ALSTOM'S DEVELOPMENT OF ADVANCED CFB BASED TECHNOLOGIES FOR CO_2 MITIGATION

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ABSTRACT

ALSTOM Power Inc. (ALSTOM) is actively working to develop advanced circulating fluidized bed (CFB) based technologies for the purpose of CO_2 mitigation. Two of the more promising ideas currently being investigated at ALSTOM are the oxygen-fired CFB and chemical looping technologies.

The oxygen-fired CFB is a near-term CO_2 capture technology, which uses pure oxygen tempered with recirculated flue gas to combust the fuel. The oxygen for combustion may be supplied by a cryogenic air separation unit, or in the future by more efficient processes such as oxygen transport membrane. This produces a flue gas stream comprising mostly CO_2 and water vapor. Simple condensation of most of the water vapor leaves a CO_2-rich product stream which can be simply compressed for sequestration or purified for use in enhanced oil recovery or enhanced coal bed methane.

Chemical looping is a longer-term development path towards CO_2 mitigation. In ALSTOM's processes, a regenerable solid carrier extracts oxygen from air and transports it for combustion or gasification of the fuel. The chemical looping combustion process produces a high CO_2 flue gas stream (similar to the O_2 fired CFB flue gas stream) and steam for a Rankine cycle. The chemical looping gasification process captures CO_2 in a separate chemical loop and produces hydrogen-rich synthesis gas for use in IGCC's, fuel cells, or for other industrial uses.

This paper discusses ALSTOM's latest test work in these areas and the technical, economic and environmental implications of these advanced CFB-based systems. These advanced power generation units can be built from proven fluid bed design features and systems.

Keywords: Oxygen Firing, CFB, Chemical Looping, CO_2 Mitigation

INTRODUCTION

ALSTOM Power, Inc. (ALSTOM) is continually advancing circulating fluidized bed (CFB) technology through improvements in the current product line, as well as developing new applications of CFB technology to mitigate CO_2 emissions from fossil-fuel fired power plants.

Over the past eight years, ALSTOM has conducted more than sixteen studies on CO_2 control technologies that have been sponsored by ALSTOM, U. S. and European government agencies, and private industry. This paper presents information from two recent studies sponsored jointly by ALSTOM and the U. S. Department of Energy:

> **Greenhouse Gas Emissions Control by Oxygen Firing in Circulating Fluidized Bed Boilers, September 2001 - October 2004**
> In **Phase I** of this study, ALSTOM developed conceptual designs, performance, and economics for 13 cases including combustion and gasification technologies with and without CO_2 control. The study identified oxygen-fired CFB as an attractive near-term technology for CO_2 control and chemical looping technologies as a long-term solution with very attractive economics. Phase I included bench-scale fluidized bed combustion tests with coal and petroleum coke burned in O_2/CO_2 mixtures. Subcontractors in this study included Parsons (Balance of Plant and IGCC cases), ABB Lummus (Gas Processing Systems), and Praxair (Cryogenic and Oxygen Transport Membrane air separation systems).
> In **Phase II** of this study, the oxygen-fired CFB was successfully tested in ALSTOM's 9.9 MMBtu/hr Multiuse Test Facility pilot plant. Based on the pilot plant test results, the oxygen-fired CFB design from Phase I was updated.
>
> **Hybrid Combustion-Gasification Chemical Looping - Coal Power Technology Development, October 2003 - December 2005**
> Based on the favorable economics of the chemical looping technologies, ALSTOM and the DOE began this program to continue their development and demonstrate technical feasibility. **Phase I** of the testing is completed; **Phase II** began in early 2005.

This paper describes (1) the basic oxygen-fired CFB, (2) a variation which uses an advanced Oxygen Transport Membrane for air separation, and (3) chemical looping applied to combustion and gasification systems. The paper presents the conceptual designs, performance and economics, as well as some results of pilot testing of the oxygen-fired CFB.

OXYGEN FIRED CFB

Combustion of coal in an air-fired furnace produces a flue gas of mostly nitrogen with about 15% CO_2. Some concepts for greenhouse gas control call for extracting the CO_2 from this flue gas and sequestering it. An alternative is to combust the fuel in oxygen, producing a flue gas containing 75 to 85% CO_2, the remainder mostly water. Economic evaluations show that purifying the flue gas from oxygen-fired systems is less costly than extracting the CO_2 from air-fired systems with current amine-based extraction technologies (Bozzuto, et al, 2001).

With air firing, the inert nitrogen in the air carries much of the fuel's heat energy from the combustor. With oxygen firing, another means must be provided to remove this heat and control the combustion temperature.

In most oxygen-fired pulverized coal designs, the furnace temperature is controlled by recirculating a part of the cooled flue gas back to the furnace. This maintains normal temperatures without added heat transfer surface in the furnace. Recirculating about 3 pounds of flue gas for every 1 pound of flue gas produced and mixing it with the pure oxygen results in a 30% oxygen concentration in the oxidant

mixture. This 30% mixture gives thermal conditions in the furnace similar to those with air firing (accounting for the different properties of CO_2 and N_2).

In a circulating fluidized bed combustor, much of the temperature control is achieved by recirculating cooled solids to the furnace through an external heat exchanger (EHE). With an oxygen-fired CFB, the additional required cooling duty can be achieved by recirculating cooled flue gas (as in the pulverized coal case), by increasing the circulation of cooled solids, or by a combination of the two.

In theory, a CFB combustor could be fired with pure oxygen and cooled with a high recirculation of cooled solids. This would eliminate the cost of the increased gas flow through the backpass and the recirculating fan. As a practical matter, we have limited our oxygen-fired CFB studies to a flue gas recirculation of roughly 0.5 pounds per pound of flue gas discharged; this gives a composite 70% oxygen into the furnace. Table 1 gives typical flue gas compositions for air firing and oxygen firing diluted to 30 and 70% O_2.

Table 1 also shows the relative mass flow and volume flow of flue gas through the furnace, cyclone, convective pass, etc. (this includes the recirculated gas) and the total flue gas produced (net of recirculation). The reduced flue gas flow yields significant size and cost savings in the combustor, cyclone, convection pass, oxygen heater, ducts, fans, and other equipment. (Note that Table 1 does not include the effect of air infiltration, which would change the numbers slightly.)

Table 1: Typical Flue Gas Composition and Flow - Air *vs.* Oxygen Fired

	Air	**30% O_2**	**70% O_2**
	Composition, volume %		
N_2	74.78	0.81	0.74
CO_2	14.49	82.78	74.91
H_2O	7.40	13.05	20.97
O_2	3.31	3.31	3.31
	Relative Flow, mass (volume)		
In Furnace	100 (100)	89 (66)	36 (28)
Net Produced	100 (100)	23 (16)	23 (16)

O_2 Fired CFB Design

Figure 1 shows a simplified process flow diagram for the boiler island of the oxygen-fired CFB concept. Coal is burned in the combustor with a preheated mixture of oxygen and recirculated flue gas. The oxygen supply is provided from a cryogenic air separation unit (ASU). Hot ash is drained and cooled to control solids inventory in the system and recover heat from the ash. Limestone may be added to the combustor for sulfur capture; Figure 1 shows a design with sulfur removal entirely in the back end.

Flue gas and entrained solids flow through a cyclone, which captures most of the solids. Some of these solids are returned directly to the combustor; a portion of the solids flows through an external heat exchanger to control the combustor temperature.

The flue gas leaving the cyclone is cooled first in the convective pass, then in a tubular oxygen heater, which preheats the oxygen/flue gas mixture. The flue gas leaving the oxygen heater is cleaned of fine particulate matter and SO_2 in the baghouse with integrated flash dryer absorber (FDA, see Ahman, et al, 2002). The flue gas is further cooled in a parallel feedwater heater by transferring heat to a feedwater stream in parallel with the low-pressure extraction feedwater heaters. Finally, the gas is cooled and partially dried in a direct contact gas cooler. After the ID fan, a portion of the gas is recirculated to mix with the incoming oxygen. The remaining flue gas product stream goes to the gas processing system where it is compressed and purified if necessary for sequestration or for use (e.g., for enhanced oil recovery).

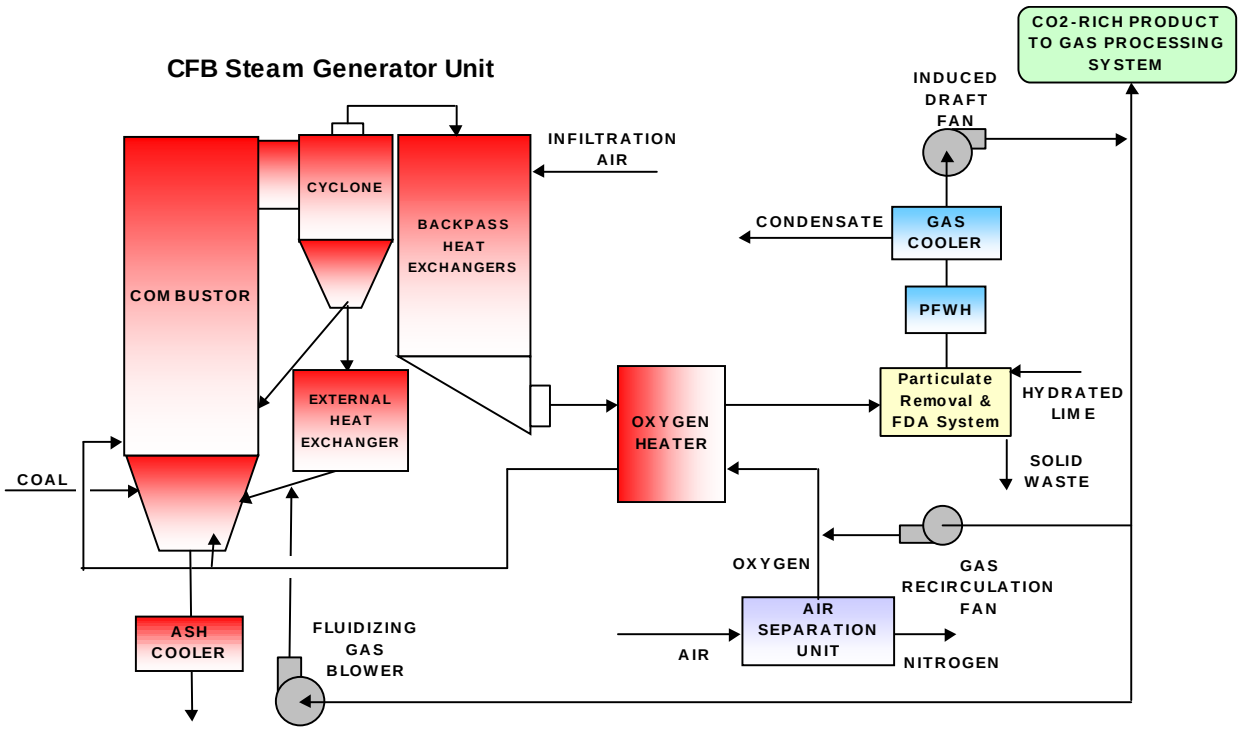

Figure 1: Simplified Process Flow Diagram – O_2 Fired CFB

Because of the lower gas flow with 70% oxygen firing, the combustor and convective pass heat absorption are each reduced to about 40% of the air-fired heat duties. This is shown in Figure 2 (which excludes the ash cooler and parallel feedwater heater.) To compensate, the external heat exchanger heat absorption for O_2 firing is about 3.4 times greater than the air-fired value. A moving bed design was selected to take advantage of counterflow of the solids and to eliminate the need for fluidizing gas in the heat exchanger.

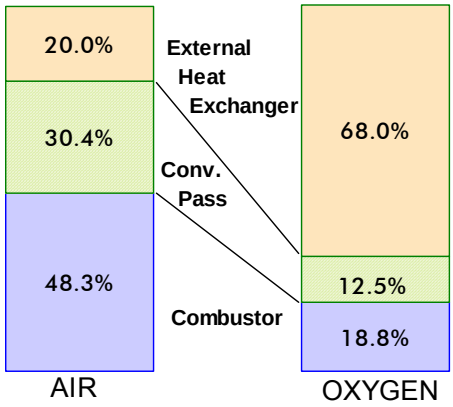

Figure 2: Boiler Heat Absorption Comparison – Air and 70% O_2 Firing

Because of the reduced gas flow with oxygen firing, much of the equipment in the boiler island (combustor, cyclones, backpass heat exchangers, air heater, fans, ductwork, baghouse, etc.) is smaller. Figure 3 compares the plan views for the air-fired and O_2-fired boilers, each producing 210 MWe-gross.

The O_2-fired unit has about 51 percent of the plan area and occupies about 56 percent of the volume of the air-fired unit. The total boiler weight is about 65 percent of the air-fired unit. This results in a boiler cost about 32 percent less than an air-fired CFB boiler. This is a greater savings than would be achieved with an O_2-fired PC or stoker unit, which recirculate larger quantities of flue gas to control the furnace temperature.

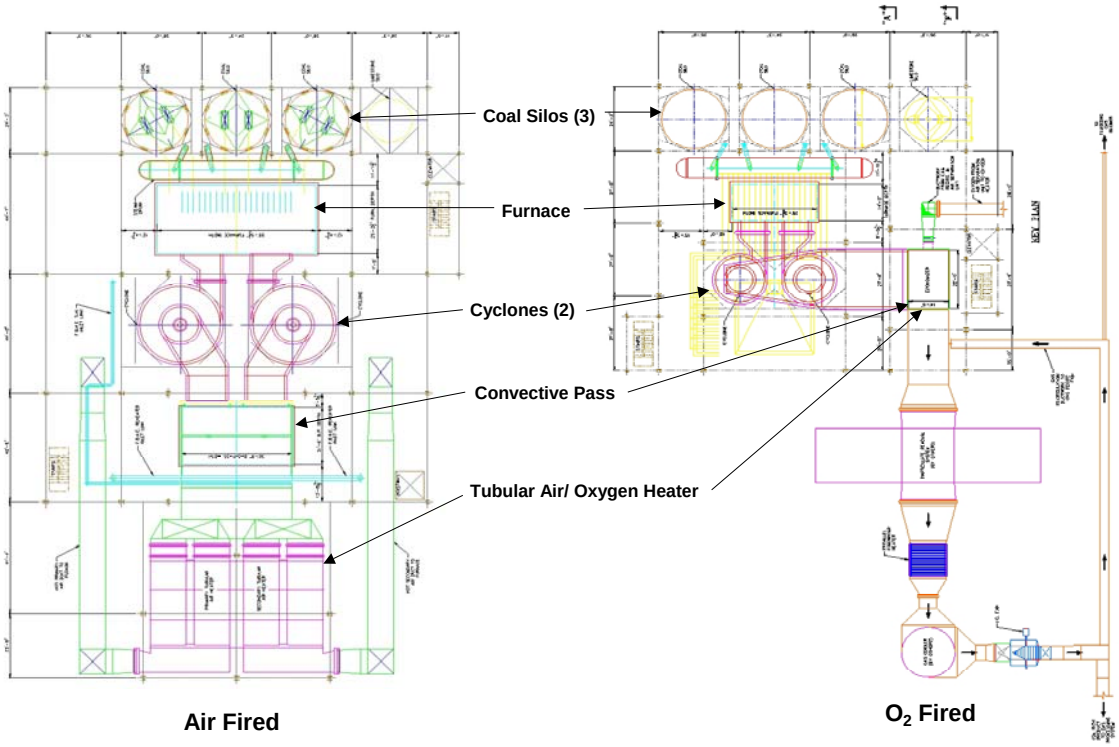

Figure 3: Air and O_2 Fired 210 MWe-gross CFB's – Plan Views

ADVANCED CFB WITH OXYGEN TRANSPORT MEMBRANE

The cryogenic air separation plant in the preceding design requires 18% of the power plant's gross electrical output (233 kWh/ton of oxygen). New technologies are being developed to separate oxygen from air using much less energy. One of these is the Oxygen Transport Membrane (OTM). This operates with a hot, high-pressure air stream on the supply side of the membrane and a low-oxygen sweep gas (or purge gas) on the permeate side of the membrane. The membrane passes most of the oxygen from the air to the sweep gas side, producing depleted air (mostly N_2) and a high-oxygen product.

A conceptual design using the OTM was developed in the Phase I study (Marion, et al, 2003). It showed the potential for improved efficiency, lower investment costs, lower cost of electricity, and lower cost of mitigated CO_2, compared to the O_2-fired CFB described above.

Figure 4 is a schematic of the system showing two aspects that are different from the oxygen-fired CFB:

- the combustor is based on the circulating moving bed (CMB) concept in order to provide the high-temperature air required by the OTM, and
- the separation of the oxygen from compressed air by an OTM is integrated into the boiler island.

The CMB combustor is a variation of the traditional CFB technology, which is being developed with DOE support under separate contracts (e.g., Jukkola, et al, 2003). In this combustion system, coal and limestone are burned in a high velocity bubbling bed at a temperature of about 2000°F. The flue gas from this combustion is cooled in the freeboard by direct contact with cool bauxite particles with mean diameter of 500 - 700 microns. (Pilot tests to date have been with bauxite; other, cheaper materials are being investigated.) These bauxite particles drop into the bubbling bed where they are heated to the bed temperature of 2000°F. From the bed they are drained to the top of the Moving Bed Heat Exchanger (MBHE) where they give up their heat to the working fluid. The cooled bauxite from the bottom of the

MBHE is transported to the top of the combustor to repeat the process of cooling the flue gas. Advantages of this CMB concept being developed for air-fired applications include:

- high heat transfer rates to the falling bauxite and in the MBHE to the steam cycle result in less heat transfer surface compared to typical convective pass heat transfer,
- lower combustor outlet temperature results in a cooler and smaller cyclone, and
- the higher temperature at the top of the MBHE (2000°F compared to 1550 -1650°F in conventional CFB's) helps to attain higher steam temperatures, and therefore higher steam cycle efficiencies.

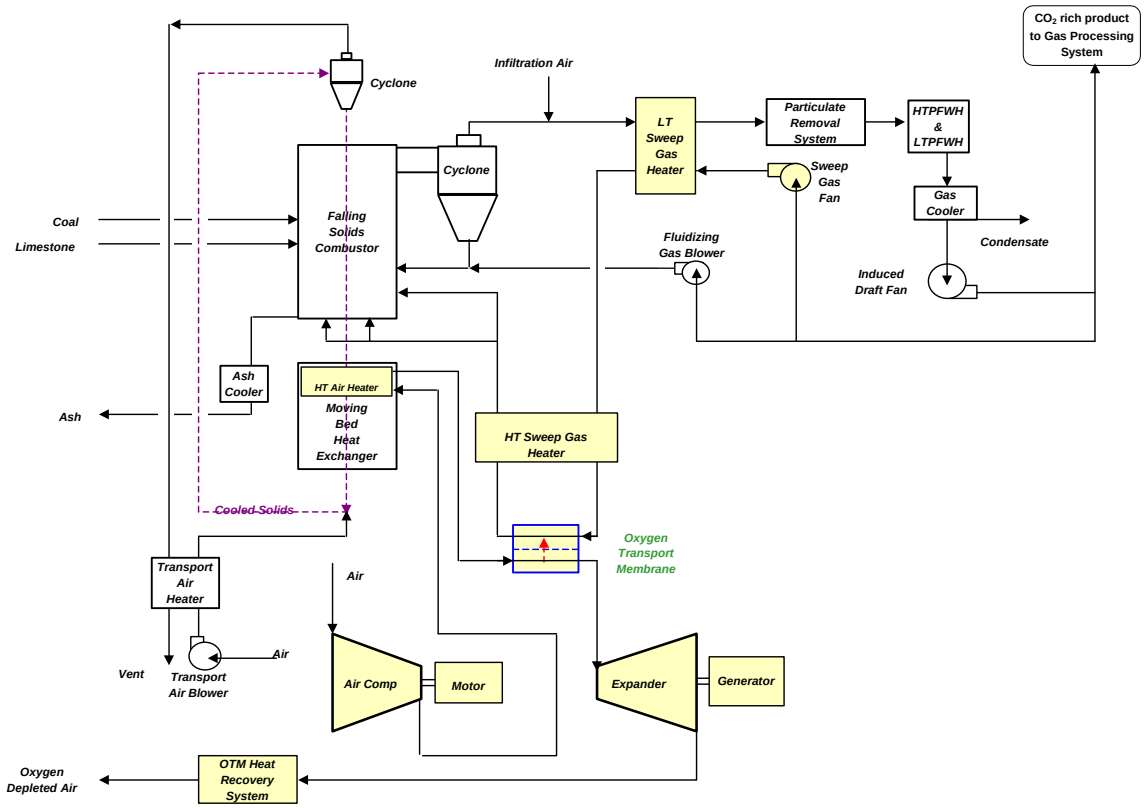

Figure 4: Simplified Process Flow Diagram – O_2 Fired CMB with OTM

The CMB concept was used in this design especially for this last reason - the high temperature bauxite can preheat the compressed air to the high temperature of 1650°F required by the OTM.

As applied to the coal-fired CMB concept here, the air is compressed, then heated in the MBHE. The sweep gas is a portion of the dried flue gas from the boiler which is about 90% CO_2. The sweep gas is preheated in tubular air heaters by the flue gas and by the hot oxygen-rich stream as shown in Figure 4.

OXYGEN-FIRED CFB PILOT PLANT TESTING

As a part of the aforementioned Phase I project, ALSTOM conducted bench-scale tests in a four-inch bubbling bed facility to investigate some of the technical impacts of an oxygen-fired CFB. Details of the bench scale tests are given by Marion, et al, (2003).

In Phase II, these technical issues were investigated at the pilot scale in ALSTOM's 9.9 MMBtu/hr Multiuse Test Facility located at the Power Plant Laboratory in Windsor, CT, USA. The pilot plant results were then used to update the oxygen-fired CFB conceptual design, performance, and economics from Phase I. The technical issues addressed in the pilot testing are discussed below.

Agglomeration – The surface temperature of burning coal particles in the fluid bed can be several hundred degrees hotter than the bulk temperature, which is usually between 1500 and 1650°F. Some of the fuel particles may become hot enough for the fuel ash to become sticky or to melt; however these few fuel particles are vigorously fluidized along with inert ash and sorbent, so there is usually no problem with agglomeration or defluidization.

With oxygen firing, the high local oxygen concentration near the oxygen injection points may increase the combustion rate, with even higher surface temperatures. Bench scale tests indicate there should be no problems with agglomeration at CFB fluidizing velocities with up to 70% oxygen. This was to be demonstrated in the pilot tests.

Heat Transfer - The higher CO_2 and H_2O concentrations with oxygen firing increase the non-luminous radiation heat transfer from the gas. The calculated impact of the increased radiation is that the heat transfer coefficient in the convective pass will be about 10% higher with oxygen firing. In the furnace and external heat exchanger (EHE), hot solids are the dominant heat transfer medium. Changes in the gas radiative properties are expected to have little effect. These pilot tests measured the in-furnace heat transfer coefficients. Heat transfer in the EHE and the convective pass will be measured in the following pilot tests in 2005.

Recarbonation - Limestone is often added to the fluid bed to capture SO_2 from the flue gas. In order to capture sulfur, the calcium carbonate in the limestone must first be calcined to calcium oxide: $CaCO_3$ + heat $\rightarrow$ CaO + CO_2. Figure 5 shows the temperature required to calcine the limestone as a function of the CO_2 content of the flue gas. With air firing, the CO_2 content of the flue gas is under 20%. Limestone will calcine at about 1450°F, which is well below the typical CFB operating temperatures.

With oxygen firing, however, the CO_2 content is above 70%. This requires a combustor temperature above 1600°F for calcination to occur. In those locations where the temperature drops below the calcination temperature (e.g., the external heat exchanger and the convective pass) the reverse reaction – recarbonation – may occur.

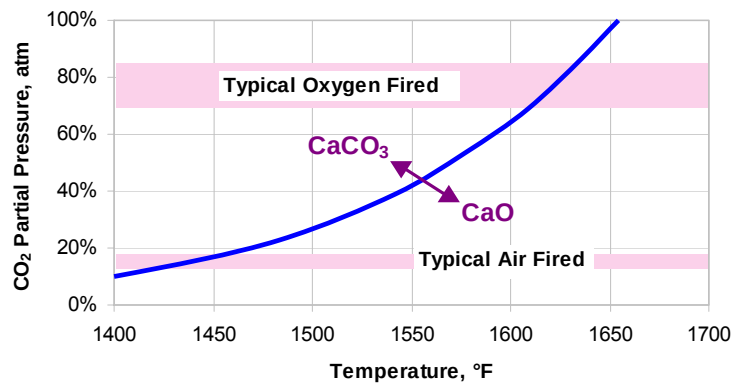

Figure 5: Equilibrium Temperature for Calcination

Sulfur Capture - There is generally an optimum temperature for sulfur capture in a fluidized bed. For bituminous coals, the optimum is around 1550°F. Lower rank fuels, such as lignite, usually have a lower optimum temperature; anthracite and petroleum coke often show improved sulfur capture up to 1650°F and beyond. For oxygen firing, the furnace should be above 1650°F to allow calcination. Except for pet coke and anthracite, the ability to capture sulfur in the furnace will suffer at these high temperatures, requiring more of the sulfur removal in a backend system such as FDA.

Nitrogen Oxides – There are three main sources of NO_x emissions from coal combustion:

- Thermal NO_x forms by dissociation of elemental nitrogen (N_2) in the air at combustion temperatures of about 2500°F or higher.
- Prompt NO_x is also formed from elemental nitrogen in the air by reaction with hydrocarbon fragments. This occurs at fluidized bed temperatures.
- Fuel NO_x forms from the oxidation of nitrogen compounds in the fuel.

NO_x formed by any of these mechanisms can be converted to elemental N_2 by reducing agents such as CO, ammonia, hydrogen, and char. This is enhanced in the furnace by staging the combustion conditions.

Thermal NO_x dominates in pulverized coal systems. Previous tests have shown up to 3-fold reductions in NO_x with oxygen firing at pulverized coal conditions (e.g., Bozzuto, et al., 2001 and Thambimuthu, et al., 1998).

Bench scale tests have also shown reductions in NO_x with oxygen firing at fluidized bed temperatures (Marion, et al. 2003). This is due to the elimination of prompt NO_x and perhaps an effect on the formation and destruction of fuel NO_x.

Carbon Monoxide - The bench scale tests showed that CO emissions are higher with oxygen firing than with air firing. The high CO_2 concentrations in the flue gas may hinder the oxidation of CO to CO_2.

Nitrous oxide - N_2O is a greenhouse gas, which is currently not regulated. Emissions depend on combustion temperature – pulverized coal firing produces less N_2O than fluidized bed combustion.

Combustion Efficiency - The bench-scale testing showed the combustion efficiency with oxygen firing to be equal to or better than with air firing.

The Multiuse Test Facility Pilot Plant

The Multiuse Test Facility (MTF) shown in Figure 6 is located in ALSTOM's Power Plant Laboratories facilities in Windsor, Connecticut. This facility has the flexibility to perform pilot-scale testing with conventional pulverized-coal firing, fluidized bed combustion, and gasification firing conditions.

The MTF allows testing with both circulating and bubbling fluidized bed conditions, as well as various other conditions being considered for advanced processes. For example, the MTF has been used in several test campaigns to develop the CMB technology described above. The facility provides detailed data on heat transfer, hydrodynamics, combustion, sulfur capture and process control.

The MTF is designed and permitted for a firing rate of 9.9 MMBtu/hr of coal, petroleum coke, biomass, oil, or gas. The furnace is 60 feet tall with 40" inner diameter. The facility includes a cyclone, sealpot, and external fluidized bed and moving bed heat exchangers to complete the circulating fluidized bed system. The flue gas is cleaned in a baghouse and a wet caustic scrubber for final particulate and SO_2 removal to meet local emissions limits. The baghouse includes an integrated FDA system. The MTF has a dedicated, commercial DCS for facility control and data acquisition.

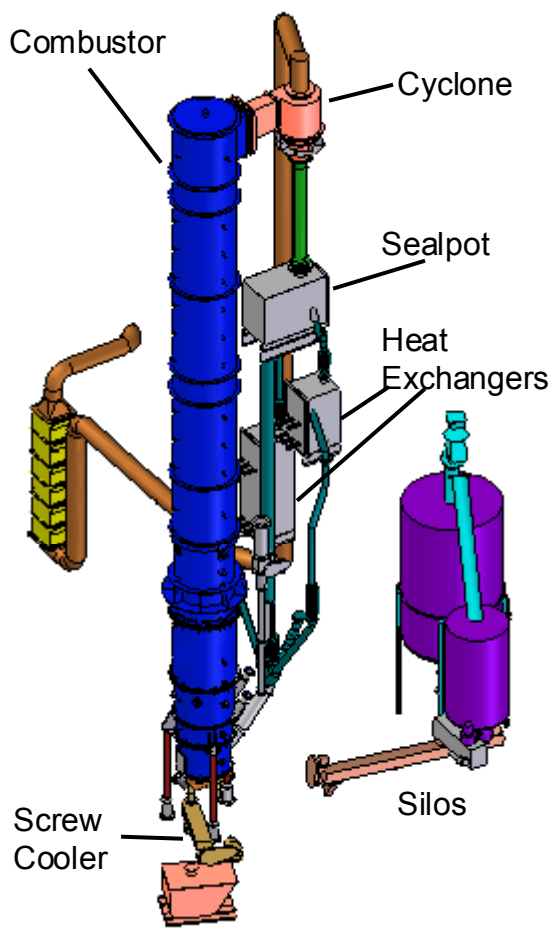

Figure 6: Multiuse Test Facility

Pilot Plant Modifications for Oxygen Firing

In order to conduct the oxygen-fired tests, several modifications were made to the MTF.

O_2/CO_2 Infrastructure - For the pilot plant testing, mixtures of oxygen and pure carbon dioxide were used to simulate mixtures of oxygen and recirculated flue gas. An O_2/CO_2 supply and control infrastructure was designed and supplied by Praxair, Inc. to enable the combustion of fuels in various O_2/CO_2 mixtures.

Reduced Furnace Diameter - When firing with an enriched oxygen mixture, the flue gas volume is reduced. To maintain the proper fluidizing velocities in the pilot plant, either the firing rate has to increase or the furnace diameter decrease. Since the pilot plant's environmental permit is limited to 9.9 MMBtu/hr firing rate, a refractory liner was added to reduce the furnace diameter from 40 inches to 21 inches. With this reduced diameter, the MTF can operate with up to 70% oxygen enrichment - see Figure 7.

Additional Heat Transfer Surface - The cooling capability of the pilot plant is adequate for oxygen firing at low enrichment (e.g., 30% O_2/70% CO_2). For the high oxygen enrichment tests (above about 50% O_2), an additional cooling coil was installed in the upper furnace to control the combustor temperature.

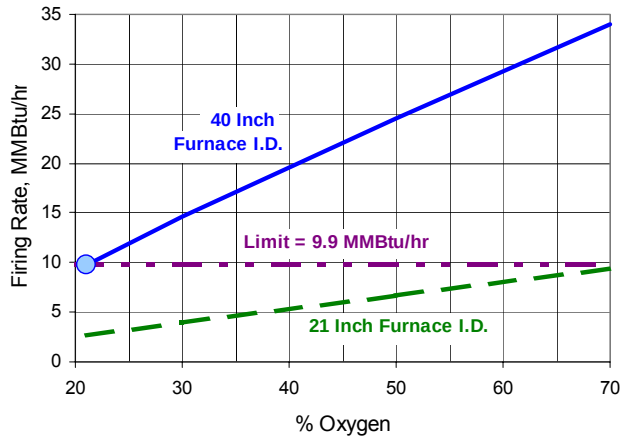

Figure 7: MTF Firing Rate *vs.* Oxygen Enrichment

Pilot Plant Test Results

In April and June 2004, ALSTOM tested a medium volatile bituminous coal and a shot petroleum coke in the Multiuse Test Facility. These tests were conducted with air firing and with O_2/CO_2 mixtures up to 50% oxygen. Most of the tests were run with furnace temperatures of around 1650°F in order to insure calcination of the limestone. This is higher than the typical air-fired temperature for bituminous coal but comparable to the normal temperature for pet coke.

Table 2: Test Campaigns

Test Campaign 1	Test Campaign 2
April 2004	June 2004
Bituminous	Bituminous & Petcoke
2.2 - 4.8 MMBtu/hr	4.2 - 7.9 MMBtu/hr
Air, 20 - 30% O_2 Mixture	40 - 50% O_2 Mixture (up to 70% O_2 locally in the feed zone)
	Additional Cooling Coil

Table 3: MTF Pilot Tests Fuel Analyses

	Bituminous Coal	Petroleum Coke
As-Fired, wt.%		
Volatile Matter	16.7	9.1
Fixed Carbon	63.4	89.0
Moisture	4.5	0.4
Ash	15.4	1.5
Hydrogen	3.8	3.7
Carbon	70.1	87.1
Sulfur	1.4	5.4
Nitrogen	1.6	1.6
Oxygen	3.2	0.3
HHV, Btu/lb	12107	14949

The basic test information is shown in Table 2. The analyses for the coal and pet coke tested are given in Table 3. A summary of the test results follows. Details are given by Nsakala et al. (2004).

Operability - The circulating fluid bed pilot plant ran well. There were no agglomeration or other problems in the lower combustor where the local oxygen concentration was up to 70%.

Recarbonation - The MTF has a water-cooled cyclone and dipleg; this cools the recirculating solids such that the dipleg and sealpot were usually below the calcination temperature (see Figure 5). When the sealpot was fluidized with pure CO_2, the CaO in the ash recarbonated.

In fact, this recarbonation used up all the fluidizing CO_2, so the sealpot did not operate. For the pilot tests, it was necessary to fluidize the sealpot with air. In a commercial unit with uncooled cyclone, the sealpot temperature is typically at least as high as the furnace temperature. Recarbonation would not occur even if the sealpot were fluidized with recycled flue gas.

In the air-fired tests, up to 4% of the calcium in the fly ash recarbonated as the flue gas cooled below the calcination temperature. In the oxygen-fired tests, up to 20% of the calcium in the fly ash showed up as $CaCO_3$ due to the higher CO_2 content of the flue gas.

NO_x - The NO_x emissions in the oxygen tests ranged from 0.05 to 0.1 lb/MMBtu. Typical results from the MTF with air firing at the same high temperatures range from 0.15 to 0.20 lb/MMBtu. Note that NO_x emissions are usually lower in a commercial unit because of poorer mixing (i.e., more staging) in large units.

SO_2 - The limestone feed rate was maintained at a calcium-to-sulfur ratio of about 2.0 throughout all the tests. The results summarized here are all with Aragonite, which is a very reactive sorbent.

With bituminous coal, the sulfur capture ranged from 70 to 90%. With air firing at the normal temperature of 1550°F, sulfur capture would be greater than 95% in the pilot plant with the same fuel and limestone. With pet coke the sulfur capture was 94 to 98%. These are comparable to results with air firing at 1650°F with the same fuel and limestone.

Further sulfur capture can be achieved in a back-end scrubber, such as ALSTOM's FDA. Testing of the FDA with oxygen firing will be included in the upcoming MTF tests in Spring 2005.

CO - At the same temperatures, the CO emissions were higher in the oxygen-fired tests due to the high CO_2 content of the flue gas - see Table 4.

Table 4: Typical MTF CO Emissions at 1650°F, lb/MMBtu

	Bituminous	Pet Coke
Air-Fired	0.03 - 0.10	0.02 - 0.03
Oxygen-Fired	0.07 - 0.20	0.05 - 0.10

Part of the reason that the CO emissions were higher in the oxygen-fired pilot tests was the lower upper furnace temperature due to the additional cooling coil. A commercial plant should have a more uniform, high temperature with emissions closer to air-fired levels.

N_2O - N_2O emissions are strongly dependent on combustor temperature. In air-fired PC systems, N_2O emissions are typically of the order of 0.01 lb/MMBtu. In the lower temperatures of fluid beds, emissions can be 0.1 lb/MMBtu and higher. In the oxygen-fired pilot tests, the N_2O emissions were 0.04 to 0.1 lb/MMBtu for the bituminous coal and 0.01 to 0.04 lb/MMBtu for the pet coke.

Unburned Carbon - The carbon heat loss in the fly ash with oxygen firing was the same as with air firing. As expected, the carbon loss was much lower with the pet coke than with the bituminous coal.

Heat Transfer - The in-furnace heat transfer coefficients were the same with air and oxygen firing, since in-furnace heat transfer is dominated by solids effects, and does not depend on the flue gas composition. Heat transfer coefficients in the convective pass and EHE will be measured in the upcoming pilot tests in Spring 2005.

CHEMICAL LOOPING

ALSTOM is also developing chemical looping processes which can extract oxygen from the air without cryogenic or membrane separation. These chemical looping processes use solid carriers to react with oxygen from air and transport the oxygen to a separate reactor to combust or gasify fuel. The chemical looping processes are enabled by commercial CFB and transport reactor technologies.

ALSTOM is evaluating metal oxide oxygen carriers for chemical looping applications in several projects in Europe. Here we describe work done with U.S. DOE sponsorship using calcium-based carriers (Marion, et al, 2003). The basic concept is shown in Figure 8.

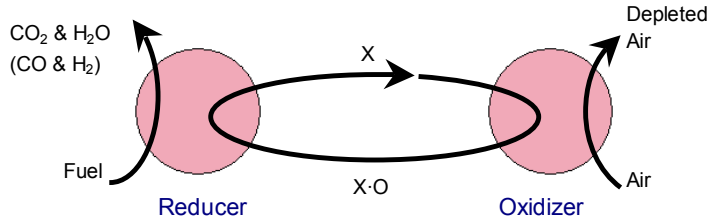

Figure 8: Chemical Looping Concept for Combustion or Gasification

Chemical Looping Combustion

In Chemical Looping Combustion (CLC), oxygen is extracted from air and used to combust coal. This is done with a carrier of CaS / $CaSO_4$ as shown in Figure 9. This avoids the large investment costs associated with either cryogenic ASU's or oxygen transport membranes. The trade off is a more complex boiler process.

Figure 10 shows a simplified process flow diagram for the CLC boiler island from the Phase I Study. The main reactions which occur in the system are given in Table 5.

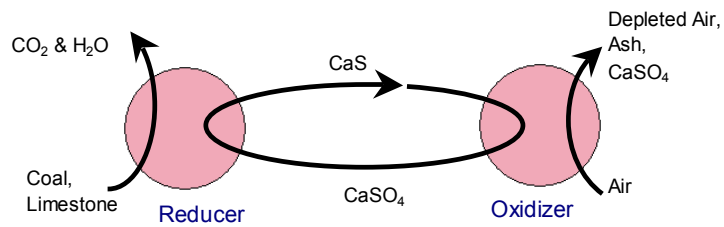

Figure 9: Chemical Looping Combustion with CaS Oxygen Carrier

Coal is fed to the reducer, where it is oxidized with the oxygen from the $CaSO_4$. Limestone is also added to the reducer to capture the sulfur from the fuel and as a makeup source for the calcium carrier. Both the limestone feed and the $CaSO_4$ react largely to CaS in the reducer. A small amount of low pressure extraction steam is added to the reducer to help initiate the reducer reactions.

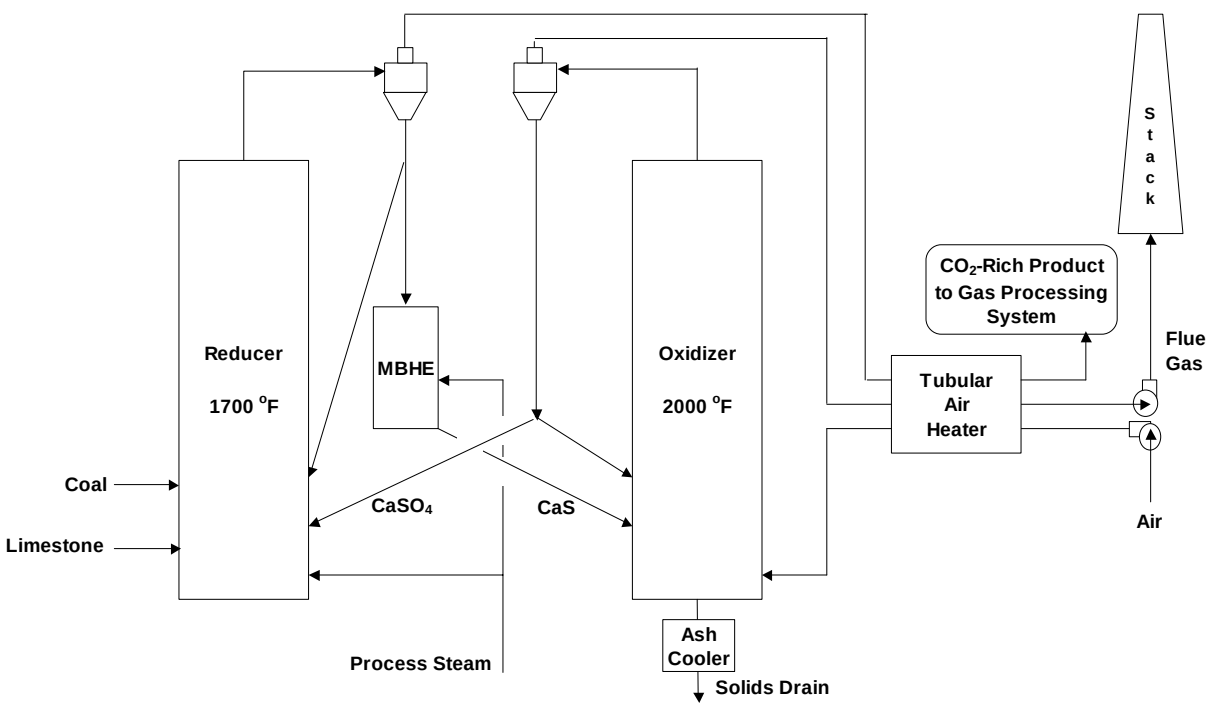

Figure 10: Simplified Process Flow Diagram – Chemical Looping Combustion

Table 5: Overall Reactions in Chemical Looping Combustion

in the Reducer	in the Oxidizer
Combustion Reactions $CaSO_4 + 2C\ (coal) + Heat \rightarrow 2CO_2 + CaS$ $CaSO_4 + 8H\ (coal) + Heat \rightarrow 4H_2O + CaS$ Calcination/Sulfidation Reaction $2CaCO_3 + 2S + C + Heat \rightarrow 2CaS + 3CO_2$	$CaS + 2O_2 \rightarrow CaSO_4 + Heat$

The flue gas from the reducer contains mainly the CO_2 and H_2O from the combustion of the coal along with pollutants such as SO_2, NO_x, and CO. This flue gas is similar to that from other oxygen-fired systems, ready for cleanup and utilization or sequestration of the CO_2.

The CaS from the reducer goes to the oxidizer where it reacts with oxygen from air to form $CaSO_4$. The gas leaving the oxidizer is mainly depleted air. A portion of the solids is drained from the oxidizer to remove fuel ash and fuel sulfur as $CaSO_4$. The solids also contain small amounts of $CaCO_3$, CaO, and unburned carbon. The solids are cooled in ash coolers for feedwater heating.

The oxidizer and reducer each operate as circulating fluidized bed systems with a cyclone and their own recirculation loop. Solids are exchanged between the two systems to transfer the oxygen carrier - the CaS and $CaSO_4$.

In order to absorb the excess heat produced in the oxidizer, the CaS solids from the reducer are cooled in a Moving Bed Heat Exchanger (MBHE) described in the above section on OTM. The MBHE generates high-pressure, high-temperature steam for the power cycle while cooling the entering solids stream. The tube bundles in the MBHE have spiral-finned surface and include superheater, reheater, evaporator and economizer sections. Very high heat transfer rates are obtained in the MBHE due to the conduction heat transfer mechanism between the solids and tube.

The high-nitrogen, depleted air from the oxidizer and the high-CO_2 flue gas from the reducer are each cleaned of solids and cooled in a tubular air heater. The N_2 stream is exhausted to the atmosphere through the ID fan. The CO_2 stream provides the feed stream to the gas processing system where a high purity CO_2 stream is produced and available for sequestration or use.

Chemical Looping Gasification

A similar chemical looping concept is also used in Chemical Looping Gasification (CLG) to provide the oxygen for the gasification of coal. This process produces a medium-Btu gas from an air fired gasifier system. A second chemical loop and a thermal loop are added to remove CO_2 from the fuel gas. This concept is shown in Figure 11

Figure 12 shows a simplified process flow diagram for the CLG gasifier island, which provides indirect gasification of coal and CO_2 capture via chemical looping. Three primary reactors are included in the CLG processes, the oxidizer, reducer, and calciner. The main reactions are summarized in Table 6.

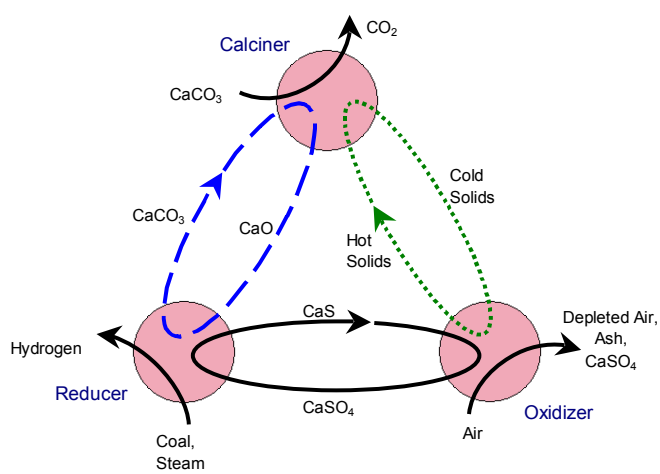

Figure 11: Chemical Looping Gasification with CaS Oxygen Carrier

The reducer operates at a lower stoichiometry than in the Chemical Looping Combustion system, so the coal is partially oxidized to CO and H_2 along with CO_2 and H_2O. Steam is added to drive the water-gas shift reaction towards H_2 and CO_2. The carbonate loop removes the CO_2 from the reducer and releases it in the calciner. This produces a hydrogen-rich fuel gas which can be cleaned and compressed for combustion in a gas turbine combined cycle for power generation with very low CO_2 emissions.

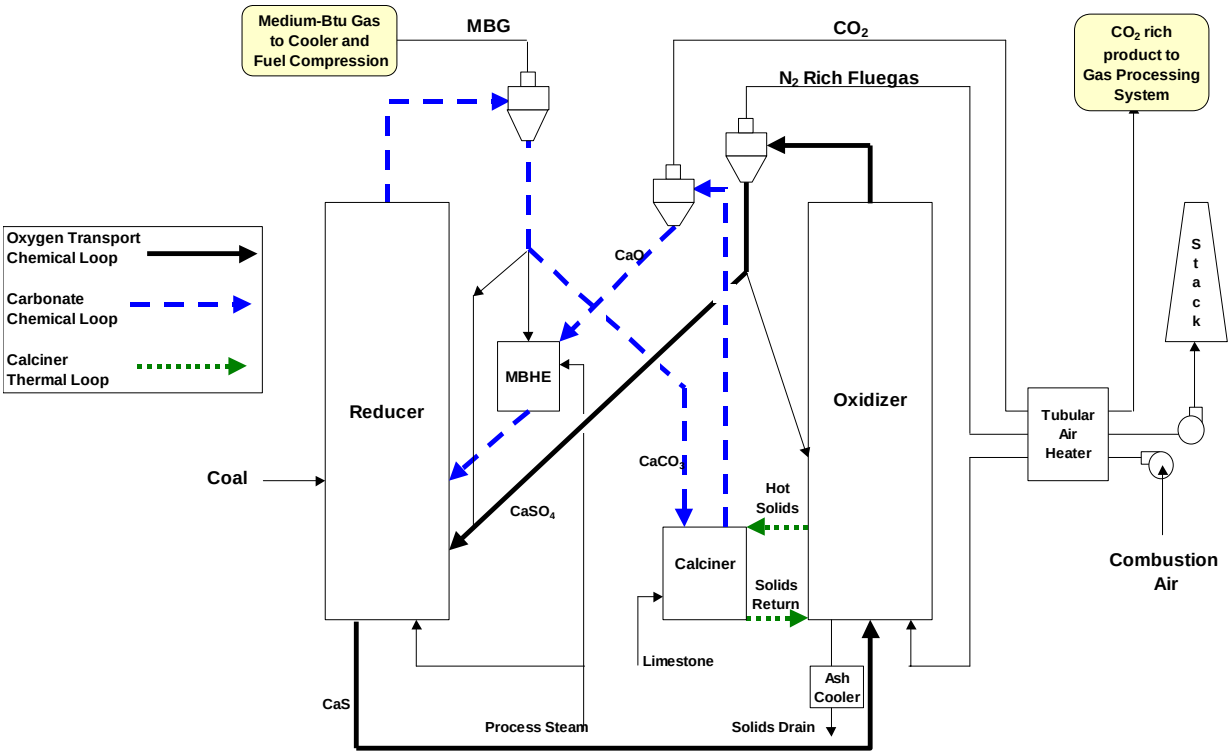

Figure 12: Simplified Process Flow Diagram – Chemical Looping Gasification

Table 6: Overall Reactions in Chemical Looping Gasification

in the Reducer	in the Oxidizer
Gasification Reactions $4C\ (Coal) + CaSO_4 + Heat \rightarrow 4CO + CaS$ $8H\ (Coal) + CaSO_4 + Heat \rightarrow CaS + 4H_2O$ $H_2O + C\ (Coal) + Heat \rightarrow H_2 + CO$ Water-Gas Shift Reaction $CO + H_2O \rightarrow H_2 + CO_2$ Carbonation Reaction $CaO + CO_2 \rightarrow CaCO_3 + Heat$	$CaS + 2O_2 \rightarrow CaSO_4 + Heat$ **in the Calciner** $CaCO_3 + Heat \rightarrow CaO + CO_2$

The oxidizer operates much like in the Chemical Looping Combustion system. Hot solids are transported from the oxidizer reactor to provide the heat of calcination in the calciner.

The calciner is a fluidized bed reactor which operates at about 1,600°F. $CaCO_3$ from the reducer and added limestone are calcined to CaO and CO_2. Hot solids (~1800°F) from the oxidizer provide the heat required for the calcination. The hot CO_2 stream is cooled before going to the gas processing system. The CaO is transported back to the reducer to repeat the cycle by removing CO_2 from the fuel gas.

CHEMICAL LOOPING PROCESS DEVELOPMENT UNIT TESTING

The chemical looping processes described above have been studied in several facilities located at ALSTOM's Power Plant Laboratories in Windsor, CT, USA. Cold flow models have been used to study the complex two-phase solid-gas transport. A Thermo-Gravimetric Reactor, small entrained flow reactors, and a 4-inch fluid bed combustor were used to investigate the individual chemical reactions required for the looping processes. These studies provided the chemical kinetic rate data necessary to develop commercial concepts for economic and engineering analysis. The tests showed that all rates were sufficiently fast to support the design of efficient, economically viable, commercial plant designs.

The reaction studies also provided the basis for designing a chemical looping process development unit (PDU). The PDU is used to study cycling reactions and also to study the two-phase solid-gas transport processes.

The PDU facility was completed in 2003 with ALSTOM funding. ALSTOM was awarded a cost-sharing contract by the U.S. DOE to use the facility to begin development of the chemical looping combustion and gasification concepts described in the previous section. The aim of the testing program is to develop sufficient information to design and test a pilot plant of the process. A schematic of the PDU is shown in Figure 13.

The facility spans three floor levels and is about 25 feet high. The facility includes a reducer loop, an oxidizer loop, and sorbent activation loops. The PDU facility enables the study of the individual cycling physical and chemical processes, including the CaS-$CaSO_4$ looping reactions to transfer oxygen between the oxidizer and reducer, the CaO-$CaCO_3$ reactions to capture CO_2, and the $CaSO_4$-carbon reactions to gasify coal.

The facility is also used to learn how to startup and operate the complex two-phase solid-gas transport processes smoothly in order to promote stable chemical reactions. Testing of the PDU facility is complemented by testing in a cold-flow facility that is identical to the PDU.

Phase I of this DOE project is completed. Tests in Phase I included cold flow development and improvement of two-phase solid-gas flow control devices, cold flow startup and operating procedures, PDU high temperature, multiple-loop operation, and successful operation of the CaS-$CaSO_4$ looping reactions between the reducer and the oxidizer.

Phase II will complete the PDU testing necessary to design, build, and test a pilot plant of the chemical looping process. Phase II tests in 2005 will include coal gasification, water gas shift, CO_2 capture via CaO-$CaCO_3$ looping, and more cold-flow development of two-phase transport.

Following Phase II, the next step in the development will be a small pilot facility where the chemical and physical processes

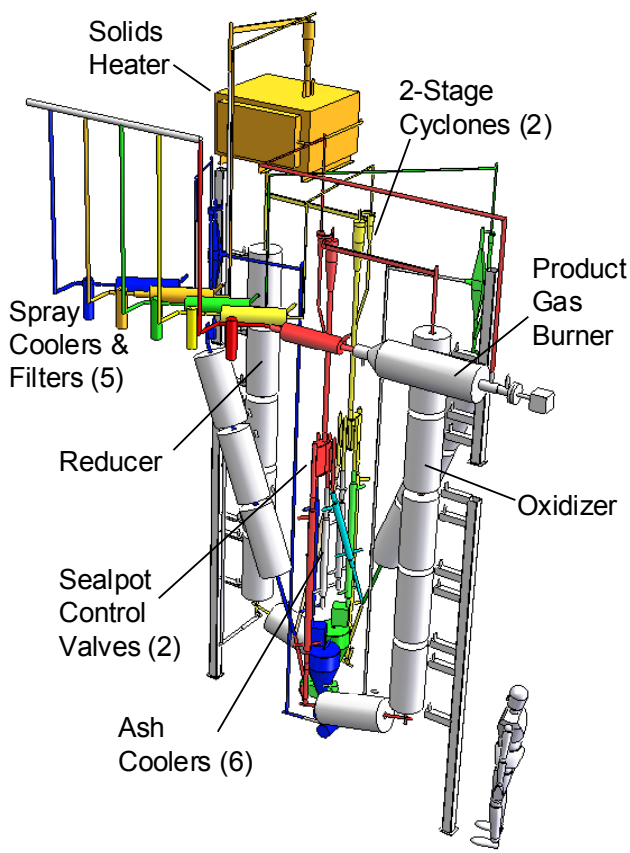

Figure 13: Schematic of the Chemical Looping PDU

can all operate simultaneously. Following the pilot testing, it is expected that a 5 - 10 MMBtu/hr prototype facility would be built and operated prior to demonstration in a commercial-sized unit.

PERFORMANCE AND ECONOMIC COMPARISON

The results of the performance and economic analyses of these combustion and gasification technologies - with and without CO_2 removal - are summarized in Table 7. The table also includes results for integrated gasification combined cycle (IGCC) cases based on Texaco quench technology for comparison. These results are taken from the Phase I study (Marion, et al., 2003), except for the O_2-fired CFB plant which has been updated in Phase II to reflect results from the pilot plant tests (Nsakala, et al, 2004).

The steam turbine for the combustion cases is a nominal 210 MWe single reheat machine with steam conditions of 1,800psi/1,000°F/1,000°F and a condenser pressure of 3.0 in. Hga. The gasification cases were all designed with a single train GE-7FA gas turbine, HRSG, and 1,800psi/1,000°F/1,000°F steam cycle. The IGCC cases include a spare gasifier for a capacity factor comparable to the other cases. The results summarized in Table 7 are also plotted in Figure 14 and Figure 15, and briefly discussed below.

Net Plant Efficiencies. An overall plant performance comparison for the oxygen- and air-fired CFB plants shows that they produce net plant thermal efficiencies of 26.0 and 35.5 %, respectively. This represents an energy penalty of about 27 percent for the O_2 fired case. The large reductions in output and efficiency are primarily the result of large power consumption requirements for the cryogenic air separation unit and gas processing system. When the oxygen transport membrane was used in lieu of a cryogenic system to produce the oxygen, the net plant thermal efficiency improved significantly to 30.0 %, thus reducing the energy penalty from 27% to 16%. The net thermal efficiency of the chemical looping combustion (CLC) plant was 30.9%, for an energy penalty of 13%. This improvement was due principally to the fact the CLC does not use an air separation system. The net thermal efficiencies of the chemical looping gasification without and with CO_2 capture were 41.4 and 36.9%, respectively, for an energy penalty of 11%. The net thermal efficiencies of the IGCC without and with CO_2 capture were 34.5 and 27.4%, respectively, for an energy penalty of 21%.

CO_2 Emissions. Carbon dioxide emission for the business as usual, air-fired CFB plant was 2.0 lb/kWh. The CO_2 capture combustion technologies reduced carbon dioxide emissions to about 0.17, 0.15, and 0.07 lb/kWh, for the O_2-fired CFB with cryogenic ASU, O_2-fired CFB with OTM, and CLC, respectively. The CO_2 emission for the chemical looping gasification plant without and with CO_2 capture were 1.71 and 0.09 lb/kWh, respectively. The CO_2 emissions for the IGCC plant without and with CO_2 capture were 1.98 and 0.15 lb/kWh, respectively. The CO_2 reduction in each case was more than 90%.

Investment Costs and Costs of Electricity. The investment costs of the combustion technologies were 1304, 2382, 2375, and 1663 $/kW for the air-fired CFB, O_2-fired CFB with cryogenic ASU, O_2-Fired CFB with OTM, and CLC, respectively. Using a Utility finance model, and economic assumptions discussed by Marion et al. (2003), the corresponding levelized costs of electricity are 4.5, 7.9, 7.1, and 5.8 Cents/kWh. These represent increases in COE ranging from 30 to 76% over the value for the air-fired CFB plant. The OTM improves the COE of the O_2-fired CFB plant by about 11% (from 7.9 to 7.1 Cents/kWh).

The investment costs of the gasification technologies were 1120, 1383, 1718, and 2364 $/kW for the CLG, CLG with CO_2 capture, IGCC, and IGCC with CO_2 capture, respectively. The levelized COE values of the CLG gasification plants without and with CO_2 capture were 4.3 and 5.2 Cents/kWh, an increase of 21% for CO_2 capture. The levelized COE values of the IGCC gasification plants without and with CO_2 capture were 5.8 and 7.8 Cents/kWh, an increase of 34% for CO_2 capture.

Table 7: Summary of Performance and Economics

		Combustion Technologies				Gasification Technologies			
		Reference Plant	CO_2 Capture Plants			CLG Reference Plant	CLG CO_2 Capture Plant	IGCC Reference Plant	IGCC CO_2 Capture Plant
		Air Fired CFB	O_2 Fired CFB w/Cryogenic ASU	O_2 Fired CFB with OTM	Chemical Looping Combustion	Chemical Looping Gasification	Chemical Looping Gasification	Texaco Quench	Quench w/ Water Gas Shift
Net Power Output	MWe	193	138	197	164	265	257	235	201
Thermal Efficiency	%, HHV	35.51	25.95	30	30.9	41.38	36.9	34.5	27.4
Investment Costs	$/kW	1304	2382	2375	1663	1120	1383	1718	2364
Cost of Electricity	Cents/kWh	4.5	7.9	7.1	5.8	4.3	5.2	5.8	7.8
CO_2 Emissions	lb/kWh	2.0	0.17	0.15	0.07	1.71	0.09	1.98	0.15
*CO_2 Mitigation Cost	$/ton avoided	---	37	27	13	---	7 (11)	---	36 (23)

* Relative to air-fired CFB Reference Plant (Relative to corresponding Reference Plant)

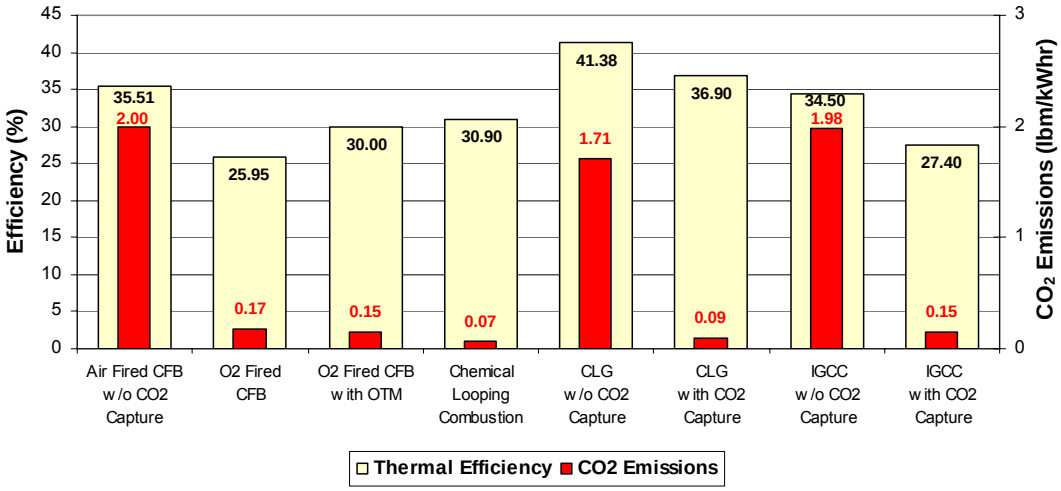

Figure 14: Net Plant Efficiency and CO_2 Emissions

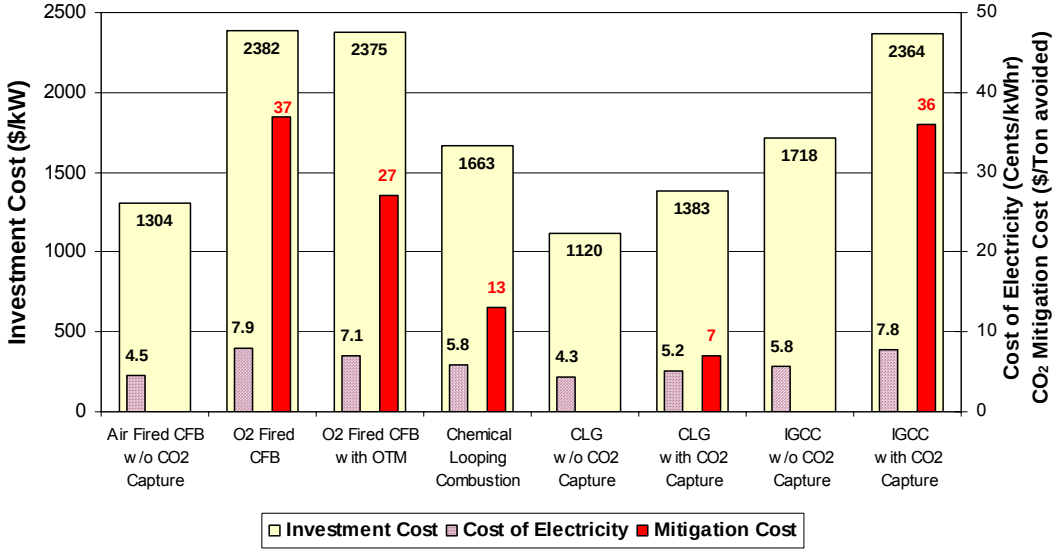

Figure 15: Investment Costs, Cost of Electricity, and CO_2 Mitigation Costs

CO_2 Mitigation Costs. The mitigation cost for the CO_2 capture plants is the additional cost of electricity ($/kWh) divided by the reduction in carbon dioxide emissions (ton/kWh). Table 7 shows the mitigation costs for each CO_2 capture technology relative to the air-fired CFB. For the Chemical Looping Gasification and the IGCC, the mitigation cost is also shown relative to the corresponding reference plant without CO_2 capture. The O_2-fired CFB with cryogenic ASU has a mitigation cost of 37 $/ton of CO_2 avoided. With the more efficient OTM used to produce the oxygen, the mitigation cost dropped to 27$/ton of CO_2 avoided. The chemical looping combustion plant reduced this to 13 $/ton of CO_2 avoided. The mitigation cost for the CLG gasification plant was the lowest at 7$/ton of CO_2 avoided (or 11$/ton relative to an CLG plant without CO_2 capture). The mitigation cost for the IGCC plant was 36$/ton of CO_2 avoided (or 23 $/ton relative to an IGCC plant without CO_2 capture). All of these results assume no credit for potentially useful byproducts (i.e., CO_2 and Nitrogen).

Comparison of Near-Term Technologies The two near-term CO_2 control technologies – O_2-fired CFB and IGCC – have similar economics. The investment costs (2382 vs. 2364 $/kW) and the cost of electricity (7.9 vs. 7.8 ¢/kWh) are within about 1% of each other. The CO_2 mitigation costs on a common basis are also similar (37 vs. 36 $/ton).

Economics without Carbon Sequestration Each of the technologies for CO_2 control cost more than the base case of an air-fired CFB – if no credit is taken for the CO_2 and nitrogen byproducts. The Phase I study by Marion, et al, (2003) also showed that the O_2-fired CFB is economically feasible even today in a situation such as enhanced oil recovery, where the CO_2 and N_2 byproducts are sold for oil field stimulation and pressurization, respectively.

SUMMARY

Combustion of fossil fuels with oxygen instead of air produces a CO_2-rich flue gas which can be readily processed for sequestration or use. Circulating fluidized bed combustion is particularly well suited to oxygen firing - the solids circulation through an external heat exchanger reduces the requirement for flue gas recirculation.

Pilot tests have confirmed the technical feasibility of an oxygen-fired CFB system. Additional pilot tests planned for Spring 2005 will investigate backend sulfur removal, trace emissions, and convective pass fouling and heat transfer.

Even today - without the requirement of CO_2 sequestration - oxygen-fired CFB can be economically feasible where the CO_2 from the combustor and N_2 from the ASU are sold for enhanced oil recovery.

Two near-term CO_2 control technologies - oxygen-fired CFB and IGCC - have similar economics. The investment costs and costs of electricity are within about 1% of each other.

Current cryogenic air separation technology consumes a large portion of the power plant's output. The more efficient oxygen transport membrane technology may be integrated into the boiler island and improve the economics of oxygen-fired systems.

The chemical looping technology is a relatively long-term development which integrates the air and CO_2 separation into the combustion or gasification process. Chemical looping may provide CO_2 capture at a very low cost of electricity. Process development tests have been successful to date and are continuing.

ACKNOWLEDGMENTS

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