using the above guidelines enabled the authors to successfully test fire the Illinois #6 coal, which is known to have a high slagging potential (see Section 3.1, above), in the FBC in O<sub>2</sub>/CO<sub>2</sub> atmospheres containing up to 50% O<sub>2</sub> without any bed defluidization-related problems. Although the test in 70% O<sub>2</sub>/30% CO<sub>2</sub> was not run, due principally to time and financial constraints, there is no reason to believe that it could not be executed successfully. The pet coke was run only in air and 30% O<sub>2</sub>/70% CO<sub>2</sub> medium, as this fuel has virtually no slagging potential.

The test conditions used here in the FBC facility are very aggressive for three reasons: (1) there was no means of recycling particles to control the bed temperature; (2) the superficial gas velocities were very low; and (3) given the prevailing stoichiometric ratios, the furnace outlet O<sub>2</sub> concentration ranged from 13% to 51% (dry basis). Conversely, the operating conditions of a commercial oxy-fuel fired CFB would be much less aggressive for the following reasons: (1) the bed temperature would be closely controlled through judicious recycling of bed materials; (2) the superficial gas velocity would be maintained at about 18 ft/sec; and (3) the O<sub>2</sub> concentration in the furnace would rapidly decline from its initial value of 70%, for Case 2 (New Compact O<sub>2</sub>-Fired FCB, see Volume I), to about 3% at the outlet.

Based on these findings, it was preliminarily concluded that the choice of 70% O<sub>2</sub>/30% recycled flue gas (essentially CO<sub>2</sub>) as a combustion medium for study Case 2 was plausible. Pilot-scale testing in Phase II will be used to evaluate this concept. Based on the pilot-scale testing the concept presented in Case 2 will be either affirmed for further commercial development or modified.

<b>HEAT BALANCE</b> $H_g + H_r + H_c = 0.0$
--

**Rate of heat generation per unit area**

$H_g = q \cdot Q$  [cal/cm<sup>2</sup>-s]

Q = Heat release at surface per unit mass of C burned

$Q_{1800K} = 7900 (2/\phi - 1) + 2340 (2-2/\phi)$  [cal/g]

$\phi$  = Mechanism factor

$q = \rho_b / (1/k_{diff} + 1/k_s)$  [g/cm<sup>2</sup>-s]

$K_{diff} = 24 \phi D / (x R' T_m)$

Hirschfelder, Curtiss & Bird (1954)

D = Binary diffusion coeff of O<sub>2</sub> in gas [cm<sup>2</sup>/s]

$D_b (T/T_o)^{1.75} (P_o/P)$

R' = Gas constant [atm-cm<sup>3</sup>/mole-K]

$T_m = (T_g + T_s)/2$  [°K]

$k_s = A \exp(-E/R/T_s)$

$A = k_{so} \exp(-E/R/T_{so})$  [g/cm<sup>2</sup>-s-atm]

E = Activation energy [cal/mole]

R = Gas Constant [cal/mol-K]

**Rate of heat loss by radiation**

$H_r = \epsilon \sigma (T_s^4 - T_w^4)$  [cal/cm<sup>2</sup>-s]

$\sigma$  = Stefan-Boltzman constant [cal/cm<sup>2</sup>-s-K]

**Rate of heat loss by conduction**

$H_c = 2l (T_s - T_g)/x$  [cal/cm<sup>2</sup>-s]

$\lambda = \lambda_o [(T_s - T_g)/(2 \cdot T_o)]^{0.75}$  [cal/cm-s-K]

T<sub>o</sub> = reference temp for  $\lambda_o$  [°K]

$\lambda_o$  [cal/cm-s-K]

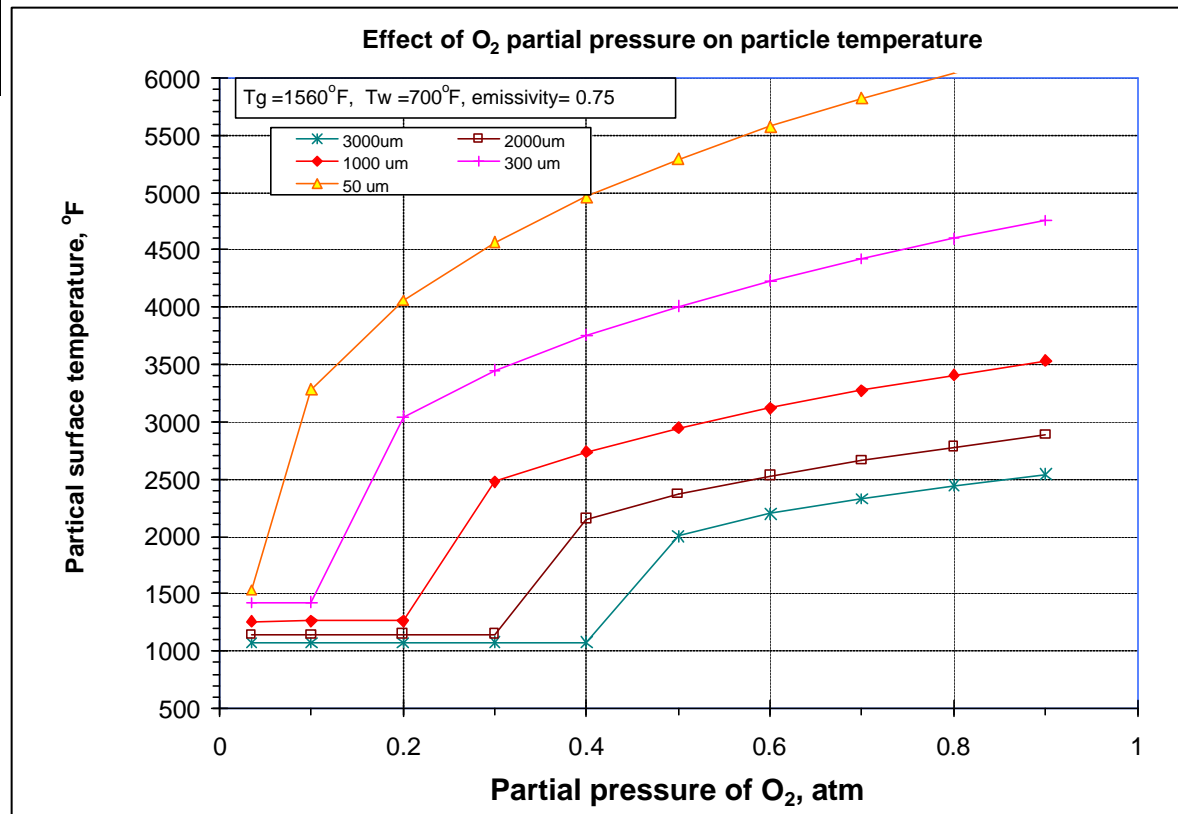


Figure 3.3.1: Variation of Burning Fuel Particle Surface Temperature with Oxygen Partial Pressure

### 3.3.2 Combustion Characteristics

As noted in the test matrix (Table 3.3.1), a number of measurements were made while observing the bed dynamics behavior (e.g., ash slagging potential), as a function of operating conditions. The fly ash samples, collected in the cyclone and Balston bag filter for each test, were first blended before being subjected to proximate and ultimate analyses. The ultimate analyses yielded the unburned carbon (UBC) values. An ash tracer technique (Nsakala, et al., 1986) was used in conjunction with the proximate analyses of the feed stock and fly ash residues to calculate the overall fuel combustion efficiencies. These results are presented in

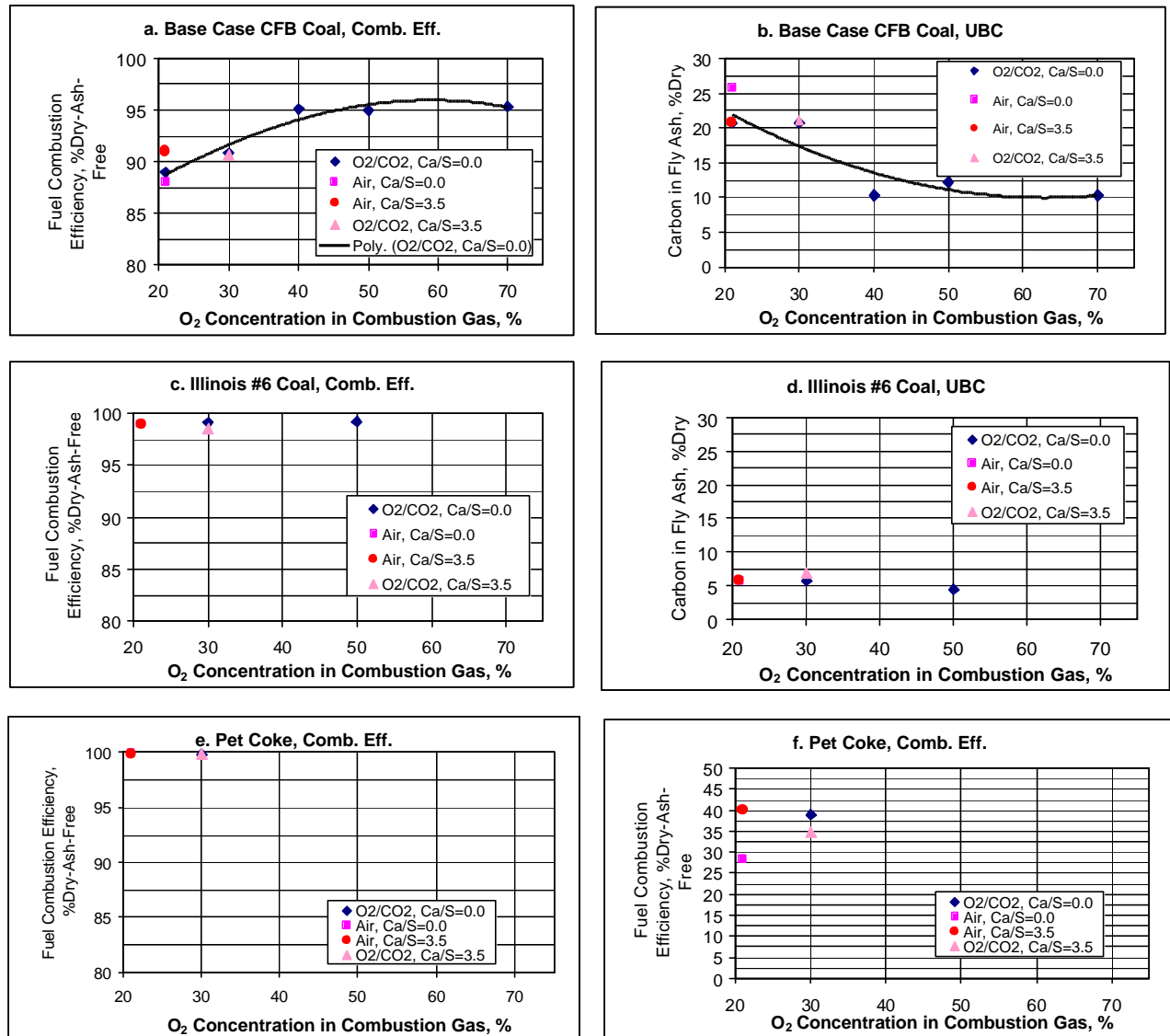
Table 3.3.2 and plotted in Figure 3.3.3. They can be summarized as follows:

- The overall Fuel Combustion Efficiency (FCE) of the medium volatile bituminous (mvb) coal from the base case CFB plant (Figures 3.3.3 a & b) increases with increasing oxygen content in the combustion gas, levelling off at about 95%. The unburned carbon (UBC) in the fly ash shows, as expected, the exact reverse trend, levelling off at about 10%.
- The Illinois #6 high volatile C bituminous (hvCb) coal (Figures 3.3.3 c & d) is so reactive that the oxygen content in the prevailing combustion gas medium does not distinctly impact its overall combustion efficiency. The FCE values for this coal are greater than 98% under all circumstances. The UBC values in the fly ashes are correspondingly low at about 5% under all circumstances.
- The pet coke sample is also highly reactive (Figures 3.3.3 e & f) and, hence, shows a similar FCE trend with the Illinois #6 coal. The high UBC values are simply indicative of the fact that this fuel has a very low ash content (0.3%, see Table 3.1.1 above).
- The addition of limestone to the combustion process to control sulfur dioxide emissions does not adversely impact overall combustion efficiency.

Based on these results, it can be concluded that oxy-fuel firing enhances overall fuel combustion efficiency, which, correspondingly, decreases carbon heat loss.

**Table 3.3.2: Summary of Bench-Scale FBC Test Data**

Fuel	Test No.	Combustion Gas Medium	Superficial Gas Velocity, ft/sec.	Stoichiometry, $\lambda$	Ca/S Mole Ratio	Gaseous Emissions, lb/MMBtu				Fuel Combustion, %DAF Basis	Unburned Carbon (UBC) in Fly Ash, % Dry Basis
						Bed Temperature, °F	NOx	SO <sub>2</sub>	CO		
Base Case CFB Coal	BCCa	Air	3.27	2.10	---	1676	1.06	2.26	0.12	88.0	25.8
	BCCa1	21% O <sub>2</sub> /79% CO <sub>2</sub>	3.18	2.02	---	1635	0.93	2.21	0.38	89.0	20.7
	BCCb	30% O <sub>2</sub> /70% CO <sub>2</sub>	1.77	2.11	---	1683	0.90	2.42	0.32	90.8	20.7
	BCCc	40% O <sub>2</sub> /60% CO <sub>2</sub>	2.77	2.95	---	1681	1.01	2.70	0.30	95.1	10.3
	BCCd	50% O <sub>2</sub> /50% CO <sub>2</sub>	2.69	2.59	---	1871	0.84	2.73	0.21	---	---
	BCCd1	50% O <sub>2</sub> /50% CO <sub>2</sub>	2.74	2.57	---	1908	0.83	2.78	0.23	95.0	12.2
	BCCe	70% O <sub>2</sub> /30% CO <sub>2</sub>	2.89	3.67	---	1805	0.82	2.96	0.48	95.3	10.3
	BCCf	Air	2.78	2.51	3.5	1669	1.32	0.42	0.21	91.0	20.6
	BCCg	30% O <sub>2</sub> /70% CO <sub>2</sub>	2.72	2.73	3.5	1708	1.27	1.61	0.35	90.7	21.1
Illinois #6 Coal	Ill#6a	Air	2.73	2.86	---	1632	1.42	5.96	0.23	98.9	5.7
	Ill#6b	30% O <sub>2</sub> /70% CO <sub>2</sub>	2.58	3.93	---	1591	1.63	5.59	0.48	99.1	5.8
	Ill#6b1	30% O <sub>2</sub> /70% CO <sub>3</sub>	2.68	2.85	---	1674	1.35	5.45	0.38	---	---
	Ill#6c	50% O <sub>2</sub> /50% CO <sub>2</sub>	2.69	4.74	--	1674	1.32	5.53	0.32	99.2	4.5
	Ill#6d	Air	2.80	3.14	3.5	1683	1.21	0.67	0.16	98.9	5.8
	Ill#6e	30% O <sub>2</sub> /70% CO <sub>2</sub>	2.70	2.80	3.5	1691	1.32	1.83	0.38	98.5	6.8
Delayed Petroleum Coke	DPCa	Air	2.77	2.80	---	1662	2.15	1.37	0.09	99.9	28.3
	DPCb	30% O <sub>2</sub> /70% CO <sub>3</sub>	2.79	2.70	---	1759	1.79	1.33	0.26	99.8	38.9
	DPCb1	30% O <sub>2</sub> /70% CO <sub>2</sub>	2.59	3.81	---	1603	1.86	1.26	0.33	---	---
	DPCc	Air	2.74	2.96	3.50	1657	1.75	0.56	0.08	99.8	39.9
	DPCd	30% O <sub>2</sub> /70% CO <sub>3</sub>	2.82	2.83	3.50	1784	1.33	0.55	0.25	99.9	34.9



**Figure 3.3.2: Variation of Fuel Combustion Efficiency and Unburned Carbon Emissions with Oxygen Partial Pressure**

### 3.3.3 Gaseous Emissions

The emissions of three gas species (NO<sub>x</sub>, SO<sub>2</sub>, and CO) were measured during each test shown in Table 3.3.2. The resulting gas traces are shown in Figures 3.3.4a – 3.3.6b. These traces show the actual time-lapse under stable conditions. The averages from these traces are, actually, the data shown in Table 3.3.2. As these average values lend themselves to easier data interpretation than the results shown in Figures 3.3.4a-3.3.6b, they are plotted in Figures 3.3.7- 3.3.8. They show, respectively, the emission trends of NO<sub>x</sub>, SO<sub>2</sub>, and CO as function of oxygen concentration (O<sub>2</sub>) in the combustion gas. It should be re-emphasised that of particular interest are the trends and relative changes rather than the actual magnitudes of the data points. A brief discussion of the emission of each gaseous species follows.

#### NO<sub>x</sub> Emissions

The medium volatile bituminous coal from the base case CFB plant, which was studied in more detail than the other two fuels, shows clear trends (Table 3.3.2 and Figure 3.3.7). Oxy-fuel firing yielded NO<sub>x</sub> emissions

equal to or less than those from air firing. For example, the reductions in NO<sub>x</sub> from firing in air to firing in 30% O<sub>2</sub>/70% CO<sub>2</sub> and 70% O<sub>2</sub>/30% CO<sub>2</sub> amounted to about 18% and 27 %, respectively (i.e., from 1.1 to 0.9 and 0.8 lb/MMBtu). These reductions are believed to be due, at least partially, to the fact that the thermal NO<sub>x</sub>, which is associated with the nitrogen in the combustion air, does not occur with combustion in nitrogen-free O<sub>2</sub>/CO<sub>2</sub> combustion mediums. This trend is consistent with results obtained previously in this Laboratory (Bozzuto, et al., 2001) and by others (Chui, et al., 2001, and Weller and Boiarski, 1985). Adding limestone to reduce SO<sub>2</sub> emissions seemed to exacerbate NO<sub>x</sub> emissions, at least for this particular coal. For example firing this coal in air without limestone and with limestone (at a Ca/S mole ratio of 3.5) led to a NO<sub>x</sub> increase of about 18% (from 1.1 to 1.3 lb/MMBtu). The corresponding increase during combustion in 30% O<sub>2</sub>/70% CO<sub>2</sub> was about 40% (from 0.9 to 1.3 lb/MMBtu). This trend, which shows the catalytic effect of Ca on NO<sub>x</sub> emissions, is consistent with ALSTOM's experience with commercial CFB units.

The NO<sub>x</sub> emissions from the delayed pet coke were consistently the highest under similar scenarios. For example, during combustion in air and 30% O<sub>2</sub>/70% CO<sub>2</sub>, the emissions from the pet coke were 2.2 and 1.8 lb/MMBtu, respectively. The corresponding values from the base case CFB and Illinois #6 coals were considerably lower. This trend is in general agreement with the fuel nitrogen loadings shown in Table 3.1.1.

### **SO<sub>2</sub> Emissions**

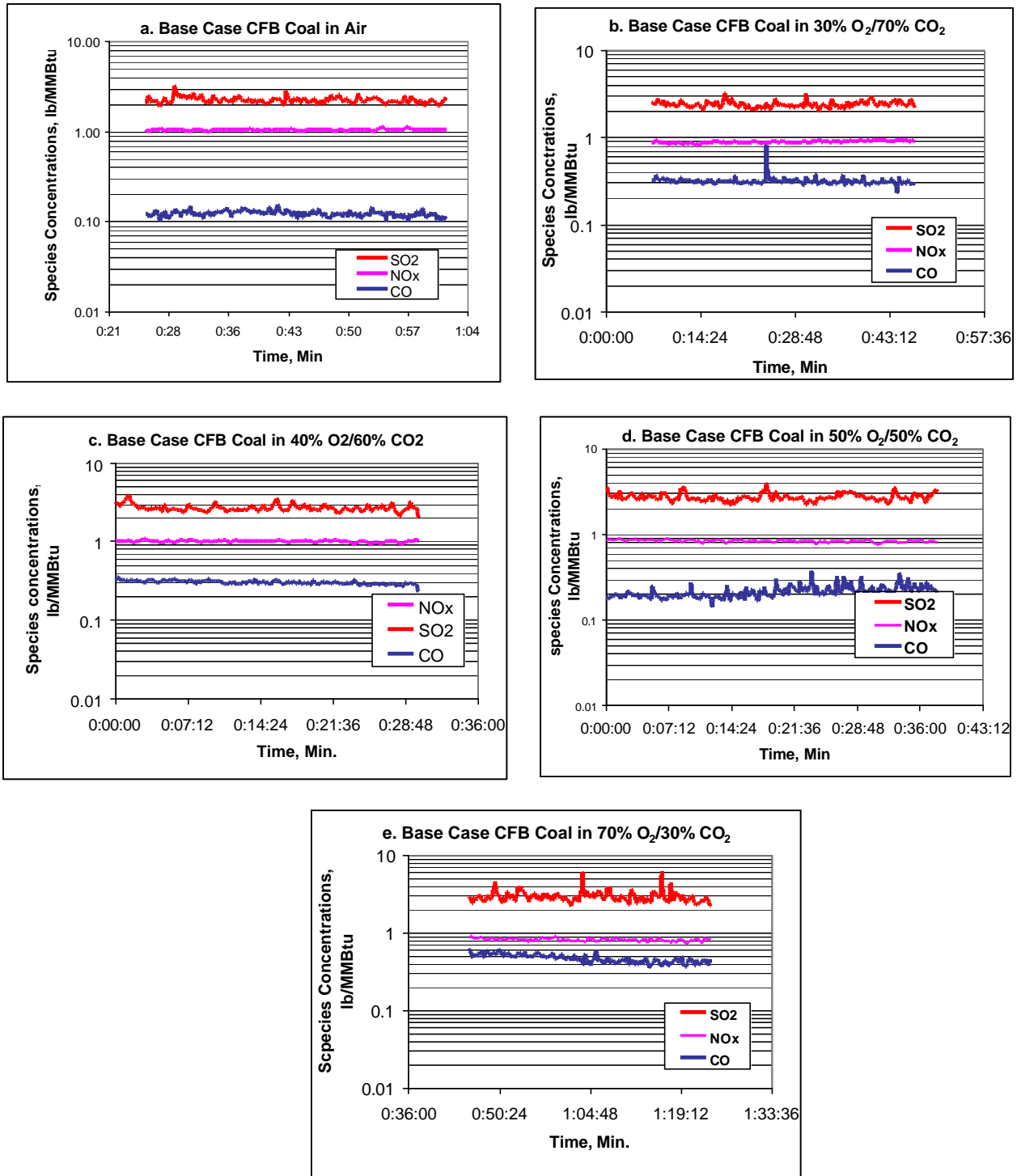
The medium volatile bituminous coal from the base case CFB plant also shows clear trends (Table 3.3.2 and Figure 3.3.8). Oxy-fuel firing yielded SO<sub>2</sub> emissions that were progressively higher than was the case when firing this coal in air. For example, the increases in SO<sub>2</sub> from firing in air to firing in 30% O<sub>2</sub>/70% CO<sub>2</sub> and 70% O<sub>2</sub>/30% CO<sub>2</sub> amounted to about 4% and 30%, respectively (i.e., from 2.3 to 2.4 and 3.0 lb/MMBtu). The increases appear to be due, at least partially, to increased bed temperatures during oxy-fuel firing. That is, for the Illinois #6 coal and the pet coke, the SO<sub>2</sub> concentrations actually went down during oxy-fuel firing, as the bed temperatures remained fairly constant.

Based on previous experience, a Ca/S mole ratio of 3.5 was used when burning each test fuel in air and in 30% O<sub>2</sub>/70% CO<sub>2</sub> (Table 3.3.2 and Figure 3.3.8). During air firing this sorbent dosage yielded a sulfur capture of 83% for the base case CFB coal (from 2.3 to 0.4 lb/MMBtu). The corresponding sulfur captures for the Illinois #6 coal and delayed pet coke were 88% (from 6.0 to 0.7 lb/MMBtu) and 57% (from 1.4 to 0.6 lb/MMBtu). Sulfur captures were consistently lower during combustion of the three fuels in 30% O<sub>2</sub>/70% CO<sub>2</sub>. The capture was only 33% for the base case CFB coal (from 2.4 to 1.6 lb/MMBtu). The corresponding captures for the Illinois #6 coal and delayed pet coke were 67% (from 5.5 to 1.8 lb/MMBtu) and 54% (from 1.3 to 0.6 lb/MMBtu).

Sulfur dioxide emissions with or without limestone addition were higher for the Illinois #6 coal than they were for the other two fuels. For example, during air firing SO<sub>2</sub> emissions were 6.0, 2.3, and 1.4 lb/MMBtu for the Illinois #6 coal, base case CFB coal, and delayed pet coke, respectively. This trend is consistent with the sulfur loading values given in Table 3.1.1.

### **CO Emissions**

Consistent with the results shown in Figures 3.3.7 and 3.3.8, the medium volatile bituminous coal from the base case CFB plant also shows clear trends (Table 3.3.2 and Figure 3.3.9). Oxy-fuel firing yielded CO emissions that were always higher than was the case when firing this coal in air. Nevertheless, CO tended to decrease as the oxygen content in the combustion gas increased. For example, firing this coal in air yielded CO emissions of about 0.1 lb/MMBtu. The values during combustion in various O<sub>2</sub>/CO<sub>2</sub> mixtures ranged from about 0.2 to almost 0.5 lb/MMBtu. It is speculated that the higher partial pressure of CO<sub>2</sub> in the flue gas may inhibit the oxidation of CO to CO<sub>2</sub> in the particle boundary layer at the prevailing conditions. A commercial CFB has a gas residence time on the order of 5 seconds versus a gas residence time of about 1.5 seconds in the current bench-scale reactor. Since gas residence time has a significant, favorable bearing on CO emissions, further testing is needed, as is planned during Phase II pilot-scale testing, to verify the magnitude of CO under conditions simulating commercial operation.



**Figure 3.3.3: Combustion of Base Case CFB Coal in Air and Various O<sub>2</sub>/CO<sub>2</sub> Mixtures without Limestone Addition**



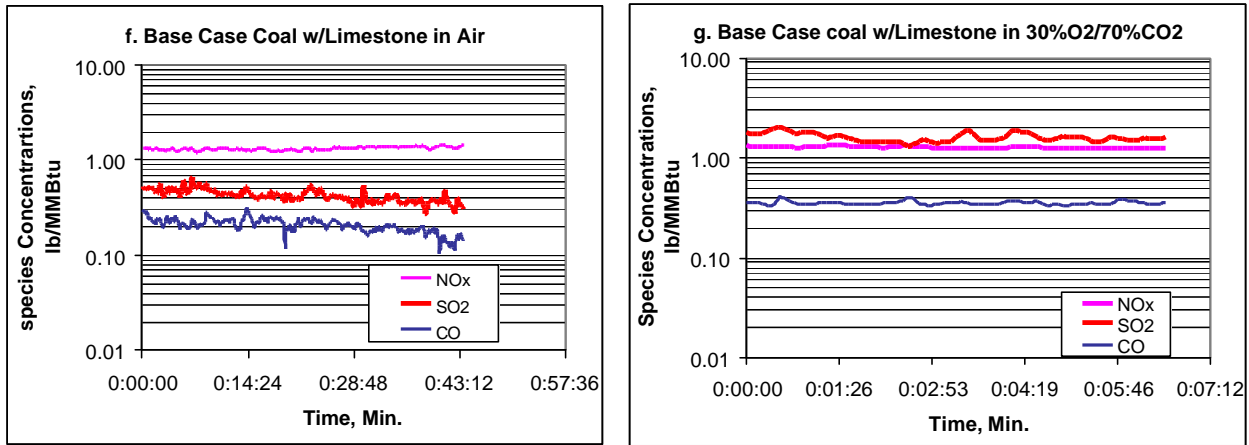


Figure 3.3.4: Combustion of Base Case CFB Coal in Air and 30% O<sub>2</sub>/70% CO<sub>2</sub>

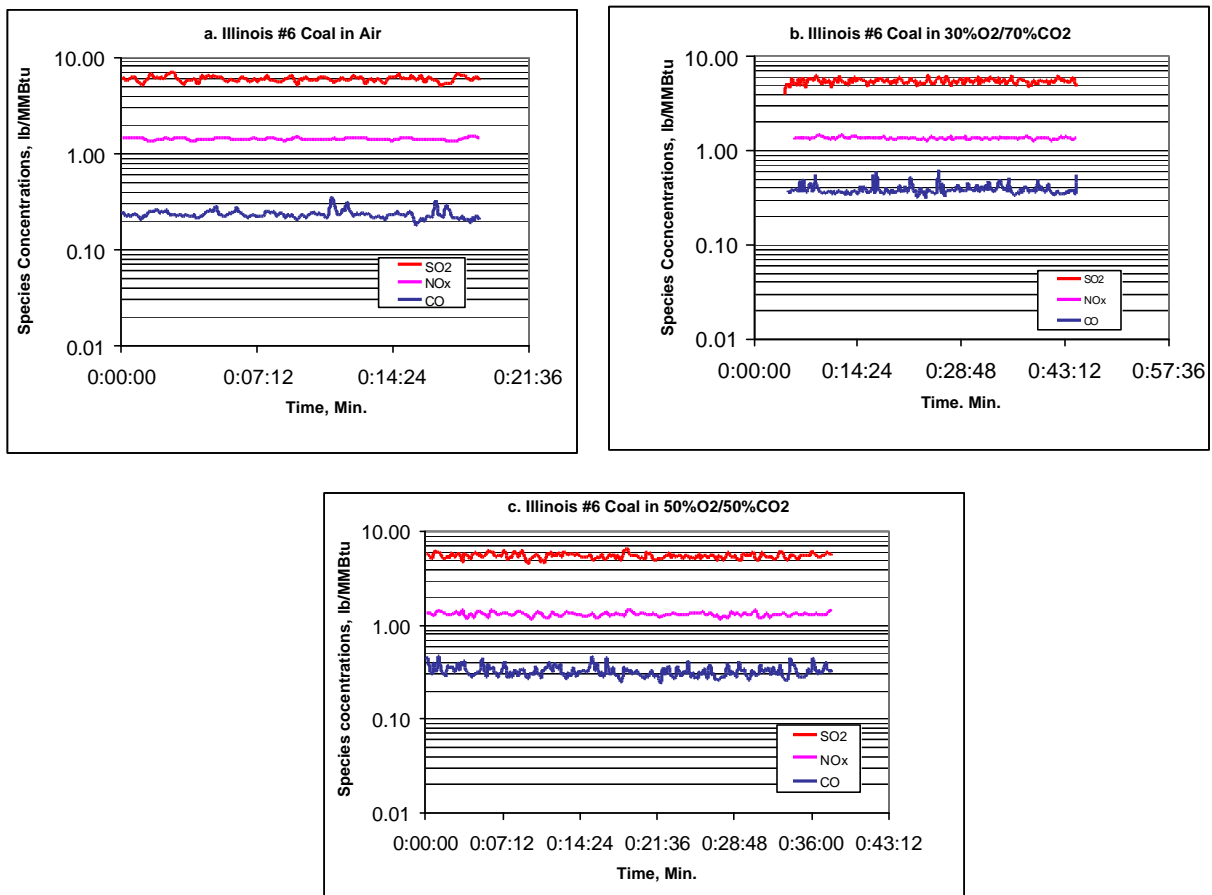
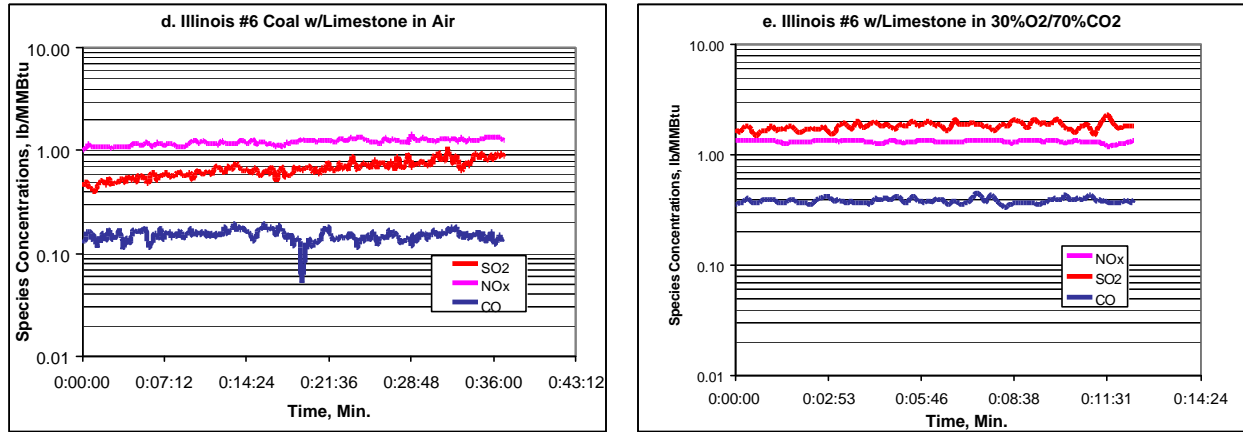
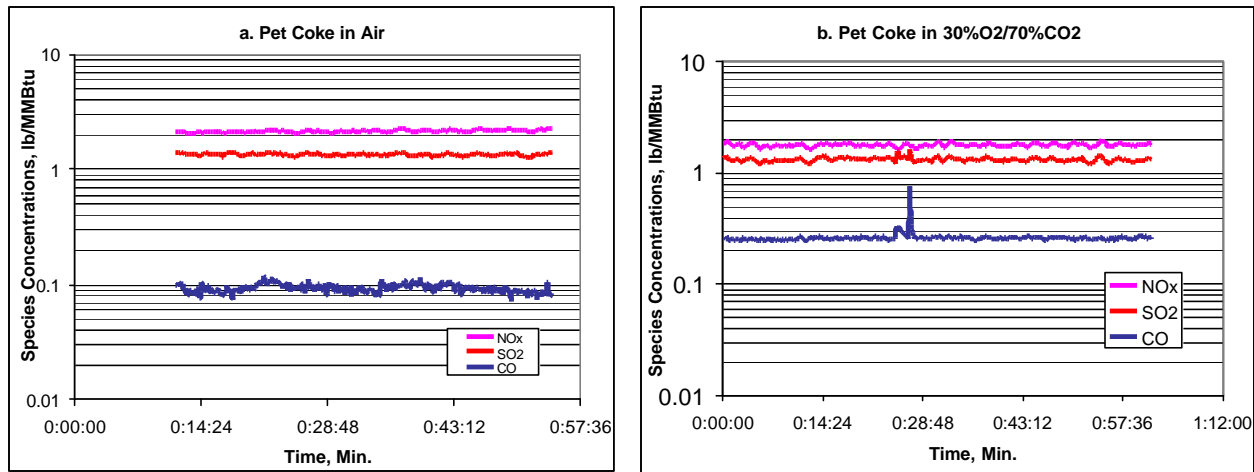


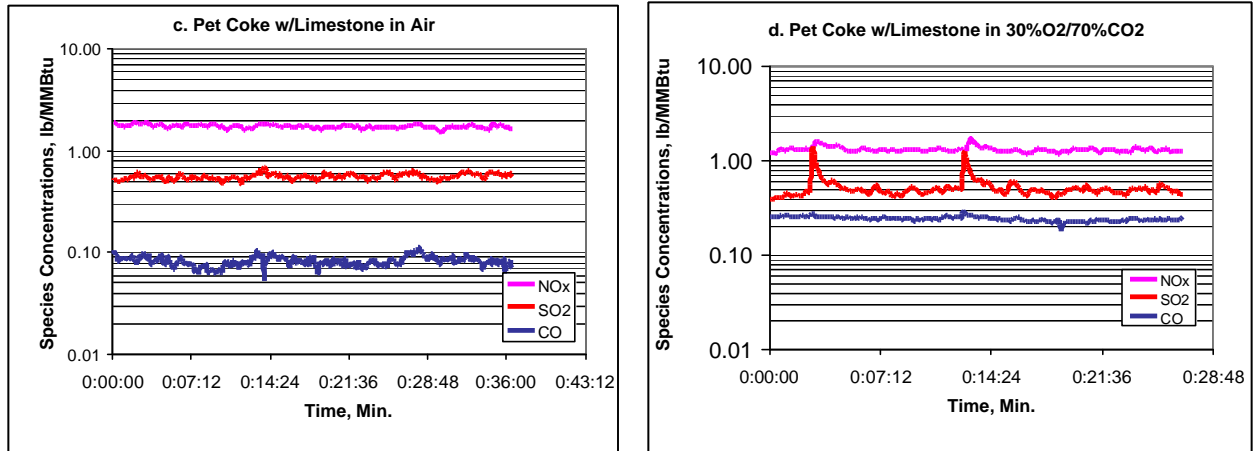
Figure 3.3.5: Combustion of Illinois #6 Coal in Air and Various O<sub>2</sub>/CO<sub>2</sub> Mixtures without Limestone Addition



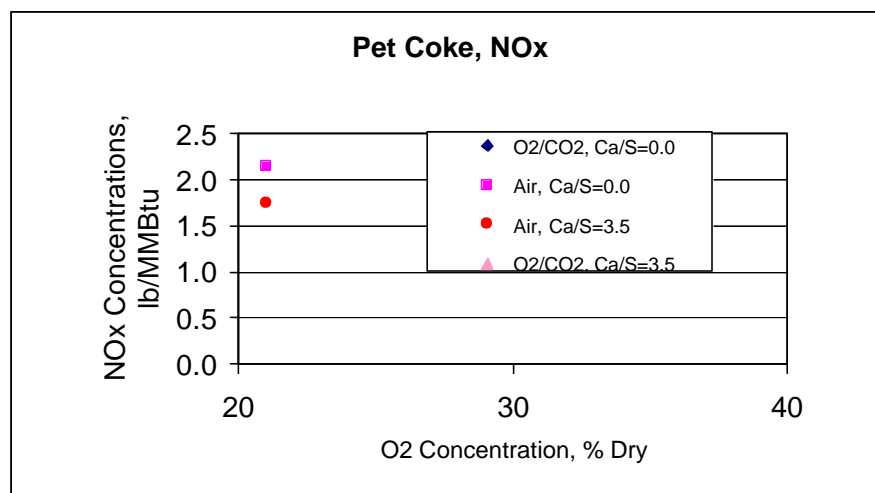
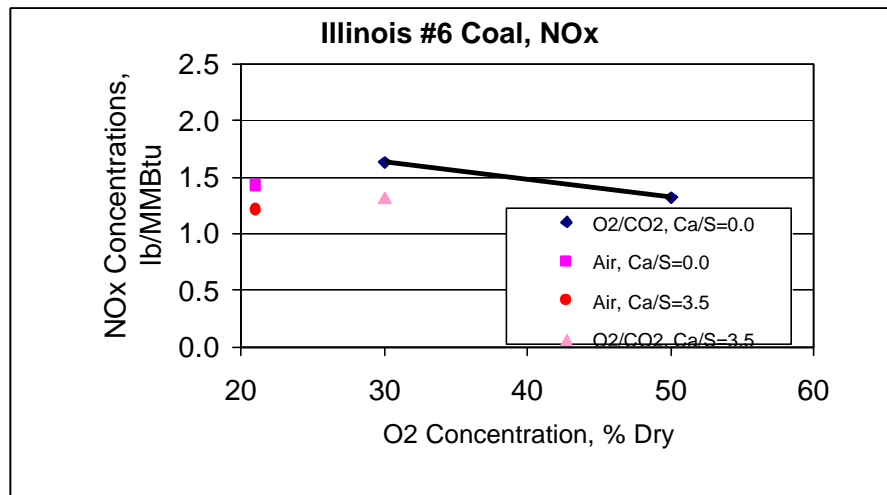
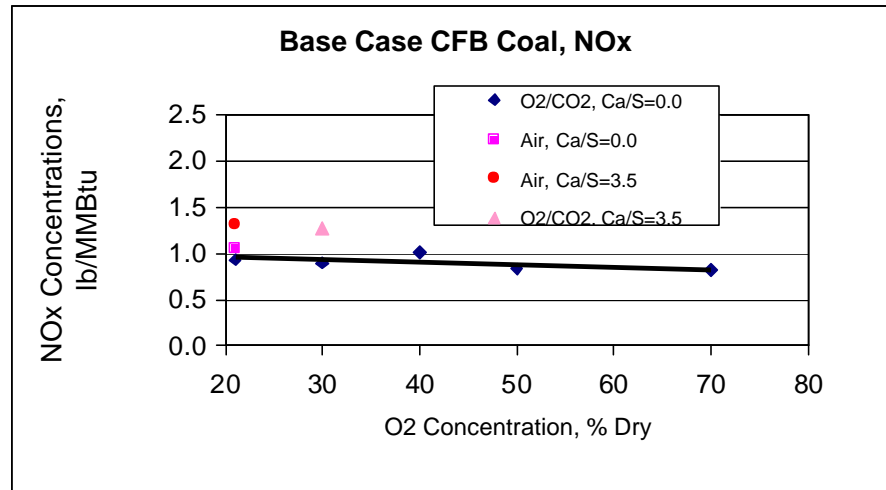
**Figure 3.3.6: Combustion of Illinois #6 Coal in Air and 30% O<sub>2</sub>/70% CO<sub>2</sub> Mixture with Limestone Addition**



**Figure 3.3.7: Combustion of Delayed Petroleum Coke in Air and 30% O<sub>2</sub>/70% CO<sub>2</sub> Mixtures without Limestone Addition**



**Figure 3.3.8: Combustion of Delayed Petroleum Coke in Air and 30% O<sub>2</sub>/70% CO<sub>2</sub> Mixtures with Limestone Addition**



**Figure 3.3.9: Variation of NOx Emissions from Test Fuels as a Function of O<sub>2</sub> in Combustion Gas**

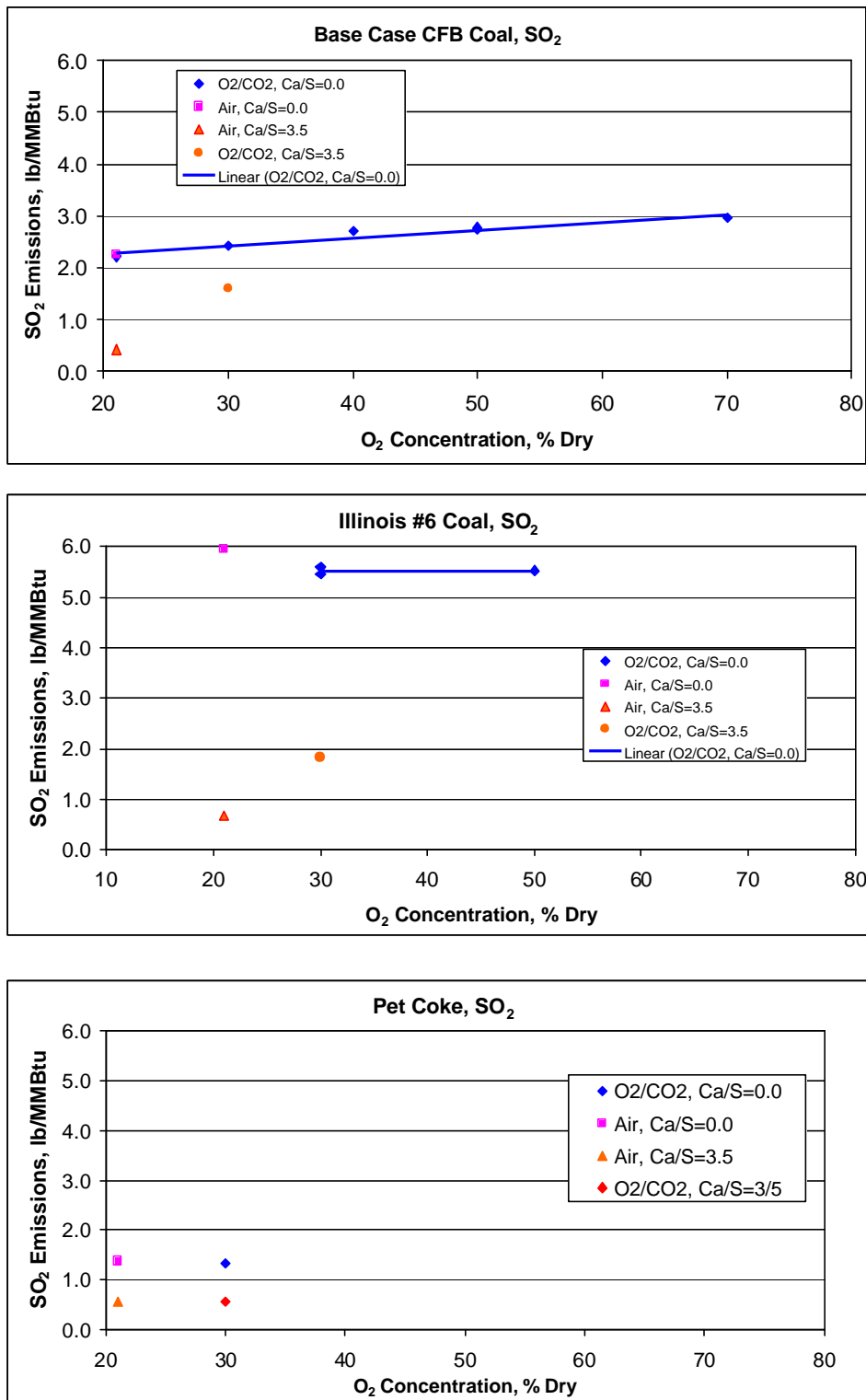


Figure 3.3.10: Variation of SO<sub>2</sub> Emissions from Test Fuels as a Function of O<sub>2</sub> Concentration in Combustion Gas

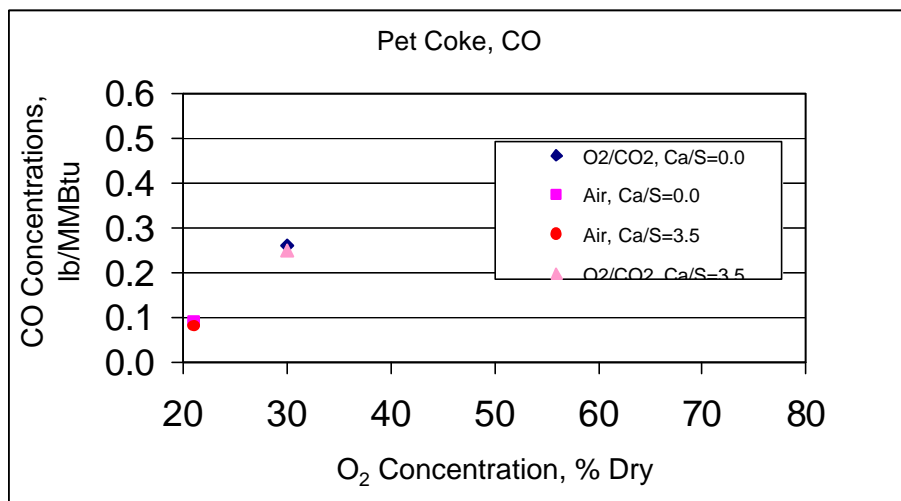
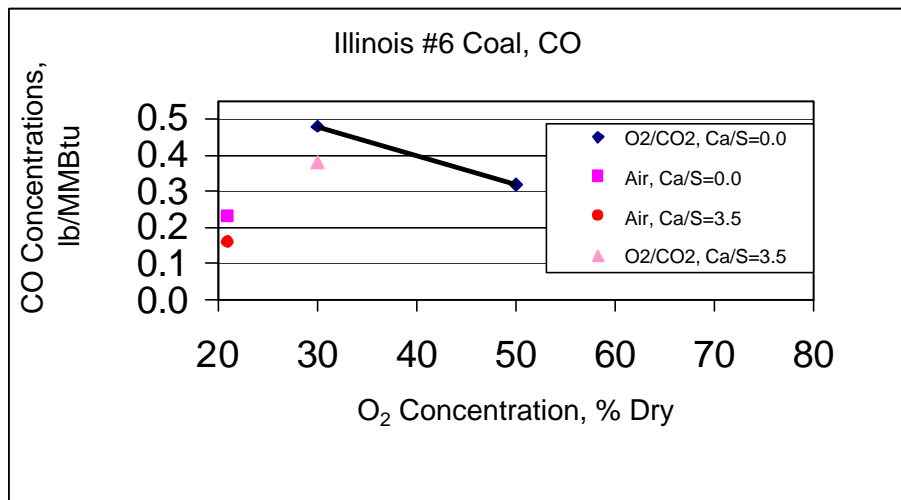
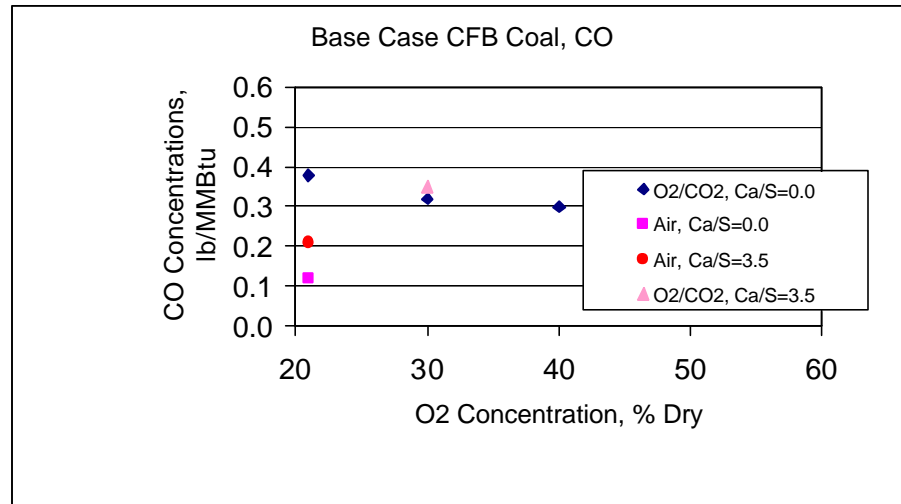


Figure 3.3.11: Variation of CO Emissions from Test Fuels as a Function of O<sub>2</sub> Concentration in Combustion Gas

### 3.4 Conclusions and Recommendations for Future Work

As stated previously, three fuels were characterized, and tested in the TGA and Bench-Scale FBC. Testing in the Bench-Scale FBC entailed burning the three fuels in air and 30% O<sub>2</sub>/70% CO<sub>2</sub> (by volume). Additionally, the base case FCB and Illinois #6 coals were burned in O<sub>2</sub>/CO<sub>2</sub> mixtures containing from 21 to 70% O<sub>2</sub> and from 21 to 50% O<sub>2</sub>, respectively. Bed temperatures ranged from about 1635 °F to 1900 °F. The limestone sample obtained from the base case CFB plant was used to determine, for each fuel, its flue gas desulfurization potential during fuel combustion in air and 30% O<sub>2</sub>/70% CO<sub>2</sub>. All tests were carried out in high excess O<sub>2</sub> (with stoichiometric ratios ranging from about 2 to about 4.7).

#### 3.4.1 Conclusions/Remarks

##### Slagging Behavior

- Testing the base case CFB coal in O<sub>2</sub>/CO<sub>2</sub> mixtures containing up to 70% O<sub>2</sub> caused bed temperature rises of up to about 250 °F. Nevertheless, it was possible to obviate bed slagging/defluidization problems as long as the bed was well fluidized. The Illinois #6 coal, which is known to have a high slagging potential, was successfully tested in O<sub>2</sub>/CO<sub>2</sub> atmospheres containing up to 50% O<sub>2</sub> without any bed defluidization-related problems. Although the test in 70% O<sub>2</sub>/30% CO<sub>2</sub> was not run on this fuel, there is no reason to believe that it could not be executed successfully. The pet coke was run only in air and 30% O<sub>2</sub>/70% CO<sub>2</sub>, as it presents virtually no slagging potential.
- The test conditions used in the FBC facility are very aggressive for three reasons: (1) there was no means of recycling particles to control the bed temperature; (2) the superficial gas velocities were very low and (3) given the prevailing stoichiometric ratios, the furnace outlet O<sub>2</sub> concentration ranged from 13% to 51% (dry basis). Conversely, the operating conditions of a commercial oxy-fuel-fired CFB would be much less aggressive for the following reasons: (1) the bed temperature would be closely controlled through judicious recycling of bed materials; (2) the superficial gas velocity would be maintained at about 18 ft/sec; and (3) the O<sub>2</sub> concentration in the furnace would rapidly decline from its initial value of 70%, for Case 2 (New Compact O<sub>2</sub>-Fired CFB, see Section 2.2, Volume I), to about 3% at the outlet.
- Based on these findings/remarks, it is preliminarily concluded that 70% O<sub>2</sub>/30% recycled flue gas (principally CO<sub>2</sub>) as a combustion medium for study Case 2 is feasible.

##### Combustion Characteristics

- Burning the three test fuels in high O<sub>2</sub> combustion mediums improved overall fuel combustion efficiency, which, correspondingly, improved carbon loss.
- The addition of limestone to the combustion process to control sulfur dioxide emissions did not adversely impact overall combustion efficiency.

##### Gaseous Emissions

- Burning the three fuels in a nitrogen-free combustion medium (i.e., in O<sub>2</sub>/CO<sub>2</sub> mixtures) leads to NO<sub>x</sub> emission reductions ranging up to 27%. The reductions are believed to be due, at least partially, to the fact that thermal NO<sub>x</sub>, which is associated with the nitrogen in the combustion air, does not occur with combustion in a nitrogen-free O<sub>2</sub>/CO<sub>2</sub> combustion medium.
- Adding limestone to the combustion process to reduce SO<sub>2</sub> emissions seemed to exacerbate NO<sub>x</sub> emissions for the base case CFB coal, as is known to happen in commercial CFB units. Unfortunately, this occurred for the Illinois #6 coal and delayed pet coke. This phenomenon needs to be investigated further.
- Burning the three test fuels in a nitrogen-free combustion medium (i.e., in O<sub>2</sub>/CO<sub>2</sub> mixtures) lead to SO<sub>2</sub> emission increases ranging up to 30%. The increases appear to be due, at least partially, to increased bed temperatures during oxy-fuel firing. This conclusion arose from a closer examination of the data. That is, for the Illinois #6 coal and the pet coke, the SO<sub>2</sub> concentrations actually went down during oxy-fuel firing, as the bed temperatures remained fairly constant.

- A Ca/S mole ratio of 3.5 led to sulfur captures ranging up to 88% when the combustion took place in air. Sulfur captures were consistently lower during combustion of the three fuels in 30% O<sub>2</sub>/70% CO<sub>2</sub>, ranging only up to 67%.

### **CO Emissions**

- Oxy-fuel firing yielded CO emissions that were always higher than was the case when firing in air. Nevertheless, they tended to decrease as the oxygen content in the combustion gas increased. It is speculated that the higher partial pressure of CO<sub>2</sub> in the flue gas may inhibit the oxidation of CO to CO<sub>2</sub> in the particle boundary layer at the prevailing conditions. A commercial CFB has a gas residence time on the order of 5 seconds versus a gas residence time of about 1.5 seconds in the current bench-scale reactor. Since gas residence time has a significant, favorable bearing on CO emissions, further testing is needed, as planned during Phase II pilot-scale testing, to verify the magnitudes of CO under conditions simulating commercial operation.

### **CO<sub>2</sub> Concentrations in Flue Gas**

- The concentration of carbon dioxide in the flue gas was not measured, as the existing analyzer could measure only values ranging up to 25%. Hence, CO<sub>2</sub> concentration was back calculated. The CO<sub>2</sub> concentration for the combustion of the base case CFB coal in the 21% O<sub>2</sub>/70% CO<sub>2</sub> - 70% O<sub>2</sub>/30% CO<sub>2</sub> was in the 47-84% range.

### **3.4.2 Recommendations for Future Work**

Testing the base case CFB coal in O<sub>2</sub>/CO<sub>2</sub> medium containing up to 70% O<sub>2</sub> caused bed temperature rises of up to 250 °F. Nevertheless, it was possible to obviate bed slugging/defluidization problems as long as the bed was well fluidized.

The added emission benefits offered by oxy-fuel firing over air firing in CFB boilers are:

- CO<sub>2</sub> in the flue gas is highly concentrated (~90% vs.~15%), thus making the processing of this stream to achieve the required CO<sub>2</sub> purity for EOR application cheaper.
- Typically, low NO<sub>x</sub> emissions in combustion-staged air-fired CFBs are further reduced, due primarily to elimination of thermal NO<sub>x</sub>.
- SO<sub>2</sub> emission reductions of up to 90% with sorbent should not be negatively impacted. Furthermore, ALSTOM has a commercial product called, "Flash Drier Absorbent (FDA)," which has been successfully demonstrated in the pilot-scale Multi-use Test Facility (MTF) to reduce SO<sub>2</sub> emissions by as much as 99%.
- Burning the three fuels in high O<sub>2</sub> combustion medium improved overall fuel combustion efficiency, which correspondingly improved carbon loss.
- The addition of limestone to the combustion process to control sulfur dioxide emission did not adversely impact overall fuel combustion efficiency.

Based on these encouraging test results, on the findings from technical and economic analyses presented in Volume I, and on practical considerations, it has been recommended and agreed to by the DOE/NETL that Phase II workscope be implemented as recommended in the Revised Statement of Work of December 13, 2002. Pilot-scale testing in Phase II will evaluate this concept, among other things. Based on the results of pilot-scale testing, the concept presented in Case 2 (see Section 2.2, Volume I) will be either affirmed for further commercial development or modified.



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