

**ALSTOM's Chemical Looping Combustion Prototype for CO₂
Capture from Existing Pulverized Coal-Fired Power Plants**

Final Report

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Abstract

Alstom's Limestone Chemical Looping (LCL™) process has the potential to capture CO₂ from new and existing coal-fired power plants while maintaining high plant power generation efficiency. This new power plant concept is based on a hybrid combustion-gasification process utilizing high temperature chemical and thermal looping technology. This process could also be potentially configured as a hybrid combustion-gasification process producing a syngas or hydrogen for various applications while also producing a separate stream of CO₂ for use or sequestration. The targets set for this technology is to capture over 90% of the total carbon in the coal at cost of electricity which is less than 20% greater than Conventional PC or CFB units. Previous work with bench scale test and a 65 kWt Process Development Unit Development (PDU) has validated the chemistry required for the chemical looping process and provided for the investigation of the solids transport mechanisms and design requirements.

The objective of this project is to continue development of the combustion option of chemical looping (LCL-C™) by designing, building and testing a 3 MWt prototype facility. The prototype includes all of the equipment that is required to operate the chemical looping plant in a fully integrated manner with all major systems in service. Data from the design, construction, and testing will be used to characterize environmental performance, identify and address technical risks, reassess commercial plant economics, and develop design information for a demonstration plant planned to follow the proposed Prototype. A cold flow model of the prototype will be used to predict operating conditions for the prototype and help in operator training. Operation of the prototype will provide operator experience with this new technology and performance data of the LCL-C™ process, which will be applied to the commercial design and economics and plan for a future demonstration plant.

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List of Acronyms

A&E's	Architect and Engineers
BP	Budget period
BSF	Boiler Simulation Facility
Cactus	Area of the Reducer where several solids streams enter the Reducer. It looks like a cactus with two branches
Calcliner	reaction vessel in Alstom's Chemical Looping Process, where CO ₂ is recovered from Calcium Carbonate
CCO	Carbon Carryover
CFB	Circulating Fluidized Bed
CFM	Cold Flow Model
Chamber Pot	Solids collection device to remove solids that are carried over through the cyclone in an upset condition.
CLC	Chemical Looping Combustion
CMB	Circulating Moving Bed
COE	Cost of Electricity
CP	Chamber Pot
DCS	Distributed Control System
dip-leg	pipe that carries solids from the cyclone bottom to the SPCV
DOE	Department of Energy
DP	Delta Pressure
EPC	Engineering, Procurement and Construction
FBHE	Fluidized Bed Heat Exchanger
FT	Fusion Temperature of solids
GPU	Gas Processing Unit
ID	Induced Draft fan or Inner Diameter
IDT	Initial Deformation Temperature of solids
IGCC	Integrated Gasification Combined Cycle
ISBF	Industrial Scale Burner Facility
kW	Kilowatt
LCL-C™	Alstom's Limestone Chemical Looping Combustion System
LSPCV	Lower Seal Pot Control Valve
MBG	Medium BTU Gas
MBHE	Moving Bed Heat Exchanger
MFT	Main Fuel Trip
MSPCV	Main Seal Pot Control Valve
MTF	Multi-use Test Facility
MWe	Megawatt Electrical
MWt	Megawatt Thermal
NEPA	National Environmental Protection Act
NETL	National Energy Technology Laboratories

NG	Natural Gas
Octopus	Area of the Reducer where gas is injected in eight equally spaced nozzles. The arrangement of feed pipes resembles eight 'legs'.
OTM	Oxygen Transport Membrane
OTO	Oxidizer Top Outlet
Oxidizer	Reaction vessel where the solids are burned in air to generate the oxygen carrying solids
P&ID	Piping and Instrumentation Diagram
PC	Pulverized Coal
PDU	Process Development Unit
PFD	Process Flow Diagram
RBO	Reducer Bottom Outlet
Reducer	Reaction vessel where Oxygen carrying solids are reduced by burning or gasifying fuel
RPC	Reducer Pressurizing Column
RTO	Reducer Top Outlet
RV	Rotary Valve
SAHE	Sorbent Activation Heat Exchanger
SCF	Standard Cubic Feet
SPCV	Seal Pot Control Valve
TCGR	Technology Concept Gate Review
TGA	Thermo Gravimetric Analyzer
UBC	Unburned Carbon in the Ash
USPCV	Upper Seal Pot Control Valve
waterwall	boiler tube walls
W-R	Warrior Run, a commercial CFB boiler

Executive Summary

Alstom Power Inc. (Alstom) is in the process of developing a novel, ultra-clean, low cost, high efficiency power plant for the global power market. This new power plant concept is based on a hybrid combustion-gasification process utilizing high temperature chemical and thermal looping technology. The process consists of the oxidation, reduction, carbonation, and calcination of calcium-based compounds which chemically react with carbon containing fuels such as coal, biomass, or opportunity fuels in two chemical loops and one thermal loop. In its most advanced configuration, this new concept offers the promise to become the technology link from today's Rankine Cycle steam power plants to tomorrow's clean coal power plants

Background

Chemical looping is a two-step process, which first separates oxygen from nitrogen in an air stream in an air reactor. The oxygen is transferred to a solid oxygen carrier. This oxygen, carried by the solid oxide, is then used to gasify or combust solid fuel in a separate fuel reactor. **Figure E-1** illustrates the basic idea. In this figure, an oxygen carrier is burned in air forming a hot oxide in the air reactor (Oxidizer). The oxygen in the hot solid oxide is used to gasify coal in the fuel reactor (Reducer), thereby reducing the solid oxygen carrier for continuous reuse in the chemical looping cycle. Chemical looping has the flexibility to be designed in a number of configurations. The reactor can be operated in a partial combustion mode, to generate a CO rich syngas, which can be shifted to hydrogen. Alternately, it can operate in full combustion mode, resulting in exhaust of CO₂ and water.

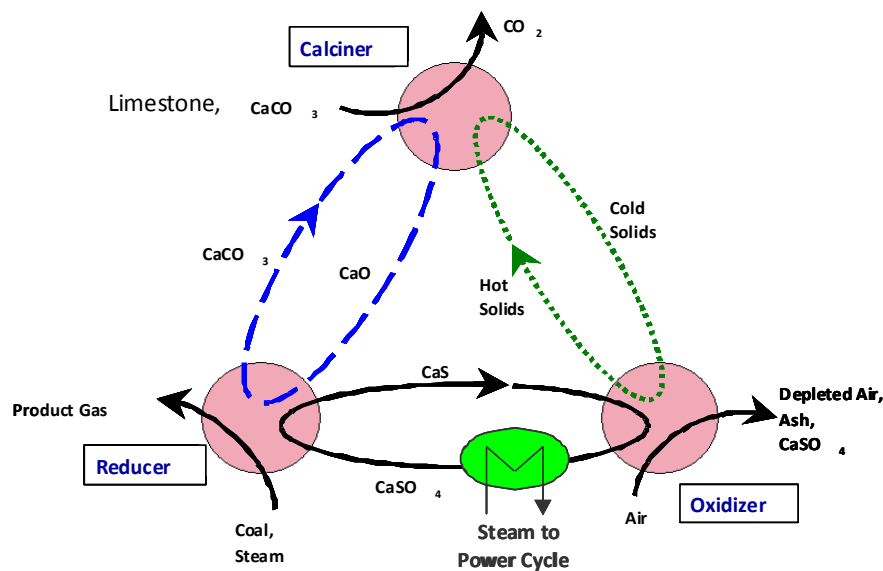


Figure E-1 – Alstom's Limestone-Based Chemical Looping (LCL™) Process Chemistry

Chemical looping is a "game changing" technology in terms of overall efficiency and cost and is the lowest costing (cost of electricity) technical approach that Alstom has identified to date for coal power with carbon capture and sequestration – **Figure E-2**.

Basis:

- Plant Size	400 Mwe-net
- Steam Conditions	3,915 psia, 1,085F, 1148F, 2.5 in. Hga
- Cost Basis	2006 \$US
- Coal Cost	1.5 \$/MM-Btu
- Levelized Capital Charge	13.5%
- Capacity Factor	80%

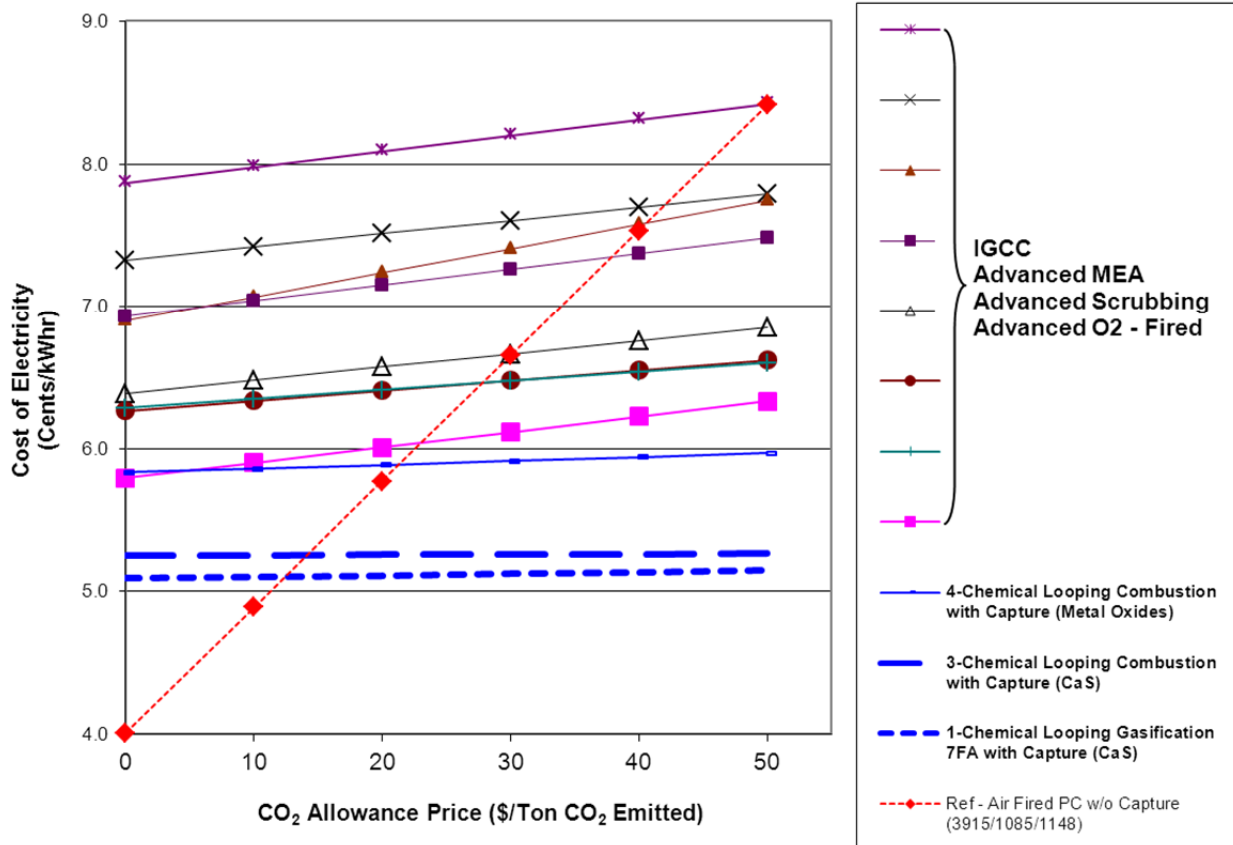


Figure E-2 – Comparison Among Various CCS Options for Coal-fired Boilers

As described in this report, Alstom is developing a chemical looping process, which uses limestone as the oxygen carrier. The process uses air, coal, limestone and steam to produce product gas and capture CO₂. Depending on the system configuration, the product gas can be hydrogen, syngas and/or CO₂. Heat and product gas produced by the process can be directly used to produce electricity via Rankine cycle, Brayton / Rankine cycle and/or fuel cell cycles in retrofit, repowered or new capacity power plants.

The U.S. Department of Energy (DOE) and Alstom have jointly funded the development of the chemical looping process since 2003. A 65 kWt Process

Development Unit (PDU) was utilized to develop and test the chemical looping combustion process with calcium sulfide (CaS) / calcium sulfate (CaSO₄). A lime (CaO) / calcium carbonate (CaCO₃) loop was added to demonstrate the feasibility of hydrogen production. The objectives were to obtain the necessary engineering information to design, build and test a viable prototype of the commercial Chemical Looping concept. This work included testing chemical reactions, determining chemical reaction rates, determining material handling properties, developing solids transport and scale-up data and developing process control information.

Project Objectives and Workscope

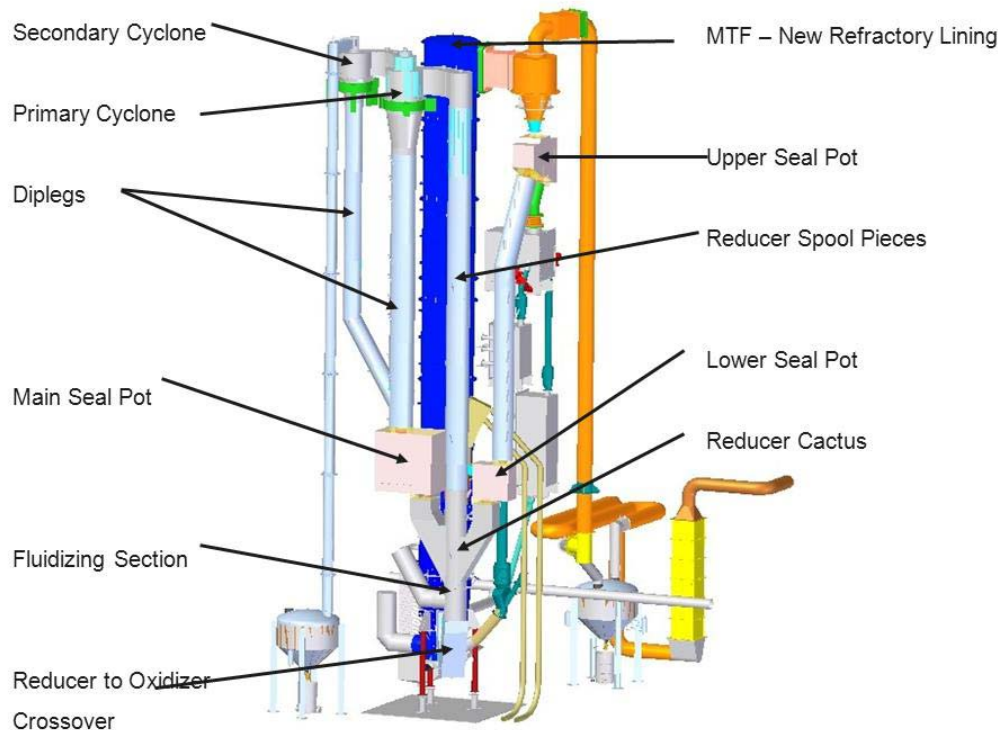
The overall objective is to develop and commercialize a novel chemical looping combustion process that is well suited for capturing nearly all of the CO₂ from existing or new pulverized-coal-fired (PC) and circulating fluidized bed (CFB) power plants. The specific project objectives are summarized below:

- Design, build, and test a chemical looping prototype plant that includes all of the equipment that is required to operate the chemical looping plant in a fully integrated manner with all major systems in service.
- Auto-thermal testing of the prototype for 40 hours at steady state.

Alstom's 3 MWt Multi-Use Test Facility was modified to operate as a 3 MWt (~1000 pounds per hour coal) chemical looping prototype test facility. Cold flow modeling tests were conducted in support of the design process and operation of the prototype facility. Shakedown tests of the prototype test facility were conducted. Series of test campaigns on the 3 MWt prototype were conducted to achieve auto-thermal operation. These efforts are summarized herein.

3 MWt Prototype

The 3 MWt chemical looping prototype was constructed by making use of Alstom's existing Multi-use Test Facility (MTF) which was originally configured as a circulating fluidized bed (CFB) boiler pilot plant. The existing CFB pilot was modified to serve as the chemical looping prototype oxidizer. A reducer system and additional auxiliary equipment were added to constitute the remainder of the chemical looping prototype. Virtually all of the MTF associated equipment were used: the existing feed system, gas handling and cleanup system, and instrumentation. The 3 MWt chemical looping prototype is shown in **Figure E-3**.



**Figure E-3 – 3-D Perspective View of the Prototype Facility
Cold Flow Modeling**

The goals of the Cold Flow Modeling (CFM) were to analyze and visualize solids transport in Alstom's chemical looping process, and to develop methods to transport, distribute and control solids flow for the operating loops. The specific needs are to establish a controllable and stable performance in the operating range, maximize solids flow control range for the given pressure system and minimize pressure drop for each looping system. The specific needs were to:

- Integrate the new Oxidizer loop into the existing cold flow model Reducer loop to form a complete solids circulation loop similar to the prototype unit,
- Trouble shoot for the prototype unit,
- Verify the conceptual design of the prototype for the solids transport in multi-loop operation,
- Demonstrate the operation methodology in multi-loop CFM operation including the start-up, shut-down and control stability of the system,
- Establishing operating guidelines for the prototype unit multi-loop operation as a training tool and as a trouble-shooting device.

All of these challenges were successfully addressed. The cold flow model demonstrated the stability of the solids transport as illustrated in **Figure E-4**.

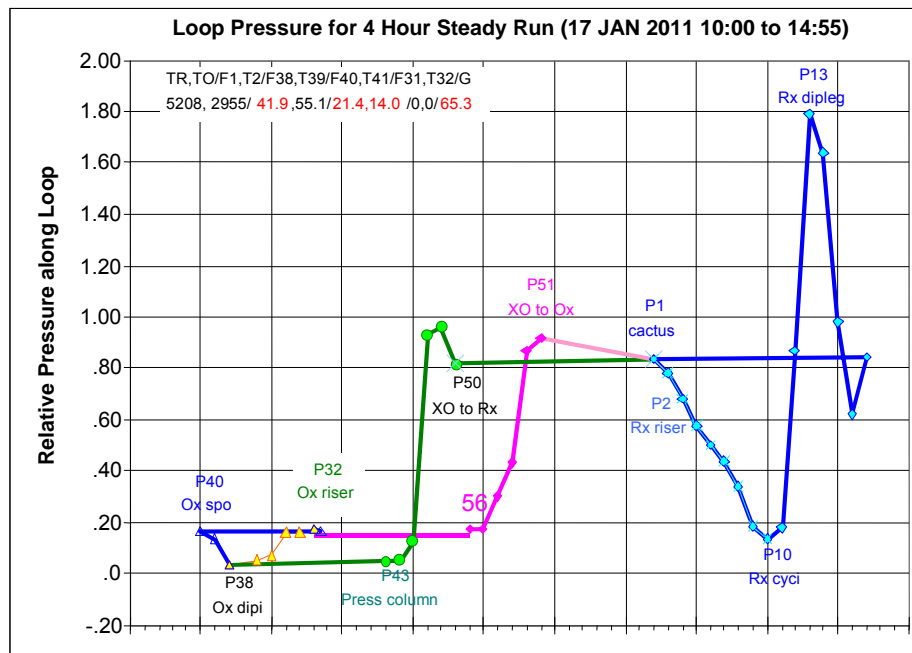
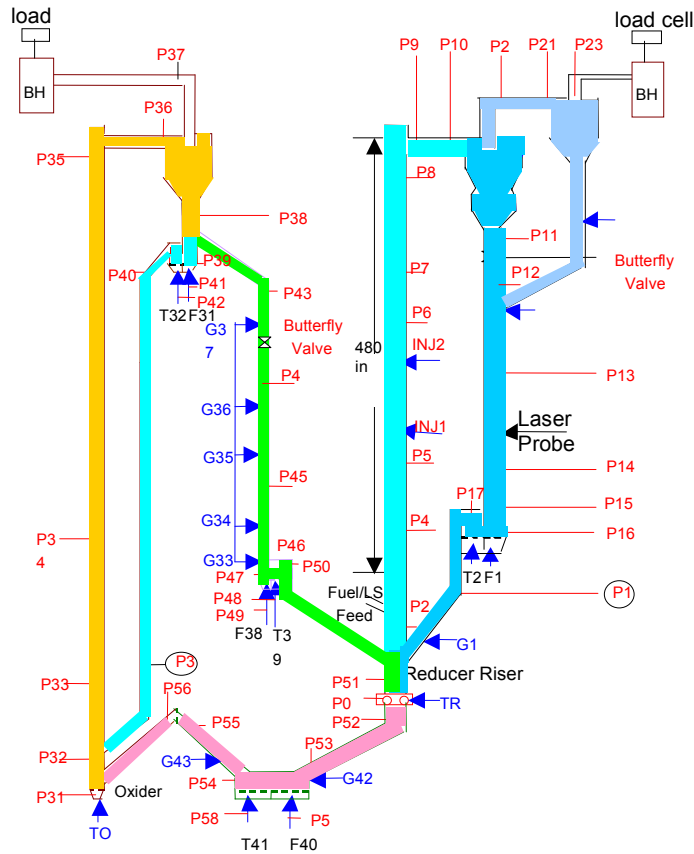


Figure E-4 – Test Results for the Prototype Cold Flow Model During a 4 Hour Test

3 MWt Prototype Test Campaigns

Commissioning of all systems to enable coal firing began in 2011. Initial coal firing tests provided operating experience and indications of chemical looping performance. Plans for 2011 called for operating the prototype auto-thermally. However, due to equipment limitations, auto-thermal operation was not achieved until 2012.

Three coal test campaigns were carried out during 2011.

- The May 2011 coal test showed that natural gas flow to the warm-up burners was below design levels, impeding coal-fired startup. The burner system was fixed.
- The June 2011 coal test showed that the chemical looping reactions were taking place (with support of natural gas firing in the oxidizer). This test indicated reaction rate performance similar to that observed during testing of the 65 kWt PDU.
- The September to October 2011 test campaign revealed deficiencies in the coal feed system (which caused coal feed interruptions) and the reducer pressurizing column (which caused solids re-circulation interruptions). Although troublesome, this test series provided valuable operator training, improved data acquisition and analysis capabilities and provided data important to future test design.

Several systematic tests were planned in 2012 to concentrate separately on the Reducer performance, the Oxidizer performance, and finally to achieve auto-thermal operation. The goals were to:

- verify the Reducer reactions,
- verify the Oxidizer reactions,
- operate with fuels of different size and reactivity, and
- achieve auto-thermal operation.

Three coal test campaigns were carried out during 2012.

- The May to June 2012 coal tests concentrated on reducer performance. Test results indicate that for nearly 1½ hours the reducer demonstrated self-sustaining chemical looping reactions.
- During July 2012, the prototype successfully achieved 12 hours of coal-only auto-thermal operation on Adaro (an Indonesian sub-bituminous with a relatively reactive char) and on Pittsburgh Seam No. 8 (a high volatile, eastern bituminous coal with relatively unreactive char).

- The August 2012 test campaign to investigate the impact of the reducer temperature on Reducer sulfur emissions. Hydrated lime was also added during this test to see the effect on sulfur emissions.

Highlights of the 2012 test campaigns include:

- 12 hours of auto-thermal operation on two coals (Pittsburgh Seam 8) and Adaro (an Indonesian sub-bituminous);
- All chemical looping reactions working in a fully integrated manner;
- Total unburned carbon (UBC) consistently < 1% of the carbon in the coal
- Up to 96% carbon capture achieved;
- Sulfur controllable to near zero for some conditions;
- Stable operation for long periods;
- Operation on 5 fuels (Pittsburgh Seam 8, Adaro, Illinois #6, wood charcoal and natural gas); and
- No major changes from Alstom's original concept or to the Prototype as originally designed and constructed were required to achieve successful auto-thermal operation.

Autothermal Operation

As mentioned above, during the July 2012 test campaign we were able to achieve autothermal operation on coal only without natural gas firing. The prototype operated autothermally for several hours each firing crushed Adaro sub-bituminous and crushed Pittsburgh #8 bituminous coals – see **Figure E-5**.

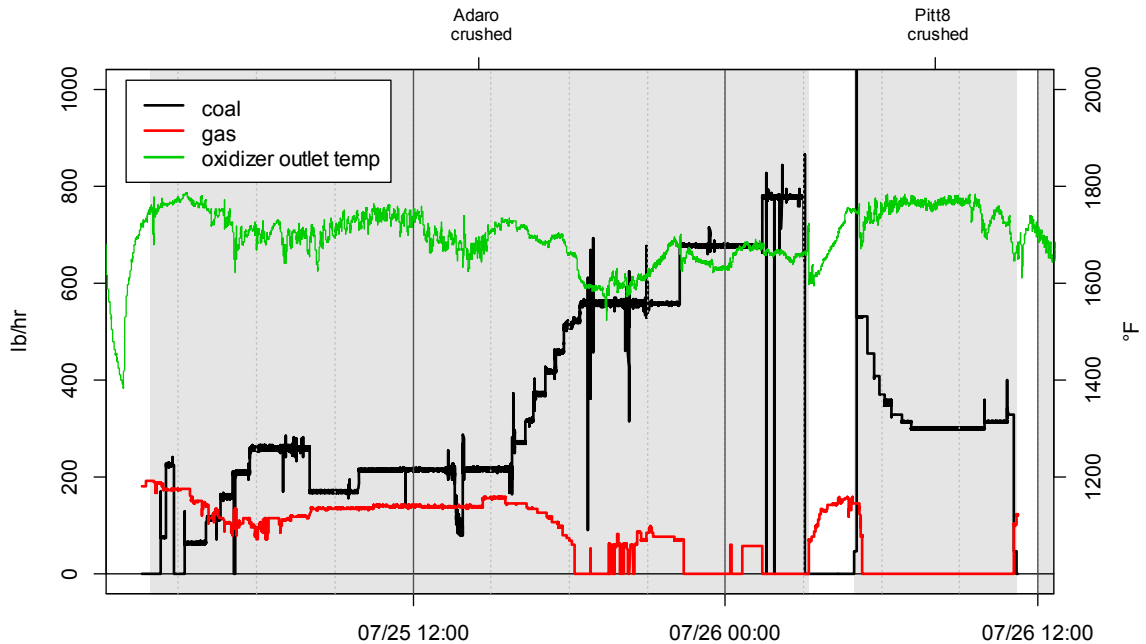


Figure E-5 – Autothermal testing during July 2012 campaign

On the afternoon of July 25, we began ramping up the coal feed rate and reducing the natural gas injection to the Oxidizer, until at about 18:00 hours the natural gas was turned off completely. As seen in **Figure E-5**, the temperatures started to drop – there was insufficient CaS being oxidized to maintain the temperature in the Oxidizer (and therefore the Reducer as well). The natural gas was turned on again to maintain the temperatures as the coal was further increased. Finally at about 01:30 on the 26th, the gas was shut off for good and the temperatures were maintained – i. e., self-sustained autothermal operation.

The Adaro autothermal test was followed by autothermal operation with crushed Pittsburgh #8 coal. The Pittsburgh #8 started at a feed rate of about 530 lb/hr, but the Oxidizer air firing rate was higher than we wanted, so it was reduced to 300 lb/hr – see **Figure E-5**.

LCL-C™ Economic Analysis

The Prototype testing has identified further steps to improve the performance towards meeting all the objectives shown in **Table E-3**, in particular the RBO Gate, the

Gas Drain, and the SAHE described above. The expected impact of these improvements are not expected to alter the conclusion of earlier studies that chemical looping combustion can be the lowest cost approach for CO₂ capture from coal-fired power plants, as shown in **Figure E-2**.

Alstom has recently completed a US DOE/NETL economic study of LCL-C™-based power plants which incorporates the results of the Prototype tests described in this report to compare Alstom's LCL-C™ to a supercritical pulverized coal power plants without CO₂ capture and to a supercritical oxy-fired pulverized coal fired power plant with 90% CO₂ capture. All three plants are designed to produce 550 MWnet.

Figure E-6 provides the process flow diagram of the LCL-C™-based power plant.

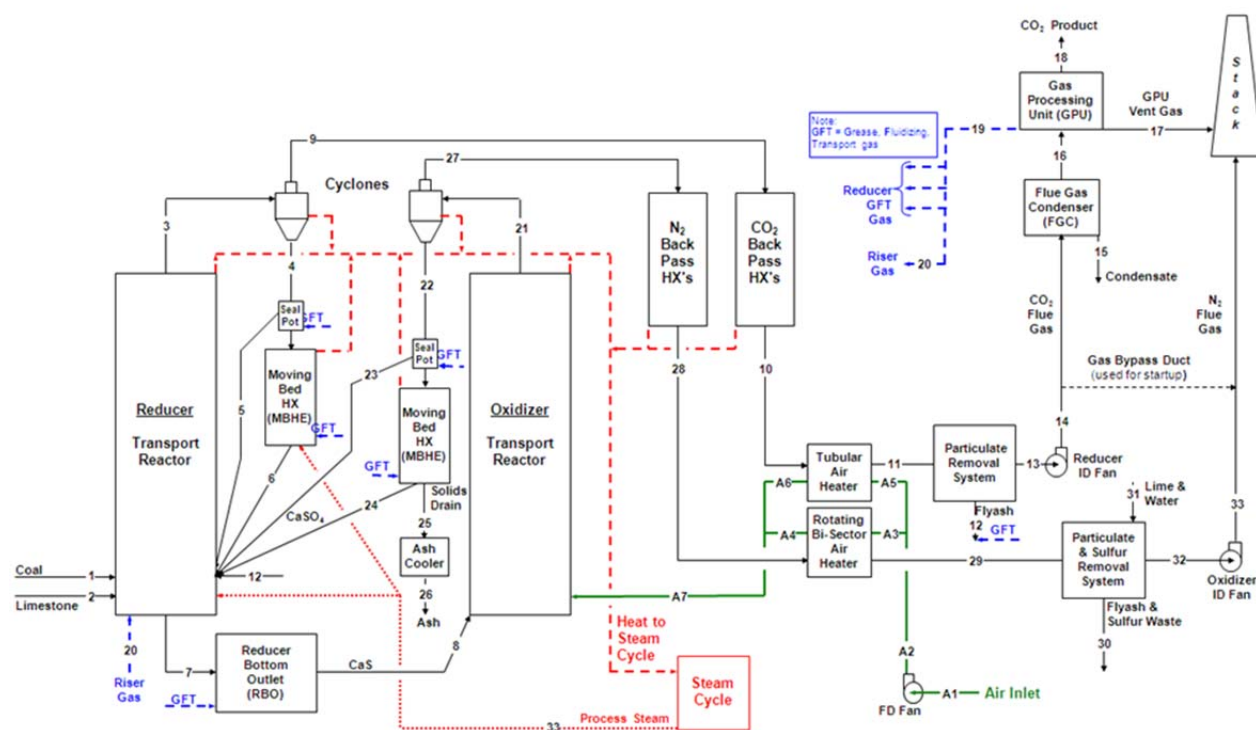


Figure E-6 – Simplified Process Flow Diagram for a LCL-C™ Power Plant – Case 1 (Transport Reactors)

Figure E-7 shows a bird's eye view of the LCL-C™ plant and a comparison of the plant with a pc boiler and CFB boiler for an idea of relative scale.

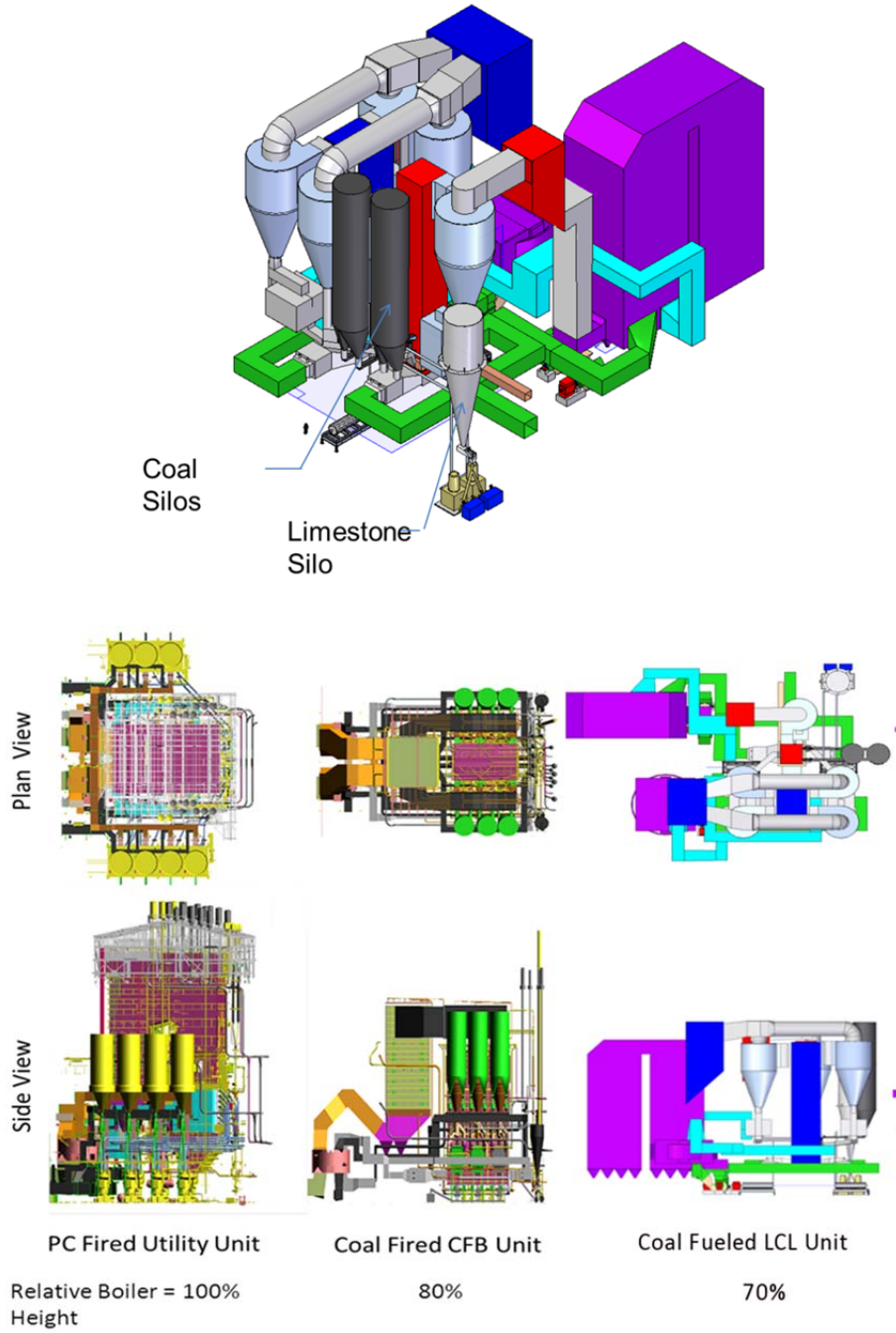


Figure E-7 - Alstom's 550 MW_{net} LCL-C™-based Power Plant

Table E-1 provides a summary of the major design and performance specifications for the three plants.

Table E-1 - Major Design and Performance Specifications

	Base Case		Case 1
	DOE Case 11 SCPC without capt	DOE Case 5C Oxy SCPC	LCL-C™ with transport reactors
Capacity	550MW _{net}	550MW _{net}	550MW _{net}
Capacity Factor, %	85	85	85
Coal	Illinois No. 6	Illinois No. 6	Illinois No. 6
Reactor Pressure, MPa (atm)	0.10 (1)	0.10 (1)	reducer 0.10 (1) oxidizer 0.10 (1)
Steam Cycle, MPa/°C/°C (psig/°F/°F)	24.1/593/593 (3500/1100/1100)	24.1/593/593 (3500/1100/1100)	24.1/593/593 (3500/1100/1100)
Condenser pressure, mm Hg (in Hg)	50.8 (2)	50.8 (2)	50.8 (2)
Cooling water to condenser, °C (°F)	16 (60)	16 (60)	16 (60)
Cooling water from condenser, °C (°F)	27 (80)	27 (80)	27 (80)
SO ₂ Control	Wet Limestone Forced oxidation	Wet Limestone Forced oxidation	Limestone added in Reducer NID™ in Oxidizer stream MDEA in GPU
NO _x Control	LNB w/OFA and SCR	LNB w/OFA and SCR	controlled by LCL-C™ process
Particulate Control (A)	Fabric Filter	Fabric Filter	Fabric Filter in Reducer and Oxidizer streams
Mercury Control	Co-benefit capture	Co-benefit capture	Halongated solution injection in Reducer Flue Gas Condenser & Activated Carbon Bed in GPU - Reducer
Mercury removal efficiency, %	90	90	>90%
CO ₂ Control	N/A	Oxy-firing & GPU	LCL-C™ & GPU
Overall CO ₂ Capture	N/A	92.65	>95%
CO ₂ Sequestration	N/A	EOR CO ₂ Specification Sequestration in saline formation	EOR CO ₂ Specification Sequestration in saline formation

The net electrical output, steam cycle, fuel, and environmental requirements are the same in all cases. For Cases 5C and the LCL-C™ case, CO₂ matches the DOE quality specification for enhanced oil recovery. The LCL-C™ plant at 95% CO₂ capture exceeds the DOE's 90% capture goal.

The plant electrical performance is shown in **Table E-2**. The % Energy Penalty is defined by the following equation:

$$\% \text{ Energy Penalty} = \frac{[\text{net plant efficiency(w/ CO}_2 \text{ capture)} - \text{net plant efficiency(SCPC w/o CCS)}]}{\text{net plant efficiency(SCPC w/o CCS)}}$$

This comparison shows that the LCL-C™ CO₂ penalty is less than 9% compared to the equivalent oxy-fired penalty at 25%.

Table E-2 - Performance Comparison

		SCPC Case 11	Oxy-PC Case 5C	LCL-C™ Case 1
Reducer Pressure	atm			1
Gross Power Output	MW	580.4	785.9	649.7
Net Power Output	MW	550.0	548.7	550.0
Coal Flow	lb/hr	409,528	549,471	449,595
Main Steam Flow	lb/hr	3,669,421	4,863,464	4,114,272
Fuel Heat Input (HHV)	MMBtu/hr	4,778	6,410	5,245
Net Plant Efficiency (HHV)	%	39.28	29.20	35.78

Auxiliary Load Summary

GPU CO2 Compressor	kW		73,390	59,579
FD Fan (Oxidizer)	kW	1,660	1,500	19,557
ID Fan (Oxidizer)	kW	7,050	7,850	
Reducer ID Fan	kW			
Primary Air Fans	kW	1,300	1,170	
Circulating Water Pump	kW	4,730	6,200	5,966
Cooling Tower Fan	kW	2,440	3,620	3,530
Condensate Pump	kW	800	1,050	1,029
Ground Water Pumps	kW	480		538
Steam Turbine Total Auxiliary	kW	400	400	448
Coal Handling and Conveying	kW	440	500	483
Coal Crush and Feed	kW			104
Pulverizers	kW	2,780	3,740	
Limestone Crush and Feed	kW			1,000
Sorbent Handling & Reagent Preparation	kW	890	1,210	
Ash Handling	kW	530	720	582
NID™ w/o Fan	kW			100
Baghouse (Oxidizer)	kW	70	90	80
Wet FGD	kW	2,970	4,050	
Transformer Losses	kW	1,820	3,000	2,037
Miscellaneous Balance of Plant	kW	2,000	2,000	2,196
SCR	kW	50		
MDEA H2S Removal	kW			701
Claus Plant	kW			1,766
ASU Compressor/Auxiliaries	kW		126,680	
Pressurized dry feeder	kW			
Total Auxiliaries	kW	30,410	237,170	99,697
Total Auxiliaries w/o GPU	kW	30,410	163,780	40,117
Auxiliary Power (% of net)		5.5%	43.1%	18.1%
% Energy Penalty		0.0%	25.7%	8.9%

The supercritical pulverized coal power plants without CO₂ capture was based on Case 11 of a recent DOE study (**Reference 8**). The supercritical oxy-fired pulverized coal fired power plant with 90% CO₂ capture was based on Case 5C of another DOE study (**Reference 9**). All economics are adjusted to the same basis and are expressed in June 2011 dollars. Alstom's LCL-C™ economic study is published as **Reference 7**.

Overnight capital costs for the three plants are shown in **Table E-3**. The LCL-C™-based plant with CO₂ capture is about 15% more expensive than the PC plant without CO₂ capture, while the Oxy-fired plant with CO₂ capture is over 60% more expensive than the pc plant without capture on a capital cost basis.

Table E-3 - Overnight Capital Costs (June 2011 \$'s)

Case	Total Overnight Cost (Including Contingencies)		Total Overnight Cost Excluding Process Contingencies)	
	1000\$	\$/kW	1000\$	\$/kW
DOE Case SCPC w/o capture	1,348,407	2452	1,348,407	2452
DOE Case 5C Oxy SCPC	2,187,217	3977	2,125,620	3865
Case 1 LCL-C™ Transport	1,537,343	2795	1,533,278	2788

Figure E-8 compares the 1st year cost of electricity (COE) for the three alternatives. The yellow portion of the graphs represents the CO₂ transportation and storage (T&S). Comparing the COEs without the T&S shows that LCL-C™ with 95% CO₂ capture adds less than 20% ($97/81=19.7\%$) to the base case cost of electricity without CO₂ capture, easily achieving the DOE goal of less than 35% more than the base case with no CO₂ capture. In comparison, oxy-fired pc with 93% CO₂ Capture adds over 50% ($124/81=53\%$) to the base case COE.

With respect to the avoided cost of CO₂ capture, LCL-C™ avoided cost during the recent study is about \$25 per ton of CO₂ while that of the oxy-fired pc case is about \$80 per ton of CO₂.

In summary, both the recent and previous economic studies of LCL-C™ show it to have great potential for the lowest COE of all CO₂ capture technologies studied to date. The studies also indicate that LCL-C™ can achieve the DOE goals of producing >90% CO₂ capture at a COE which is less than 35% greater than the no-CO₂ capture case.

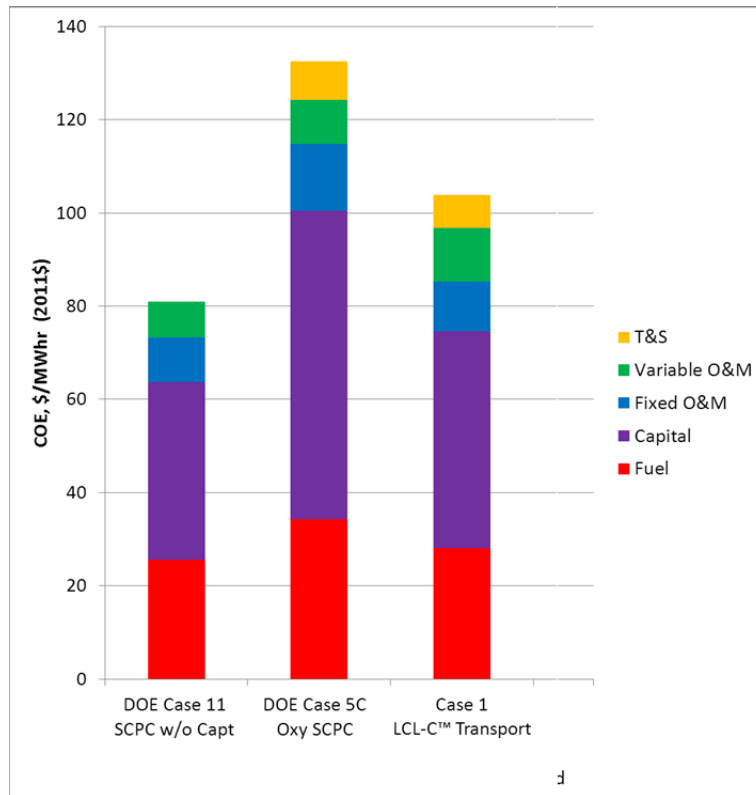


Figure E-8 – Cost of Electricity Breakdown

Conclusions

The project objectives of the LCL-C™ prototype testing project were to design and build a chemical looping prototype plant that includes all of the equipment that is required to operate the chemical looping plant in a fully integrated manner with all major systems in service and to conduct 40 hours of auto-thermal testing of the prototype.

Alstom designed an LCL-C™ prototype and built it around an existing 3 MWt Multi-Use Test Facility utilizing the existing infrastructure and support systems. Cold flow modeling tests were conducted in support of the design process and operation of the prototype facility. From 2011 to 2012, Alstom conducted series of shakedown tests and test campaigns leading up to achieving 12 hours of coal-fired auto-thermal operation. While not achieved during the Phase IVA performance period, the objective of extended (40 hours) autothermal operation was achieved in Alstom-sponsored testing effort immediately after the Phase IVA program.

During the successful auto-thermal tests, the 3 MWt Prototype was operated exclusively on coal feeding to the Reducer and with air feeding only to the Oxidizer. No supplemental fuel of any kind was required. Attaining auto-thermal performance necessarily required that all of the following factors are occurring:

- Coal is combusted in the Reducer to CO₂ via hot CaSO₄, forming CaS;

- CaS is burned in the Oxidizer forming hot CaSO₄ for the Reducer;
- LCL-C™ chemical looping reactions are self-sustaining;
- Long-term, stable operation is attained; and
- Both the Reducer and Oxidizer systems are properly sized and configured.

These results justify further testing which can be reasonably expected to provide a firm basis for a successful LCL-C™ demonstration plant. Chemical looping is a "game changing" technology in terms of overall efficiency and cost and is the lowest costing (cost of electricity) technical approach that Alstom has identified to date for coal power with carbon capture and sequestration.

Recommendations

It is important to note that although noteworthy as a first effort, the auto-thermal test performance is not perfect and there is plenty of work left to do towards optimizing the chemical looping process. These initial results are sufficient to show that Alstom's LCL-C™ concept is viable and that the prototype is correctly sized and configured. The results also indicate directions for improvement. Future prototype test work is recommended in the following areas:

- 40 hour auto-thermal run
- Sulfur control with Sorbent Activation Heat Exchanger and limestone testing
- Gas generation control and solids control
- Full load operation
- Condensing heat exchanger
- Automatic solids control
- Commercial startup and operation (full load / part load / load change / long runs / demo coal test)
- Maximum pressure tests

The 40 hour auto-thermal run was achieved after the conclusion of Phase IVA.

The cold flow model facility will continue to be a tool to analyze and visualize solids transport in Alstom's chemical looping process and to develop methods to transport, distribute and control solids flow.

Alstom has recently completed a 12 month technical-economic study of an LCL-C™ plant for CO₂ capture (DOE/NETL Cooperative Agreement No. DE-FE0009484). (Some of the preliminary results are included in this report.) The results will enable the DOE to compare Alstom's limestone chemical looping technology against other developments and against pressurized oxy technology. Alstom intends to continue testing at its 3 MWt prototype chemical looping facility in Windsor, CT based on the technical-economic study. Alstom seeks a 10 to 25 MWe (or 30 to 75 MWth) small-scale demonstration plant based on design guidelines and tools developed from the R&D efforts. This proposed plant is a prerequisite to a 100 MWe+ full commercial scale demonstration plant. Alstom's commercial vision of the technology is a 350 to 600 MWe ultra-supercritical CLC boiler and power plant.

1. Introduction

Since 2003, the Department of Energy (DOE/NETL) and Alstom Power Inc. (Alstom) have collaborated on developing an entirely new, ultra-clean, low cost, high efficiency power plant for the global power market. This new power plant concept is based on a hybrid combustion-gasification process utilizing high temperature chemical and thermal looping technology. The process consists of the oxidation, reduction, carbonation, and calcination of calcium-based compounds which chemically react with carbon-containing fuels such as coal, biomass, or opportunity fuels in two chemical loops and one thermal loop. In its most advanced configuration, this new concept offers the promise to become the technology link from today's Rankine cycle steam power plants to tomorrow's clean coal power plants. Based on previously performed engineering and economic studies at Alstom, such a process has been shown to have the potential to achieve near-zero CO₂ emissions, exceed all current environmental requirements and cost (in 1997 \$) less than \$800 per kilowatt without CO₂ capture (based on conventional power plants at \$1000/kW) and less than \$1000 per kilowatt including CO₂ capture for the world-wide power generation market. The Chemical Looping concept is exceptionally flexible. There are many potential commercial options. Alstom believes the chemical looping may first be employed near-term for advanced steam cycle applications for clean, high-efficiency coal fired boilers. Other options include producing hydrogen while capturing nearly all of the CO₂ from the fuel. The hydrogen, in turn, can be used for advanced boilers of all types or for advanced IGCC and/or fuel cell power plants of the future

In 2003 Alstom proposed and was awarded a contract to complete a two-year, two-phase program to develop and verify the high temperature chemical looping process at a small-scale process development facility. Alstom has completed Phase I and Phase II work under the DOE/NETL Cooperative Agreement No. DE-FC26-03NT4186. Additionally, Alstom successfully completed Phase III under a 1-½ year extension to the original two-year, two-phase program. The Phase 1 results have been reported in **Reference 1**, while the Phase 2 results have been reported in **Reference 2** and the Phase 3 results were reported in **Reference 3**.

1.1 Chemical Looping Overall Objective

The overall objective of the proposed work is to develop and verify the high temperature chemical and thermal looping process concept and to design, construct and demonstrate a pre-commercial demonstration version of this advanced system. In support of this objective, Alstom proposed an extension to the original 3 ½ year, three-phase program. This Phase IV of the program was divided into two additional parts, i.e., Phase IVA and Phase IVB to bring the Chemical Looping concept to commercial status.

The Objectives of the first three phases of the program were to obtain the necessary engineering information to design, build and test a viable **Prototype** of the commercial Chemical Looping concept. This work included: testing chemical reactions, determining chemical reaction rates, determining material handling properties,

developing solids transport and scale-up data and developing process control information. All of these objectives have been successfully met on-time and on-budget.

1.2 Phase IV Objective

The objective of **Phase IV** is for Alstom to design, build, operate and test a **Prototype**. The **Phase IV Prototype** was designed for the range of 500 to 1000 lb/hr of coal (about 3 MWt Max depending on fuel type). The prototype presents the first opportunity to develop the entire integrated process at a size which eliminates the requirement for external heating (as required for the PDU), i.e., able to operate under auto thermal conditions. This size also enables thorough investigation of solids transport and control. The objective of the **Prototype** is to develop sufficient engineering information to design, build and operate a successful commercial-sized demonstration plant at an existing electrical power plant. The size of the Prototype is sufficient for successful scale-up to a commercial-sized demonstration plant (25 to 100 MWe) in Phase V.

Phase IV work includes the prototype testing and development. The performance from the prototype was compared with the basis of the earlier economic analyses to determine if the earlier assumptions would still hold. The performance and economic implications are presented in Section 9 of this report. Section 9 also includes results from a new economic study of LCL-C™-based power plants done for the US DOE/NETL (**Reference 7**) which compares Alstom's LCL-C™ to a supercritical pulverized coal power plants without CO₂ capture and to a supercritical oxy-fired pulverized coal fired power plant with 90% CO₂ capture. All three plants are designed to produce 550 MWnet.

Supplementary cold flow tests were performed. Planning for the demonstration plant will also be performed including reviewing demonstration sites, finding sponsors, contacting A&E's, and addressing other demonstration plant requirements. This report describes the results of the prototype construction and testing and includes the updated demonstration and commercialization plans. Phase IV is divided into two parts Phase IVA and Phase IVB. This report covers the work done in Phase IVA.

1.2.1 Phase IVA

Phase IVA includes about ½ of the required prototype effort; specifically, EPC and a limited amount of initial testing. Phase IVA project was done in two budget periods that correspond to the DOE's fiscal year. The objective of Budget Period 1 (BP1) is to design and complete a substantial portion of the Prototype EPC. The objective of Budget Period 2 (BP2) is to complete the Prototype and perform initial testing.

1.2.2 Phase IVB

The objective of Phase IVB was to perform parametric testing of the prototype to obtain operational and design information to enable Alstom to design a chemical looping

demonstration plant. The scope of this Phase IVB is now planned for a separate follow on program.

2. Chemical Looping Options

The chemical Looping concept represents a new high temperature process whereby limestone derived calcium based compounds are “looped” in a regenerative manner to extract oxygen from air for purposes of combustion (**Figure 2-1**) or gasification and then to extract CO₂ from reformed syngas for purposes of hydrogen production (**Figure 2-2**). Surplus heat from the exothermic oxidation reactions is transferred by the thermal loop of solids to satisfy the energy requirements for the endothermic reduction reaction. The thermal looping can employ either chemically inert solids (e.g. Bauxite) or (more likely) excess calcium solids.

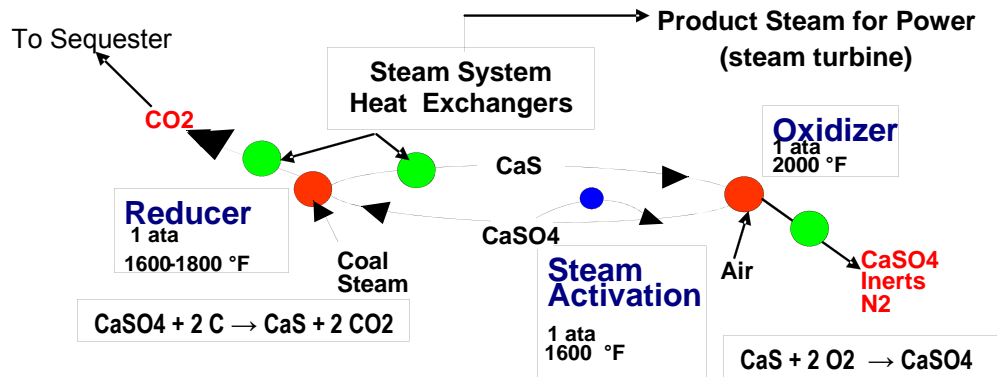


Figure 2-1 – Chemical Looping Combustion with CO₂ Capture

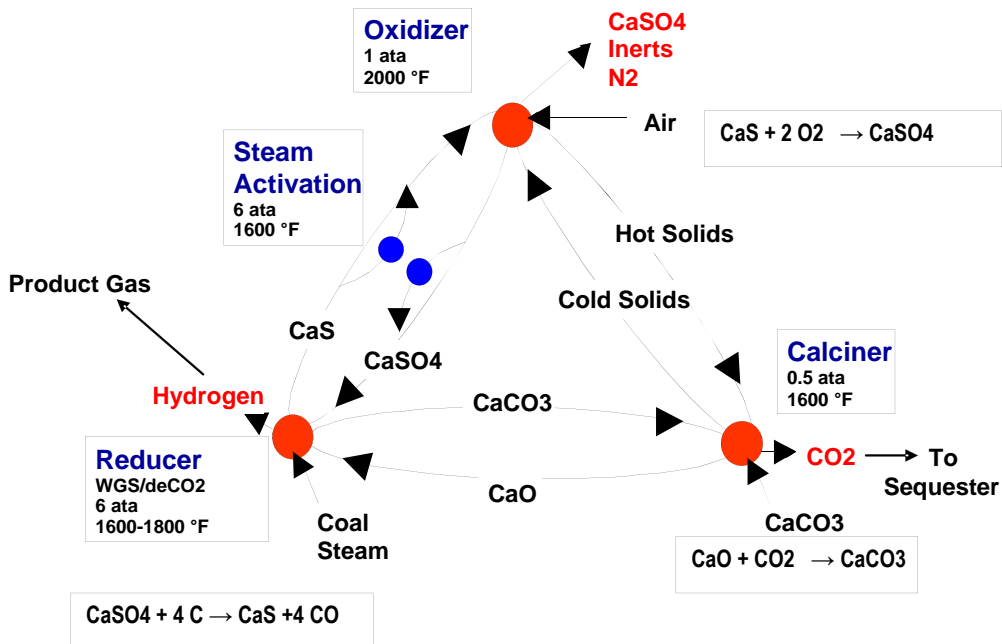


Figure 2-2 - Chemical Looping Hybrid Gasification\Combustion with CO₂ Capture

In reference to **Figure 2-1**, the exothermic Oxidizer reactor oxidizes CaS to form CaSO₄ using pre-heated air: $\text{CaS} + 2\text{O}_2 \rightarrow \text{CaSO}_4$. The hot, oxygen rich CaSO₄ is transported to the Reducer reactor where coal is introduced and strips the oxygen from the CaSO₄ to form CaS (solid) plus pure CO₂ (gas). The CO₂ gas product is available for use or sequestration: $\text{CaSO}_4 + 2\text{C} \rightarrow \text{CaS} + 2\text{CO}_2$. By decreasing the air-to-coal ratio, this system can produce a syngas of carbon monoxide (CO) and hydrogen (H₂). The CaS is then transported back to the Oxidizer to repeat the process (i.e. regenerate) and thus completes the “loop”. Fresh CaCO₃ is added to the system to capture fuel bound sulfur and form CaSO₄. The excess CaSO₄ must be drained from the Reducer to maintain the mass balance. The continuous requirement to capture fuel-bound sulfur to form CaSO₄ regenerates calcium compounds in the loop to keep the chemical reactivity high. The heat balance between the exothermic Oxidizer and the endothermic Reducer can be satisfied by recirculation of solid particles between the reactors.

The CaS / CaSO₄ loop can be configured in either one of two freestanding chemical processes. When the amount of oxygen delivered is sufficiently high to burn all the coal, the loop becomes a combustion system. The end products are pure CO₂ for sequestration and steam for electric power. The steam is generated by heat from the Oxidizer (**Figure 2-1**). Alstom considers this option to be the early commercial application.

If in **Figure 2-1**, the amount of air delivered to the coal is only sufficient for partial oxidation, then the end product is a sulfur free syngas consisting mainly of CO and H₂

(up to about 300 Btu/ft³, dry, HHV basis) suitable for a gas turbine combined cycle. Cold gas efficiency can exceed 85%.

Figure 2-2 shows the modification of the combustion loop to the syngas loop from **Figure 2-1** with the addition of a calciner and the lime (CaO) / calcium carbonate (CaCO₃) loop. In this modification, the Reducer uses steam to shift the CO rich syngas to H₂ and CO₂. Lime (CaO) is added to the Reducer to capture the CO₂ as CaCO₃, thereby producing a hydrogen rich stream (about 300 Btu/ft³, dry, HHV basis) suitable for an advanced steam cycle, gas turbine combined cycle, fuel cell cycle, etc. Cold gas efficiency can exceed 85%. The CaCO₃ is drained from the shift reactor and sent to the calciner where it is mixed with hot solids from the Oxidizer to drive off CO₂ gas and to regenerate CaO. The CaO is then returned to the shift reactor to capture more CO₂, completing the loop. The CO₂ capture reaction is an exothermic reaction that drives the gasification reaction. The calciner is a high temperature endothermic reactor that receives its heat in the form of hot solids from the Oxidizer. Hot CaSO₄ / CaO (or inert bauxite) from the Oxidizer can be used for this purpose. The need to capture sulfur and dispose of spent CaSO₄ keeps both loops well stocked with chemically fresh "looping material."

Chemical Looping Product Options

Alstom's Chemical Looping process can be deployed in three options (**Figures 2-3, 2-4 and 2-5**).

Option1 - In **Figure 2-3**, the limestone based sorbent (CaS) is burned in the circulating fluidized bed Oxidizer/Boiler (at about 1800 to 2000 °F) to produce hot CaSO₄. Steam is also generated as in a CFB boiler. CaSO₄ is used in the circulating fluidized bed (CFB) Reducer to combust the coal at a temperature range of 1600 to 1800 °F to form CO₂ for use or sequestration. The CaS is formed when the limestone captures the sulfur in the coal. This option can be employed when CO₂ capture is required. It can be used with conventional steam cycles – both sub-critical and supercritical steam conditions. This equipment will be smaller than Alstom's traditional CFB boiler for a given steam generation because of rapid reactions and higher gas velocities in the two reactors. The process requires about 85% of the materials of construction used in today's CFBs. This configuration separates CO₂ from the nitrogen flue gas. Such a plant could be deployed in the relatively near term at a capital cost near that of a CFB. The use of modified, but essentially commercial, CFB technology provides equipment that is readily recognizable in the power industry, making commercial acceptance easier to achieve.

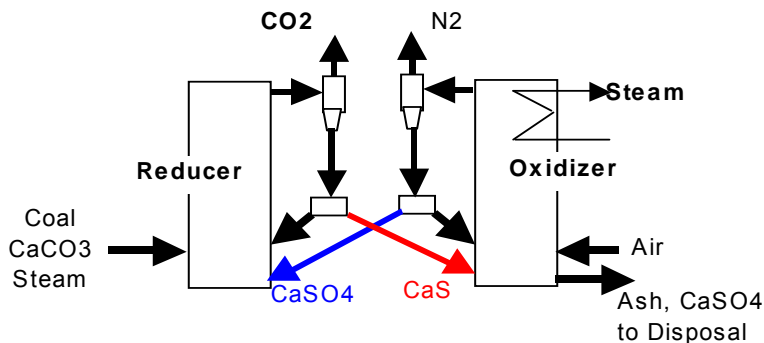


Figure 2-3 - Option 1 – Chemical Looping Combustion with CO₂ Capture

Option 2 - The second option is shown in **Figure 2-4**. The major difference between Option 1 and Option 2 is that the air-to-coal ratio for Option 2 is about 1/4th that of Option 1's. Because of this lower air-to-coal ratio, medium-Btu syngas (CO and H₂) is produced instead of CO₂. Since less air is required, the equipment for this option is smaller than that of Option 1. Less than 2/3rd of typical CFB materials are required for this option.

This option is adaptable to more power cycles (e.g. advanced steam cycles, combined cycles, fuel cell, etc.) than Option 1. Although, CO₂ capture is not inherently accomplished with Option 2, it can be added downstream of the Chemical Looping system (as is the case with conventional IGCC) by including water gas shift reactors to shift the CO via steam to CO₂ and H₂ with subsequent removal of the CO₂ via scrubbing (via ammine, ammonia, etc.) Compared with conventional IGCC with CO₂ capture, the Option 2 approach avoids the cost and efficiency penalty of an oxygen plant.

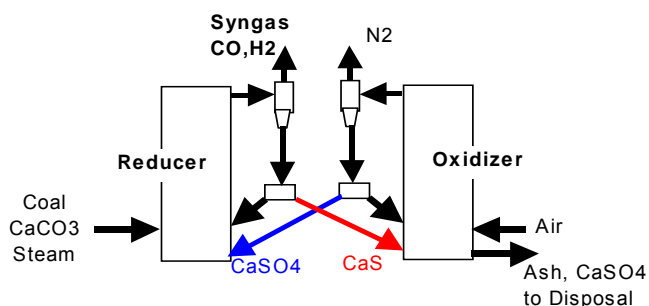


Figure 2-4 - Option 2 – Chemical Looping Gasification with Syngas Production and with CO₂ Capture

Option 3 -The third option is shown in **Figure 2-5**. This option operates at the same air-to-coal ratio as Option 2, but more steam is used in order to form mostly hydrogen and CO₂ rather than syngas. The CO₂ is captured by the lime (CaO generated from the limestone) and liberated in the Calciner using hot solids from the Oxidizer to supply the heat of reaction. The pure CO₂ can be used or sequestered. This equipment is about the same size as Option 2, requiring about 2/3rd of typical CFB construction

materials. Option 3 provides the highest net plant efficiency of all of the Chemical Looping options and can be used for clean, high efficient, low cost power plant applications or for hydrogen production. As this concept requires the operation of more loops which are inter-related, it will need additional development and can be considered a longer term option. The Phase IV Prototype will be configured as Option 3, but will be flexible enough to test Option 1 and Option 2 as well.

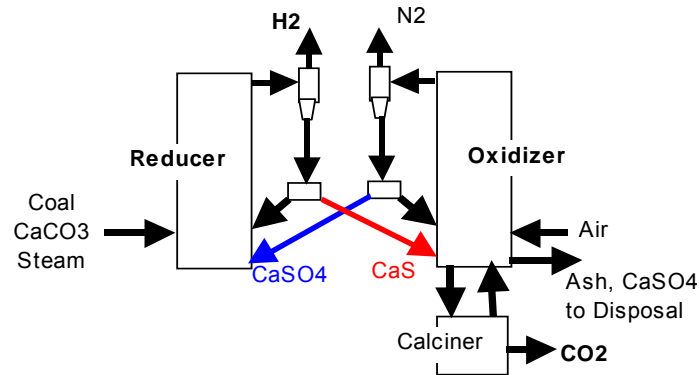


Figure 2-5 - Option 3 – Chemical Looping Gasification with CO₂ Capture and H₂ Production

Chemical Looping Applications

Chemical Looping has been under development at Alstom since 1997. Since that time significant progress has been achieved in the development of the technology and engineering/commercialization studies have helped to identify customer requirements and applications. During the course of this work, Alstom has come to realize that the application of Chemical Looping is more flexible from a product standpoint than originally envisioned. Some of this flexibility is shown in **Table 2-1**.

Table 2-1 – Chemical Looping Applications

OPTION	SUB OPTION	PRODUCTS	CO2 CAPTURE	APPLICATIONS
1	-	CO2/Steam	Yes	Coal-fired Advanced Steam Cycles
2	A	SynGas	No	Feedstock for Transportation/Liquid Fuels Feedstock for Chemical Applications Industrial Applications
2	B (Note1)	H ₂ /CO ₂	Yes	Coal-fired Advanced Steam Cycles Coal-fired Advanced Gas Turbine Combined Cycles Coal-fired Advanced Cycles Industrial/Oil Refinery/Petrochemical Applications
3	-	H ₂ /CO ₂	Yes	Coal-fired Advanced Steam Cycles Coal-fired Advanced Gas Turbine Combined Cycles Coal-fired Advanced Cycles Industrial/Oil Refinery/Petrochemical Applications

NOTE: 1.Additional Water-Gas Shift System and CO₂ Scrubber is required.

Table 2-1 summarizes the chemical looping product options described in the last sections along with their associated product streams. Also shown are some of the specific uses (i.e. applications) of the particular product option. The wide range of application shows the flexibility of Alstom's Chemical Looping Technology. Each product option is capable of capturing nearly all of the CO₂ from the coal (or any other carbonaceous fuel). Applications can serve nearly every major industrial market sector. Alstom's Chemical Looping provides the lowest cost option for capturing CO₂ from coal-fired power plants. Concerning power plant applications, **Table 2-2** shows that Chemical Looping can be applied to advanced steam cycles, to advanced gas turbine combined cycles and (in the future) to fuel cell power cycles.

Table 2-1 also shows that product gas from Chemical Looping can be used in petrochemical/oil refinery applications to provide, for example, hydrogen for increasing refinery yields and can be specifically tailored to provide a perfect feedstock for producing Fischer-Tropsch or other liquid fuels from coal (or any other carbonaceous fuel such as biomass, waste or opportunity fuels).

Table 2-2 shows potential performance and range of usage for some of the applications in **Table 2-1**.

Table 2-2 – Performance of Chemical Looping Applications

Index	Market	Chem Looping Application	Chem Looping Option	Power Cycle	Power Plant Efficiency (% , HHV basis)		Plant Efficiency Ratio (2)	Basis
					NO CO ₂ Capture	95% CO ₂ Capture		
1	Coal Power	Steam Power Plant	n/a	Sub-Critical Steam (1)	36			Reference 4
2	Coal Power	Partial CO ₂ Capture	Option 1	Sub-Critical Steam (1)	36	31	0.86	Reference 4
3	Coal Power	PC/CFB Retrofit	Option 3	Supercritical Steam (1)	42	34	0.80	Preliminary
4	Coal Power	IGCC	GE/Texaco (Quench)	Combined	35	27	0.79	Reference 4
5	Coal Power	Turbo-Charged Boiler	Option 3	UltraSupercritical Steam (1)	45+	41+	0.91	Preliminary
6	Coal Power	Chem Looping CC	Option 3	Combined	42	37	0.88	Reference 4
7	Coal Power	Fuel Cell	Option 3	Combined	60+	60+	0.91+	Preliminary

Notes: 1. Also applicable to other steam cycles.

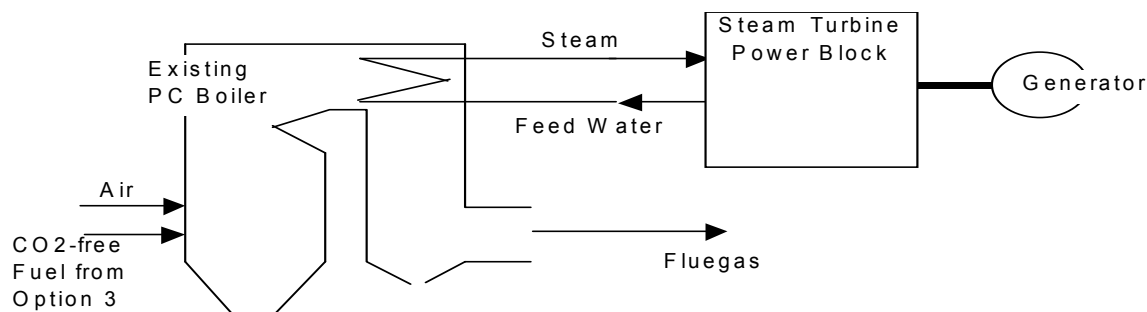
2. This column equals the plant efficiency with 95% CO₂ capture divided by the plant efficiency without CO₂ capture.

Referring to **Table 2-2**, Index 1 and 4 represent the performance for conventional steam plants and IGCC, respectively from **Reference 4**, and are included for comparative purposes.

The concept of Partial CO₂ Capture for power plants is shown in Index 2. The sixth column from the left shows the plant efficiency with no CO₂ compression/liquefaction while the seventh column shows plant efficiency with nearly all of the CO₂ being compressed/liquefied. Partial CO₂ Capture/Sequestration would fall somewhere in between. For example, the efficiency at 50% CO₂ Capture/Sequestration would be about 33.5%. The value of this Partial CO₂ Capture approach might be that for some critical period of time, if allowed by the plant permit, more power could be made available for use by customers by reducing the CO₂ capture/sequestration rate. In this example, reducing the CO₂ capture rate from 95% to 50% would provide about 7 % more power at full load coal flow. Of course, other partial capture scenarios are possible as well. Although this option is shown for a sub-critical steam cycle, it is applicable for high efficiency supercritical cycle. For example, with a supercritical cycle (e.g. steam conditions of 3915psi/1085°F/1148°F/2.5in.Hg), the efficiency would be about 42% (HHV basis) without CO₂ capture (**Reference 4**) and with 95% capture would be 86% of this value (36%). These performance examples compete well against both conventional steam plants (Index 1) and IGCC (Index 4).

Index 3 indicates how Chemical Looping Option 3 can provide a retrofit alternative for existing Pulverized Coal-fired (PC) and CFB steam power plants. Since this option produces a CO₂-free fuel (hydrogen), it can be used to provide boiler fuel for existing PC and CFB Boilers. **Figure 2-6** shows how CO₂-free hydrogen from Chemical Looping Option 3 can be used to re-power the existing boiler when CO₂ capture is required. For current day PC and CFB units, this concept could be implemented if sufficient space for Option 3 were available fairly near the PC boiler's location. When CO₂ capture is required, the Option 3 system can be added for about 20-25% of the original power plant cost. The 95% CO₂ captured by the Chemical Looping system can be put to use (e.g. for enhanced oil recovery, etc.) or sequestered. After conversion the system would retain 80% of the original plant's net power. This same approach is

compatible with future ultra-supercritical steam cycles (e.g. steam conditions of 5075 psi/1292°F/1328°F/2.5in.Hg) with efficiencies of about 43.5% (HHV basis) without CO₂ capture (**Reference 4**) and about 35% with 95% CO₂ capture.

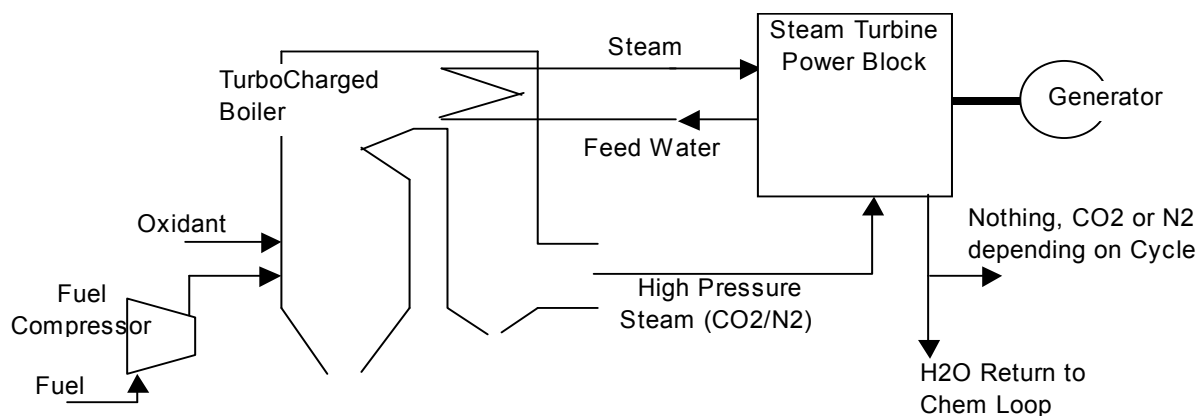


Boiler Fuel:

1. Initial boiler fuel is coal,
2. if CO₂ capture is required, Chem Loop hybrid gasification/combustion is installed and CO₂-free gas (H₂) is fired in the existing boiler.

Figure 2-6 – Retrofit CO₂-Capture Pulverized Coal-fired Power Plant Concept

Table 2-2 shows Chemical Looping applications for an advanced steam cycle concept (Index 5) and for a combined cycle (Index 4). The ultra-supercritical (USC) turbo-charged boiler concept (Index 5) is shown in **Figure 2-7**.



Boiler Fuel: Gas from Chemical Looping Hybrid Gasifier/Combustor (**Option 3**).

Oxidant: Air or Hot CaSO₄ from integration with Chemical Looping Gasifier.

Figure 2-7 – Chemical Looping Option 3 Turbocharged Boiler Concept

In this concept, a pressurized USC boiler is integrated with Chemical Looping Option 3 which provides the source of pressurized CO₂-free fuel (hydrogen) and oxidant (CaSO₄). High-pressure steam is produced by the reaction of hot CaSO₄ and hydrogen. This high-pressure steam is used by the steam turbine to make additional power.

Table 2-2, Index 6 shows Chemical Looping **Option 3** used in an IGCC system. This concept provides a coal-to-hydrogen chemical process that is more efficient than an oxygen blown IGCC (**Table 2-2**, Index 4). The absence of parasitic power of the oxygen plant and heat losses due to water-gas shift cooling and low-temperature sulfur recovery more than offset the power for the required syngas compressor in the chemical looping process. Dry solids will flow into and out of the reactor from both loops at a pressure close to atmospheric. The sensible heat in the gaseous N₂, CO₂ and H₂ streams is recovered by heating the air required by the Oxidizer. Finally, particulate clean-up of all streams is done at cold conditions without the need of high temperature ceramic filters or the heat losses of a quench column.

As a final comment, **Table 2-2**, Index 7 shows Chemical Looping potential performance when supplying hydrogen to future Fuel Cell cycles.

Alstom's Perspective on Chemical Looping

Over 40% of the world's installed power boilers are of Alstom design. As the world's leading supplier of coal-fired power plants, a major part of our current business is supplying steam generation systems for the power industry. This factor combined with the current regulatory uncertainty in the power market means the flexibility of Chemical Looping with respect to the applications listed in **Tables 2-1** and **2-2**, is extremely important to Alstom.

From our customers' perspective, given the uncertainty of future CO₂ regulation, our customers are asking how Alstom can provide steam generators with CO₂ capture capability (both new and retrofit) so that they can be assured that their generating plant projects will move ahead and will not be made obsolete by future CO₂ regulatory requirements. Later, when the CO₂ regulatory landscape is more discernible, we expect that our customers' emphasis will shift to more advanced applications with higher efficiencies.

Accordingly, Alstom sees Chemical Looping as a breakthrough technology leading to the lowest cost coal-based power with CO₂ Capture. We expect that the first step commercially will be Chemical Looping applied to steam power plants (supercritical and ultra-supercritical cycles) according to Option 1 (**Figure 2-3**). Following that, we expect that the hydrogen option (Option 3 in **Figure 2-5**) will be next, perhaps in Industrial applications (**Table 2-1**) and later in advanced power plant applications (**Table 2-1**).

Considering the above factors, Alstom intends to concentrate the Chemical Looping development toward chemical looping combustion as a way to provide a cost effective, CO₂ capture options to the company's PC and CFB customers in the relatively near term. Accordingly, Alstom intends to develop Chemical Looping Option 1 (Combustion) through the Prototype stage, as the option which is most applicable to our customer's time-phased requirements. With respect to Demonstration, the most suitable

demonstration plant option can be chosen based on commercial considerations as part of the next phase program.

3. Chemical Looping History

3.1 Alstom's Background in Gasification Technology

Alstom has significant experience in studying and developing advanced combustion and gasification processes for coal based power generation. In the time period 1974-1981, the company was involved in the development of a coal gasification process aimed at producing a 140 BTU/SCF gas. The process was air blown, but also suited for O₂ blown technique. A 120-ton per day pilot plant (equivalent to 12-15 MW) was built and operated for 3.5 years, **Figure 3-1**.



Figure 3-1 - The Windsor Connecticut Coal Gasification Pilot Plant.

The DOE selected this technology for two demonstration projects:

- 150 MW Gulf States Utilities (1980-1982).
- 65 MW IGCC for CWL&P (City Water Power and Light) in Springfield, Illinois (1990-1995).

In addition, the technology was selected as a Japanese National Project to build a 200TPD (equivalent to ~20 MW) pilot plant. The project was initiated in 1985 and successfully completed in 1995. Further plans for commercialization continue in Japan.

In the mid-80's, Alstom pioneered the introduction of CFB (Circulating Fluid Bed) technology in the US. Sizes have increased from 15 MW in the 80s to nearly 400 MW today. The company is currently developing a large scale 600MWe+ ultra-supercritical CFB unit. With the aim to advance Alstom's CFB technology further, the company initiated a new effort in the gasification field in 1997. The objective was to develop a process concept that can produce syngas for gas turbines without an O₂ plant. This process, Hot Solids Gasification, would use a solids recycle loop to transfer the necessary O₂ to the system. The solids could be oxidized using air in an Oxidizer step and separately the oxygen from this oxidized material would be used to oxidize the fuel - chemical looping. The chemical reactions of FeO to Fe₂O₃ and CaS to CaSO₄ were studied in laboratory TGA (Thermo Gravimetric Analyzer) and drop tube tests. The measured kinetic reaction rates for the CaS/CaSO₄ loop were used in a design study in 1998. Calcium was used because it can carry more O₂ per pound than metal oxides and it is more readily available with limestone as a precursor. The study showed that, with this technology, a coal-based power plant can be designed significantly smaller than a state of the art PC fired boiler, illustrated in **Figure 3-2**.

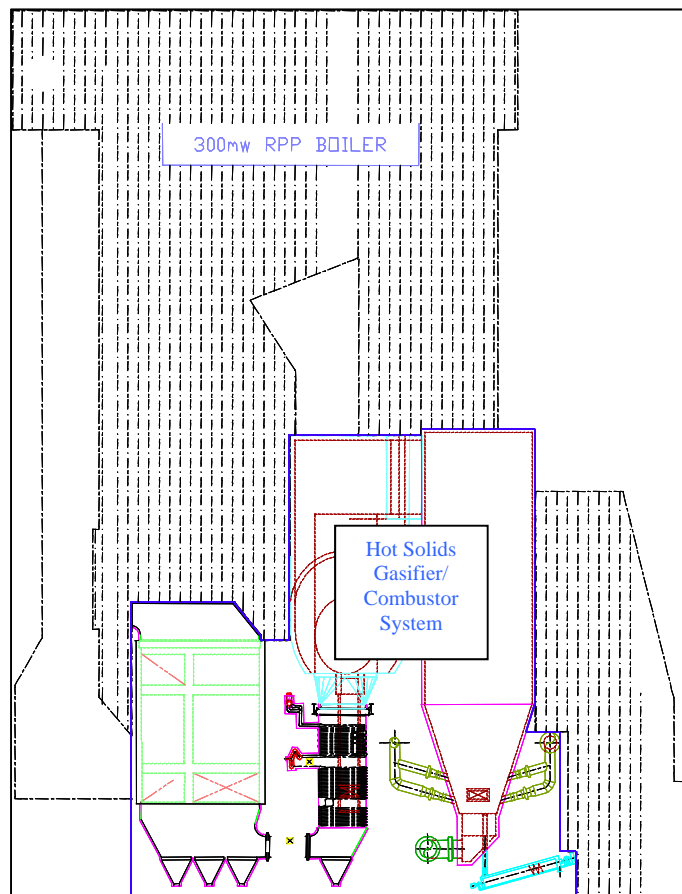


Figure 3-2 - Process Size Comparison between a PC Fired Boiler and a Hot Solids Gasifier/Combustor System.

Greenhouse Gas Economic Study

Under the U.S. DOE NETL Cooperative Agreement No. DE-FC26-01NT41146, Alstom carried out a project entitled "Greenhouse Gas Emissions Control by Oxygen Firing in Circulating Fluidized Bed Boilers" (**Reference 4**). As part of this project, a comprehensive conceptual design study was done comparing the technical feasibility and economics for several alternative process concepts involving control of CO₂ emissions. Plant types included in this study were coal combustion and coal gasification type power plants. Comparisons of plant performance, investment costs, and economics were developed. The complete results of the study are reported in the Phase I Topical Report (**Reference 1**). In that study two chemical looping based plants with CO₂ capture were analyzed and were evaluated very favorably as compared to other CO₂ capture options studied. Costs used for all of these studies are accurate to within 25% on an absolute basis, but are more accurate on a relative basis and provide a firm basis for economically comparing power plant alternatives.

A total of thirteen (13) Greenfield case studies, listed below, were analyzed in this evaluation. The thirteen cases were subdivided into three groups. Seven of the cases were grouped as Coal Combustion cases, four were IGCC cases, and two were Chemical Looping gasification cases. One Combustion case, two IGCC cases and one Chemical Looping gasification case were analyzed without CO₂ capture. These cases without CO₂ capture represent Base Cases for comparison with the respective CO₂ capture cases. Inclusion of the Base Cases allows accurate quantification of the impact of CO₂ capture and gas processing on plant efficiency, cost, and cost of electricity. CO₂ mitigation costs (\$/Ton of CO₂ avoided) were also calculated relative to the appropriate Base Case. Within each technology group, the order of the various cases roughly represents increasing levels of technology development complexity (i.e., within the combustion cases with CO₂ capture, Cases-6 & -7 would require the most development and Case-2 the least).

- Coal Combustion Cases:
 - Case-1: Built and operating Air Fired Circulating Fluidized Bed (CFB) without CO₂ Capture (Base Case for Comparison to Cases 2-7)
 - Case-2: Oxygen Fired CFB with CO₂ Capture (trace O₂ and SO₂ removed for EOR)
 - Case-3: Oxygen Fired CFB with CO₂ Capture (sequestration-only, less pure than Case -2)
 - Case-4: Oxygen Fired Circulating Moving Bed (CMB) with CO₂ Capture (advanced boiler concept)
 - Case-5: Air Fired CMB with CO₂ Capture utilizing Regenerative Carbonate Process
 - Case-6: Oxygen Fired CMB with Oxygen Transport Membrane (OTM) and CO₂ Capture
 - Case-7: Indirect Combustion of Coal via Chemical Looping and CO₂ Capture

- IGCC Cases:
 - Case-8: Built and Operating Present Day IGCC without CO₂ Capture (Base Case for Comparison with Case-9)
 - Case-9: Built and Operating Present Day IGCC with shift reaction and CO₂ Capture added
 - Case-10: Commercially Offered Future IGCC without CO₂ Capture (Base Case for Comparison with Case-11)
 - Case-11: Commercially Offered Future IGCC with shift reaction and CO₂ Capture
- Chemical Looping Gasification Cases:
 - Case-12: Indirect Gasification of Coal via Chemical Looping (Base Case for comparison to Case-13)
 - Case-13: Indirect Gasification of Coal and CO₂ Capture via Chemical Looping

All plants were designed for the identical coal and limestone analyses, ambient conditions, site conditions, etc. such that each case study provided results which are directly comparable, on a common basis, to all other cases analyzed within this work. The ambient conditions used for all material and energy balances were based on the standard American Boiler Manufacturers Association (ABMA) atmospheric conditions (i.e. 80 °F, 14.7 psia, 60 percent relative humidity).

Performance results are shown in **Figure 3-3**. Case-1 is the base case without CO₂ removal. With CO₂ removal all of the combustion cases incur significant heat rate penalties, but Case-7 had the lowest penalty (Chemical Looping Combustion).

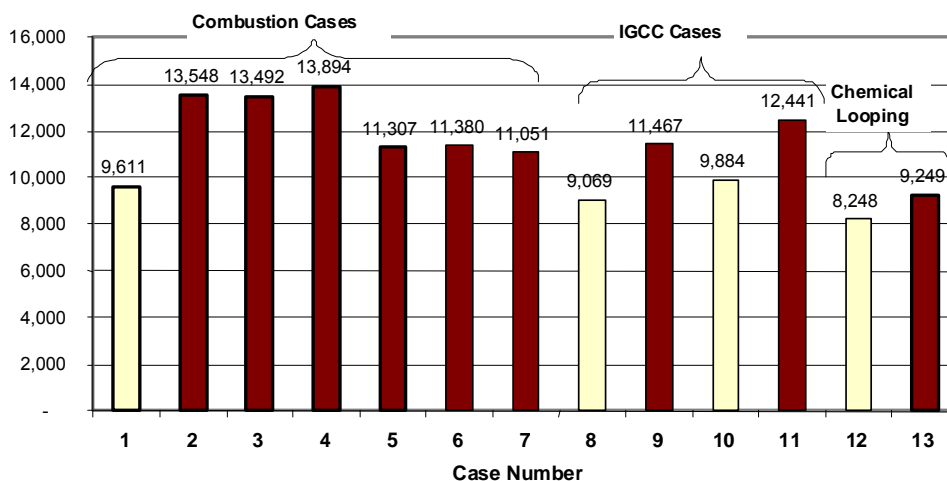


Figure 3-3 - Greenhouse Gas Project Results – Efficiency.

Case-7, the chemical looping combustion case with CO₂ capture, shows the highest net plant thermal efficiency at about 30.9 percent. For this case, the efficiency reduction is almost entirely due to the power required for the compression and

liquefaction of the captured CO₂. For this case there is essentially no energy penalty associated with the capture of CO₂ other than the energy required to recirculate the solids between the Oxidizer and Reducer vessels.

CO₂ capture Cases-9, -11 and -13 all incur significant power output degradation as compared to their Base Case counterparts (Cases-8, -10, and -12), due to the heavy demands of auxiliary power for gas processing which includes CO₂ compression. The efficiency differences among these cases are a reflection of the differences in gasification processes, CO₂ capture processes, and auxiliary power requirements.

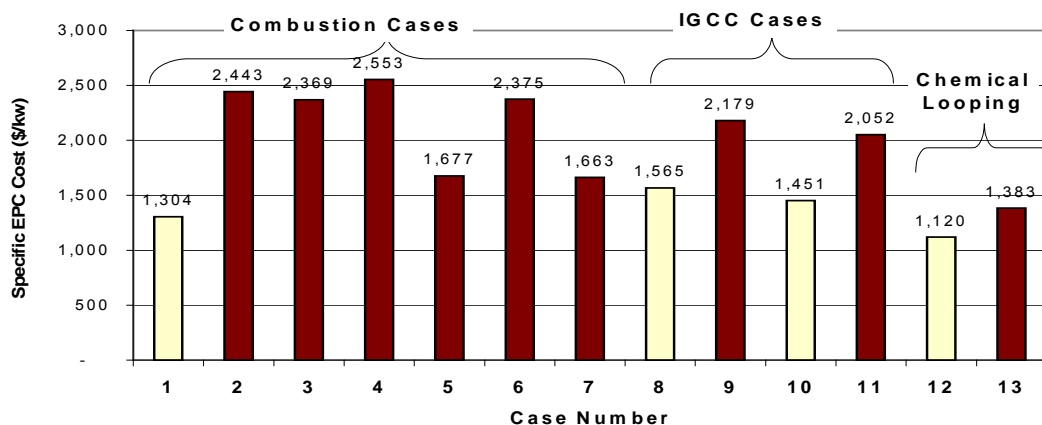


Figure 3-4 - Greenhouse Gas Project Results – EPC Costs

The Chemical Looping gasification cases (Cases-12 and -13) were found to be more efficient both with and without CO₂ capture (36.9 and 41.4 percent HHV, respectively) than all other CO₂ control cases including the comparable Texaco based IGCC cases. Case-12 was 10 and 20 percent more efficient than Cases-8 and -10 respectively, while Case-13 was 24 and 34 percent more efficient than Cases-9 and -11 respectively.

The capital cost for the Base Case without CO₂ capture was 1,304 \$/kW (2003 \$). The plant investment cost range for the remaining combustion cases (Cases-2 thru -7) with CO₂ capture was from about 1,660 to 2,550 \$/kW. Case-7 (Chemical Looping Combustion) was found to be the lowest cost of the combustion based capture cases (1,663 \$/kW) followed closely by Case-5, the Regenerative Carbonate Process, at 1,677 \$/kW. Cases-2, -3, and -4, all variants of the cryogenic based oxygen fired process, were found to have significantly higher EPC (Engineered, Procured and Constructed) costs (2,370 – 2,550 \$/kW). Case-3, which used a simplified Gas Processing System (drying and compression only), showed a savings of about 74 \$/kW or about 3 percent as compared to Case-2. Case-6 (oxygen fired via an advanced OTM system) was slightly less costly than the comparable cryogenic case at about 2,375 \$/kW, a savings of about 7 percent as compared to Case 4.

The plant investment costs (EPC basis) for the Texaco Base Cases (Cases-8 and -10) without CO₂ capture was 1,565 and 1,451 \$/kW. The plant investment costs for the corresponding cases (Cases-9 and -11) with CO₂ capture were 2,179 to 2,052 \$/kW respectively. Case-13 (Chemical Looping gasification) was found to be the lowest cost of the capture cases (1,383 \$/kW) as compared to Case-12 without CO₂ capture at 1,120 \$/kW, a 23.5% differential.

Figure 3-5 summarizes the economic results for all thirteen cases in this study. It shows levelized cost of electricity for all cases.

For cases with CO₂ capture, Case-13, Chemical Looping gasification, represents the best of the cases studied based on both levelized COE (Cost of Electricity) and CO₂ mitigation cost evaluation criteria. Case-7, Chemical Looping combustion, and Case-5, the regenerative carbonate process, were about 12 and 14 percent higher than Case-13 with respect to levelized COE. These three cases showed significant COE advantages as compared to all other capture cases in this study.

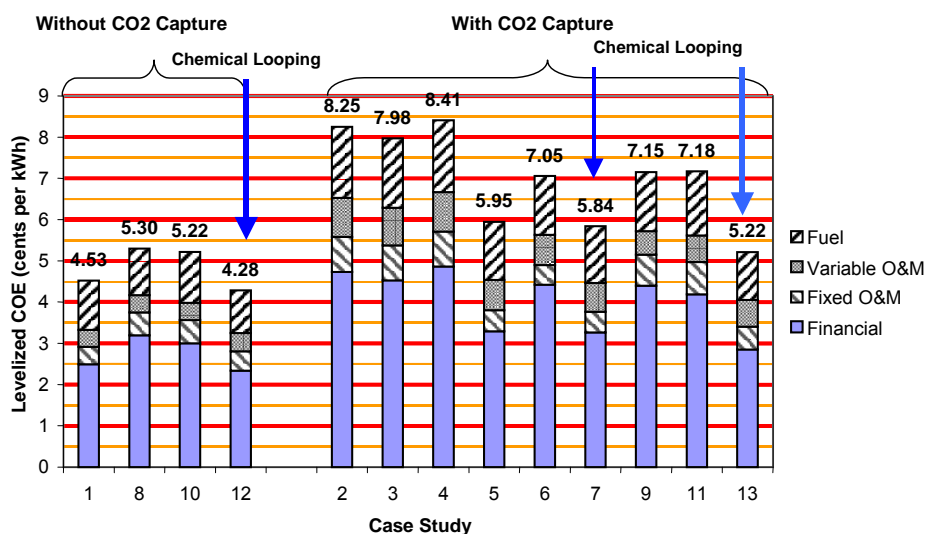


Figure 3-5 – Greenhouse Gas Report - Cost of Electricity

3.2 Results from Phases I, II and III

Before the contract started, in a preliminary phase (Phase 0) Alstom funded and built the required small-scale pilot facility (Process Development Unit, PDU) at its Power Plant Laboratories in Windsor, Connecticut. Construction was completed in calendar year 2003.

The objective for Phase I was to develop the indirect combustion loop with CO₂ separation, and also syngas production from coal with the calcium sulfide (CaS) / calcium sulfate (CaSO₄) loop utilizing the PDU facility. The results of Phase I were

reported in **Reference 1**, "Hybrid Combustion-Gasification Chemical Looping Coal Power Development Technology Development Phase I Report"

The objective for Phase II was to develop the carbonate loop – lime (CaO) / calcium carbonate (CaCO₃) loop, integrate it with the gasification loop from Phase I, and ultimately demonstrate the feasibility of hydrogen production from the combined loops. The results of this program were reported in **Reference 2**, "Hybrid Combustion-Gasification Chemical Looping Coal Power Development Technology Development Phase II Report"

The objective of Phase III was to operate the pilot plant to obtain enough engineering information to design a prototype of the commercial Chemical Looping concept. The activities include modifications to the Phase II Chemical Looping PDU, solids transportation studies, control and instrumentation studies and additional cold flow modeling.

A small pilot plant was constructed by modifying the existing Chemical looping PDU. All of the existing capabilities were retained and additional capabilities were added. Automatic controls were added to the seal pot control valve (SPCV) gas feed lines. A second vacuum pump, scrubber and stack were added to simulate the control action required in the commercial concept where separate outlet streams must be controlled independently because they cannot be mixed. In addition, several upgrades and repairs were made to the PDU including a new gas burner, chamber pots (solids knock out cans), spray nozzles in the heat exchangers, gas outlet controls and an upgraded control system computer and software.

The cold flow model designed and built for the Phase I and Phase II tests was used extensively in Phase III to measure the transport characteristics of the solid material used in the tests. The plastic model was also used to visualize the flow characteristics of the transporting solids. The 15-ft cold flow model was modified by adding a second identical loop to conduct dual loop testing.

A forty-foot tall plastic model was constructed for use in Phase III. This model was used to test higher solids flow rates with a taller static solids seal.

Tests were conducted on both cold flow models to characterize solids transport flow and to provide information for developing an automatic control system for the PDU. Results from the cold flow modeling also provided design information for the prototype, and helped analyze scale-up issues.

The solids flow characteristics of each component of the chemical looping reactors and transport piping were investigated to determine pressure drop versus solids mass flow relations, solids flow choking conditions, fluidizing requirements, grease air methods and other important data.

Results from the cold flow testing were used to make design improvements to system components. Testing of the new designs was successful. An improved SPCV

was able to smooth the solids flow pulses. The cyclone demonstrated 99.9954% efficiency and captured all particles above 7 micron.

The PDU was run to test the feasibility of using automatic controls to control two separate outlet streams, automatically control fluidizing air and transport air to the SPCV, control main air flow with temperature changes and load changes and control start-ups, shut-downs and emergency plant shut-downs. These tests were successful and showed that there was a feasible method for automatic control.

Engineering studies were done to develop a design for the Prototype plant, Phase IV. A preliminary prototype was developed to size equipment. Materials of construction were investigated for areas of the system that had unique issues. For example, the Reducer vessel and associated piping is expected to operate at high temperatures with a high H₂ content. This required specifying special materials and construction techniques. A set of material recommendations and construction recommendations were developed for the entire chemical looping island.

The prototype plant was sized to run without external heating as needed in the PDU. Heat transfer studies were done to determine that the heat loss was small enough to achieve this condition. It was also determined that the prototype could be heated up in a reasonable time.

An independent economic update of the commercial design was conducted and shown to be consistent with previous studies that showed chemical looping has the potential to be the lowest cost option for CO₂ capture.

Several technical reviews were conducted. Among them was an independent third party review conducted by the ASME for the DOE. A list of comments and recommendations were generated. These recommendations were incorporated into the Chemical Looping Program. The consensus from this review was that the program should proceed to the prototype phase. Several other reviews were conducted by the DOE and Alstom conducted a Technology Concept Gate Review (TCGR).

The Chemical Looping Program has made significant progress in the three program phases. The Phase I and Phase II program produced the following accomplishments:

The program provided the chemical validation of Alstom's chemical looping process. The following processes were demonstrated and significant data was generated for each:

- CaS – CaSO₄ looping
- CaO - CaCO₃ looping
- Water gas shift: $\text{CO} + \text{H}_2\text{O} \Leftrightarrow \text{H}_2 + \text{CO}_2$
- Hydrogen production
- Sorbent reactivation
- CO₂ removal

- Char gasification/combustion via CaSO₄
- Coal devolatilization
- The PDU was used to show the simultaneous operation of four solids transport loops at elevated temperatures. The temperatures were about 1800 °F at a pressure of about 1 ata.
- The PDU was operated with five solids transport loops simultaneously at ambient temperatures.
- Multi-loop control requirements were established.
- The seal pot control valve (SPCV) operation requirements were established and the operation was controlled and steady for most of the testing.
- Startup requirements were established for smooth startup.
- Emergency quick shut-down and quick restart procedures were established.
- Inspection and maintenance procedures were determined.
- A water condenser, water trap and gas reheater system for the vacuum pump inlet was designed, built and successfully operated.
- The PDU successfully transported four very different solids (inert sand, commercial gypsum, coarse CFB bed material and the normal chemical looping sorbent). It was learned that the angle of repose tests for each solid are required for SPCV design and that cold flow model testing for fluidization rates was directly applicable to the hot case.
- The project team successfully passed the 'Product Development Quality Specification Gate Review' and the Technical Peer Review with very few changes required in the development plan.
- The Phase III program produced the following accomplishments:
- A feasible automated control system for the chemical looping process was demonstrated using two separate outlet streams, and automatic SPCV flow control.
- Automated startup and shutdown was demonstrated including emergency shutdown.
- The cold flow modeling characterized pressure drop versus solids flow relationships for the 15-ft model, dual-loop 15-ft model and the 40-ft model.
- Scale-up from a ¾" diameter riser to a 4" diameter riser was shown to be very easy.
- Cyclone performance was demonstrated to be 99.9954% with the 40-ft cyclone system. All particles above 7 micron were captured.
- Controllable and smooth solids flow was demonstrated in all the cold flow models.
- A new SPCV valve was designed and successfully tested.
- A prototype design was created and material specifications were developed.
- Economic studies were done for retrofit applications for Chemical Looping combustion. The COE for producing hydrogen as a boiler fuel were shown to be competitive.

- The project team successfully passed an independent third party review by the ASME, several DOE technical reviews, internal risk reviews and a Technical Concept Gate Review without any major project revisions.

Conclusions:

The main conclusion from Phase I and Phase II is that all of the PDU chemistry required for the chemical looping process has been validated. The main conclusion from Phase III is that a prototype plant is feasible based on flow control studies, automatic control tests, material and heat transfer studies and economic estimates.

Additional conclusions are as follows:

From Phase I (Reference 1)

- It is practical to build a chemical looping system using the CaS to CaSO₄ reaction without losing sulfur as either SO₂ or H₂S.
- High gasification rates can be obtained in a chemical looping system even with low reactivity coals. A carbon conversion rate of 5%/sec ata was used for the commercial plant economic studies, while the minimum rate achieved in the Chemical Looping PDU was twice the required rate with low reactive char.
- It is possible to operate three interactive solids transport loops (Oxidizer, Reducer and sorbent activation), at elevated temperatures (1800 °F).
- It is possible to start up and heat up the solids transport loops interactively.
- The Chemical Looping PDU design concept is validated.
- Cold flow modeling provides a valuable tool for simulating the hot chemical looping system. The cold flow model is useful for determining fluidization and solids transport control settings for fluidizing and transport gases.
- The original economic conclusions were still valid after determining the Phase I chemical reaction rates at the PDU. The original costs studies were based on equipment sizes determined from bench-scale reaction rates. Phase I showed these rates to be conservative.

From Phase II (Reference 2)

- Operation with five parallel loops is becoming routine. The PDU demonstrated five parallel loops cold and four parallel at operating temperatures.
- CaO + CaCO₃ kinetics were demonstrated in the PDU at operating temperatures.
- Water gas shift reactions occurred rapidly at PDU operating conditions.
- Cold flow bench test scale-up methods reveal what the hot PDU behavior will be like.

- Economics assumptions are still valid after detailed peer review and detailed specification review.
- Important control strategies were tested and validated.
- The sorbent activation system vent system can accurately measure flow from the sorbent reactivation reactor.
- The original economic conclusions are still valid after determining the Phase II chemical reaction rates at the PDU. A CO₂-Capture rate (i.e. Rate of conversion of CaO to CaCO₃) of 5%/sec-ata was used for the commercial plant economic studies. CaO conversion rates achieved in the Chemical Looping PDU were an order of magnitude greater than the required rate for normal-sized sorbent material (i.e. 16 mesh).

From Phase III

- It is feasible to build an approximately 3 MW Prototype chemical looping plant that is auto-thermal (requiring no external heaters).
- It is possible to design and operate an automatic control system for the chemical looping system.
- It is possible to design reactors for the chemical looping system using standard materials of construction and standard design methods.
- Cyclone performance of 99.9954% can be achieved with the proper design. It is also possible to keep all solids greater than 7 microns in size in the loop.
- Controllable and smooth solids flow can be maintained.
- Scale-up of 28 times in flow area and 2.6 times in height is possible for the chemical looping concept. Scale-up from the 4" diameter CFM to the 18" diameter prototype is only 20.25 times in flow area and 1.5 times in height. Scale-up to the prototype should be feasible.
- The performance of the cold flow models has shown a very good correlation to the performance of the hot PDU.
- The Chemical Looping concept is ready for the Prototype Phase.

4. 3 MWt Chemical Looping Prototype Project

4.1 Objectives

The overall objective of the chemical looping development program is to develop and commercialize a novel chemical looping combustion process that is well suited for capturing at least 90% of the CO₂ at a 20% or less increase in the cost of energy services from existing or new pulverized-coal-fired (PC) and circulating fluidized bed (CFB) power plants.

The overall objective will be met by designing, building and testing a prototype facility that includes all of the equipment that is required to operate the chemical looping plant in a fully integrated manner with all major systems in service. Data from the design, installation, and testing will be used to characterize environmental performance,

identify and address technical risks, reassess commercial plant economics, and develop design information for a demonstration plant planned to follow the proposed prototype. The objective of the prototype program is to construct and learn how to operate the prototype. This includes initial testing of non-reactive solids transport and 40 hour auto-thermal operation of the prototype, which justifies further testing in a follow-on phase. It also includes applying the lessons learned to the commercial design and economics and plan for a future demonstration plant (25 to 100 MWe).

4.2 Scope of Work

As shown in Figure 4-1, Phase IV was estimated to take about three years to complete, including about twenty-four months for engineering, procurement, and installation, with the remaining time for testing and development. Phase IV includes EPC and nine months of testing that includes 40-hour auto-thermal operation. The Phase IV project was executed in two budget periods. The objective of Budget Period 1 (BP1) was to complete the prototype design and cost estimate. The objective of Budget Period 2 (BP2) was to complete the prototype EPC and perform initial testing, analyze performance data, and develop a technical and cost plan to continue the development program under a separate future project. The future work would include additional prototype optimization testing and pre-engineering leading to a demonstration project.

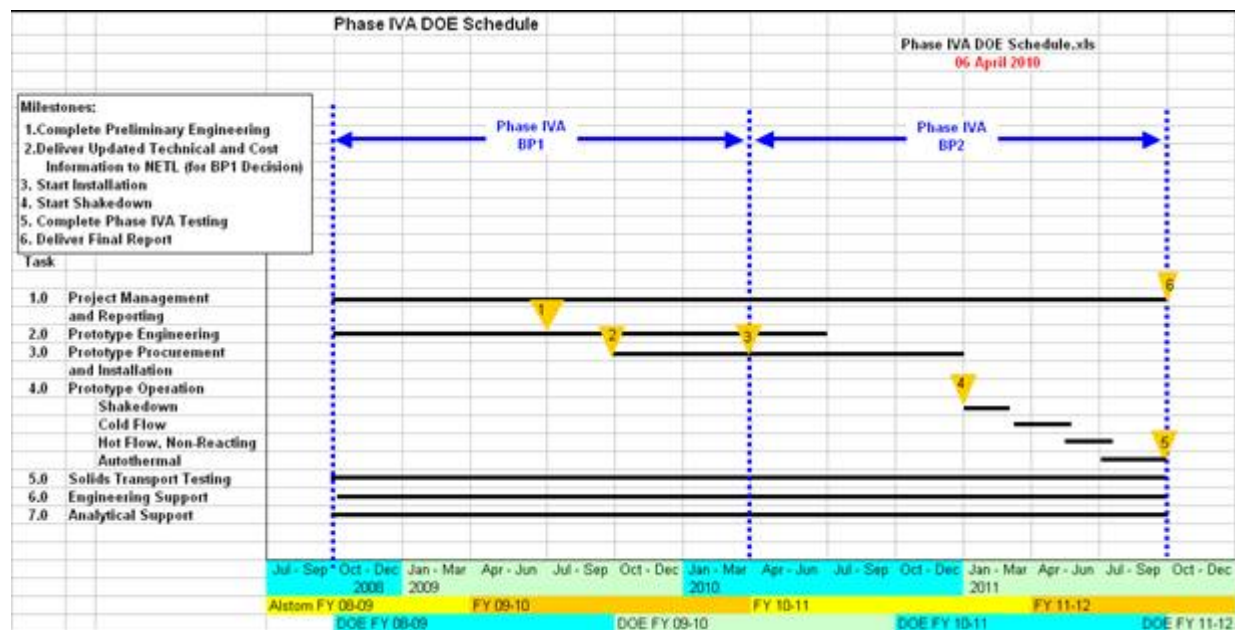


Figure 4-1 - Phase IV Project Schedule (Original)

The following provides the schedule status of the project milestones and deliverables planned and as executed.

Milestone and Deliverables	Planned	Actual
Budget Period 1		
M1. Complete Engineering of Prototype	6/30/09	6/12/09
M2. Updated technical and cost information to NETL	9/30/09	9/30/09
D1. Project Management Plan update		9/02/08
D2. Information for NEPA update		10/18/08
D3. Topical report prototype plant design and cost estimate		4/30/10
D4. Application for Continuation to Budget Period 2		3/17/10
Budget Period 2		
M1. Start Phase IV BP 2	4/30/10	1/30/10
M2. Start Prototype Installation	4/30/10	1/30/10
M3. Start Prototype Shakedown Testing	12/31/10	10/26/10
M4. Complete Prototype Testing	09/30/11	8/31/12
D1. Complete Proposal	12/31/12	deferred
D2. Preliminary Test Plan	9/30/10	9/30/10
D3. Final Report	12/30/11	12/31/12

A 3 MWt chemical looping prototype facility was designed, constructed, shaken-down, and tested with auto-thermal operation achieved by July 2012. Greater detail of the prototype design, cold flow modeling work, and prototype test results are discussed in the following sections. Described below are the steps the project team took to realize this achievement.

Design and Construction of the Prototype

The 3 MWt chemical looping prototype was constructed by making use of Alstom's existing Multi-use Test Facility (MTF) which was originally configured as a circulating fluidized bed (CFB) boiler pilot plant. The existing CFB pilot was modified to serve as the chemical looping Oxidizer. A Reducer system and additional auxiliary equipment were added to constitute the remainder of the chemical looping prototype.

The support structure in the original estimated budget was based on a modification in which the chemical looping prototype equipment would be added to the existing MTF structure. Once the project was underway, an outside architect was hired to better define the support structure costs. The outside architect advised Alstom that the assumption to tie in a support structure to the existing building was more costly than originally estimated. They provided an initial budget estimate for a standalone structure and for integrating the prototype into the existing MTF structure. However, it was determined the integrated option was still less expensive, faster and therefore it became the basis for the revised BP 2 estimate. The integrated option, as priced for the BP 2

estimate, was higher than the original estimated budget and the continuation request reflected the new cost in the BP 2 budget.

The integrated option uses the MTF and virtually all of its associated equipment in the prototype. The MTF vessel itself is used as the Oxidizer. In this option, the existing feed system, gas handling and cleanup system, and all of the MTF instrumentation are used to reduce the amount of new equipment added.

Alstom continued with the integrated option as the basis for the revised budget estimate. Alstom continued to work to find lower cost options and ways to reduce costs within the integrated option.

Cold Flow Modeling

A Cold Flow Model (CFM) was used to analyze and visualize solids transport in Alstom's chemical looping process and to develop methods to transport, distribute and control solids flow for the operating loops. The specific needs were to:

- integrate the new Oxidizer loop into the existing cold flow model Reducer loop to form a complete solids circulation loop similar to the prototype unit,
- trouble shoot for the prototype unit,
- verify the conceptual design of the prototype for the solids transport in multi-loop operation,
- demonstrate the operation methodology in multi-loop CFM operation including the start-up, shut-down and control stability of the system, and
- establish operating guidelines for the prototype unit multi-loop operation as a training tool and as a trouble-shooting device.

Prototype Operation

Prototype operation began by October 2010 with shakedown and operational testing. This effort revealed the necessity for some minor equipment, controls, and electrical modifications.

The air tests included increasing Oxidizer and Reducer air and recycle gas flow, defining the flow and stall characteristics of the Oxidizer air supply fan and the Reducer startup fan, defining and improving the operation of the Oxidizer and Reducer burners, testing and improving the operation of the steaming heat exchangers and testing and tuning the startup electric heaters.

Initial operations with solids included testing and then modifying the solids handling and storage facility to successfully size-grade and transport the CFB solids to the storage hopper. The solids pneumatic fill-up system was tested and successfully used to load the CFB solids into the prototype for solids transport cold flow testing.

Following initial operation, there were a series of test operations with the prototype facility ranging from cold solids flow to hot combustion. Each operation built experience levels and insight with the fully integrated chemical looping process.

In early April 2011 solids flow was initiated in the prototype. Using air settings suggested by the cold flow model, solids began transporting in a stable operating mode. Settings for the operation were recorded and data was logged for analysis. The air heaters were started up. The solids transport was stable enough to allow 'hands off' operation for about an hour of operation.

In mid April 2011, the prototype was started up and run for a 24-hour period. The process was heated up to about 600 to 700°F using a combination of natural gas burners and electric air heaters. In May 2011, the unit was again started up and run for over 24 hours with improved natural gas flow to the burners. Coal was fired for 16 hours to about 100 lb/hr with supplemental natural gas and the unit briefly reached 1450°F. Syngas was made in the Reducer for the first time.

In early June 2011, the prototype was restarted after minor equipment modifications and upgrades to the natural gas delivery system. Natural gas was fired in both the Oxidizer and Reducer burners and then directly into the Oxidizer when sufficiently heated by the burners. The Oxidizer was heated up to full operating temperature. Coal was fired along with natural gas in the Reducer.

In mid-June 2011, the prototype was started and quickly heated up to operating temperatures. Coal was fired for about an hour to 360 pounds per hr. **Chemical looping reactions were achieved on June 11, 2011.**

Additional testing was attempted in September and October 2011. However, there were mechanical and design issues which prevented long-term test operations. By October 2011, the project team decided to systematically review and address prototype design. Despite the setback, the project team had realized the following technical achievements.

- Learned how to detect the height of the SAHE solids.
- Learned how to generate significant SAHE flow.
- Learned how to light natural gas in the reactor vessels at a lower temperature which reduced heat up time and also reduced the formation of solid agglomerates, which can impede solids flow.
- Learned how to start up the prototype to operating temperature in one shift.
- Learned how to operate without generating solids build up in the condenser and chiller.
- Achieved less frequent solids loss to the chamber pots.
- Operators were getting more proficient in controlling the prototype.

By May and June 2012, prototype testing resumed as part of a comprehensive plan to attain auto-thermal operation. Testing started with the Reducer operating in a

“decoupled” mode. Decoupling means that the Reducer heat was supplied by supplemental natural gas firing in the Oxidizer. Normally, the chemical looping process would totally rely on the Oxidizer exothermic chemical reactions to supply heat, as would be the case in the auto-thermal mode of operation. In this mode the Oxidizer is still used because the solids must still be recirculated, but it allows the testing of just the Reducer without have to characterize the Oxidizer at the same time. The objectives of the Reducer test were to show the Reducer chemical looping reactions and to evaluate the Reducer performance. The data produced was the coal and CaSO₄ conversions, solids recycle rate and the Reducer solids loading.

The Reducer tests were very successful. The results showed the following.

- All chemical looping reactions were realized.
- There was a high carbon burn-up efficiency of greater than 98%.
- There was negligible carbon carryover to the Oxidizer.
- Oxygen demand was 15 to 20%.
- SO₂ release can be controlled by varying the excess air to fuel ratio.

In July the prototype was prepared for the Oxidizer characterization testing. The purpose of the test was to verify the Oxidizer reactions. The intent was to use fuels of varying reactivity in the Reducer and determine carbon carryover and CaS conversion in the Oxidizer. Alstom achieved stable, auto-thermal, coal-only operation with the 3 MWt prototype on July 2012 for 12 hours on Pittsburgh and Adaro coals.

During the auto-thermal tests, the 3 MWt prototype was operated exclusively on coal which was fed to the Reducer with air fed only to the Oxidizer. No supplemental fuel of any kind was required. Nearly full design coal flow was attained. Attaining auto-thermal performance necessarily required that all of the following factors are occurring.

- Coal is combusted in the Reducer to CO₂ via hot CaSO₄, forming CaS.
- CaS is burned in the Oxidizer forming hot CaSO₄ for the Reducer.
- LCL-C™ chemical looping reactions are self-sustaining.
- Long-term, stable operation is attained.
- Both the Reducer and Oxidizer systems are properly sized and configured.

These initial results are sufficient to show that Alstom's LCL-C™ concept is viable and that the prototype is correctly sized and configured. The results also indicate directions for process optimization. Future work is anticipated in the following areas.

- 3 MWt chemical looping prototype optimization tests
- 3 MWt chemical looping prototype 40 hour Auto-thermal run
- Sulfur control (sorbent activation, limestone testing)
- Main dip-leg gas generation control – solids control
- Reduce bottom outlet gate [counter-current gas (up) and solids (down)]
- Full load operation

- Condensing heat exchanger
- Automatic solids control
- Commercial startup and operating (full load, part load, load change, long runs, demonstration coal test)
- Maximum pressure tests
- Cold flow modeling support

5. Prototype Plant Description

5.1 Design and Engineering

The Prototype Chemical Looping process is scaled down from the Greenhouse Gas Report Case 13 (**Reference 4**). This Case is the most general and the equipment can be used to operate in either, a) the combustion mode Case 7, b) the syngas production mode Case 12 or c) the hydrogen production mode Case 13.

The chemical looping concept is used to indirectly provide the oxygen for the gasification of coal rather than direct utilization of ambient air. The chemical looping concept supplies the oxygen to the gasification process without the large efficiency penalty associated with a cryogenic type Air Separation Unit. Additionally, the large investment cost associated with both cryogenic Air Separation Units or Oxygen Transport Membrane oxygen supply systems is avoided.

Additionally, CO₂ is captured with a second chemical loop in this concept. These chemical loops provide a very energy efficient method for oxygen transport and CO₂ capture. The trade off, of course, is a more complex gasification process. Through the use of this chemical looping process, Medium Btu Gas (MBG) is produced from an air fired gasifier system as in Case 12. In the combustion mode, CO₂ is produced as in Case 7 and in the last mode, Hydrogen and CO₂ are produced as in case 13.

5.1.1 Process

This section describes the Prototype processes and includes a process flow diagram (PFD), material and energy balance and equipment description. The process and equipment description includes only the major components included in the Chemical looping Island.

Process Flow Diagrams

Figure 5-1 shows a simplified process flow diagram for the Prototype. In **Figure 5-1**, components are identified by text boxes, streams are labeled with a number or letter identifier. (See **Table 5-1** for flow rates). Red colors indicate items associated with the Reducer, green indicates calciner items and blue indicates Oxidizer items. This process description briefly describes the function of the chemical and thermal loops, major equipment and systems included within the Prototype. Selected mass flow rates (lb/hr) and are shown in **Table 5-1**.

Table 5-1 - Overall Plant Stream Report

	Stream No.	Gas			Solid lb/hr
		lbmole/hr	lb/lbmole	lb/hr	
Coal	1				1000
Limestone	2				231
Disposal	3				423
	4				1231
	A	90	2.8	252	503603
CO2	B				490944
H2O	C	14	18.0	253	54549
	G				545493
CO2	I	0	44.0	21	
CO2	J	4	44.0	185	
H2O	K	56	18.0	1011	
H2O	L	14	18.0	253	
	M	4	44.0	758	
	N				43209
	P2	92	22.5	2078	502882
	P3	90	2.8	252	
	P6A	58	44.0	2570	
	A3, A6, A7	88	28.6	2515	
	G1	73	27.9	2033	
Hot CaSO4	14				40659
CaS	20				43070
CaCO3	7				112330
CaO	8A				104720
	O	72	28.2	2033	81319
	P				40659

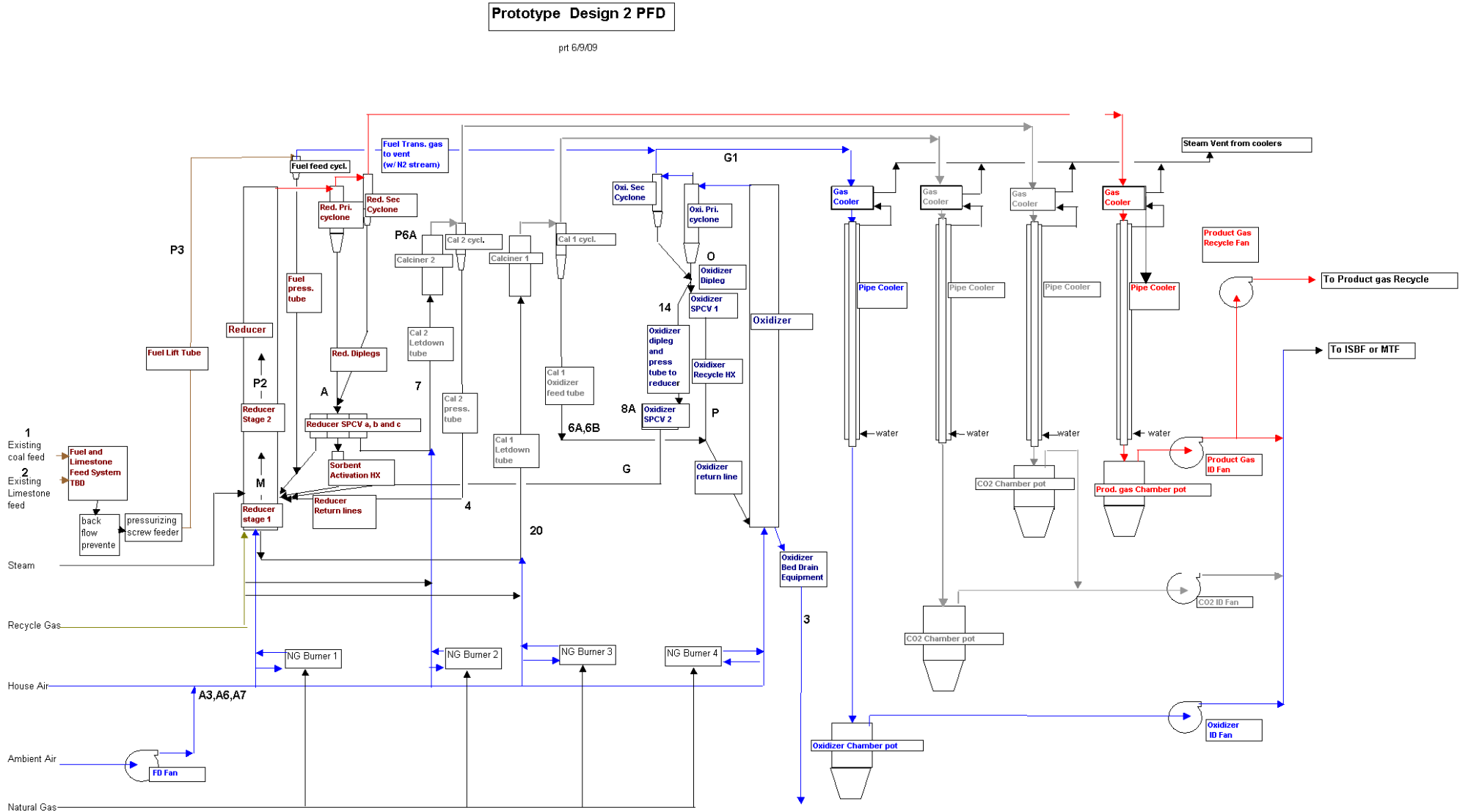


Figure 5-1 - Simplified Prototype Process Flow Diagram

U.S. DOE NETL Cooperative Agreement No. DE-NT0005286
 ALSTOM's Chemical Looping Combustion Prototype For CO₂ Capture From Existing
 Pulverized Coal Fired Power Plants

Table 5-2 - Prototype Reactor Design Conditions

Stream	PDU Data	REDUCER w/ H ₂ Production										OXIDIZER w/ H ₂ Production			CALCINER w/ H ₂ Production			OXIDIZER for Case 7 35% Load			CALCINER for Case 7 50% Load - No CO ₂											
		Stage I		Stage I		Stage I		Stage II		Stage II		Stage II		Stage III		Stage III		Stage III		Stage III			Stage III									
		Carbon Burnout	Carbon Burnout	Carbon Burnout	Carbon Burnout	Carbon Gasif	Carbon Gasif	Carbon Gasif	Carbon Gasif	Carbon Gasif	Carbon Gasif	Carbon Gasif	WGS deCO ₂	WGS deCO ₂	WGS deCO ₂	WGS deCO ₂	WGS deCO ₂	WGS deCO ₂	WGS deCO ₂	Inlet	Outlet	Average	Inlet	Outlet	Average	Inlet	Outlet	Average	Inlet	Outlet	Average	
		Inlet	Outlet	Average	Inlet	Outlet	Average	Inlet	Outlet	Average	Inlet	Outlet	Average	Inlet	Outlet	Average	Inlet	Outlet	Average	Inlet	Outlet	Average	Inlet	Outlet	Average	Inlet	Outlet	Average	Inlet	Outlet	Average	
Temp	1700	1800	1800		1800	1800		1800	1800		1800	1800		2000	2000		1800	1800		2000	2000		1800	1800		2000	2000		1800	1800		
Press	1	2.0	2.0		2.0	2.0		2.0	2.0		2.0	2.0		1.0	1.0		0.3	0.3		1.0	1.0		0.3	0.3		1.0	1.0		0.3	0.3		
Stream		I	M		M+J+G	P2		P2+K	A		A3,A6,A7	0		n/a	P6A																	
Gas	(lbmole/hr)	0.139	0	4	22	92		146	90		88	72		0.35	58		123	101		123	101		1.39	1		123	101		1.39	1		
	(lb/lbmole)	10	44.011	44.0	27.345	22.5		20.6017409	2.8		28.6	28.2		44	44		28.6	28.2		44	44		44	44		44	44		44	44		
	(lb/hr)	1.393	21	160	598	2078		3089	251		2515	2033		15	2570		3521	2846		3521	2846		61	61		3521	2846		61	61		
	(scfh)	50	168	1305	7853	33172		53308	32241		31532	25918		125	20967		44145	36285		44145	36285		499	499		44145	36285		499	499		
	(act/s)	0.061	0	1	5	21		34	21		44	36		1	89		61	50		61	50		2	2		61	50		2	2		
	(lb/act)	0.0063	0.053	0.053	0.033	0.027		0.025	0.003		0.016	0.016		0.008	0.008		0.016	0.016		0.016	0.016		0.008	0.008		0.016	0.016		0.008	0.008		
Stream		N	20		G	P2+N		P2	A		P+20	0+3		20	20	P6A																
Solid	(lb/hr)	279	43,209	43,070	545,493	546,091		502,882	503,603		83,729	81,742		43,070	40,499		117221	114439		117221	114439		172279	172279		117221	114439		172279	172279		
Solids Bulk Density	(lb/ft ³)	82.5	82.5	82.5	82.5	82.5		82.5	82.5		82.5	82.5		82.5	82.5		82.5	82.5		82.5	82.5		82.5	82.5		82.5	82.5		82.5	82.5		
Solids Apparent Bulk Void Frac	(vol frac)	0.45	0.45	0.45	0.45	0.45		0.45	0.45		0.45	0.45		0.45	0.45		0.45	0.45		0.45	0.45		0.45	0.45		0.45	0.45		0.45	0.45		
Solids Apparent Particle Density	(lb/ft ³)	150	150	150	150	150		150	150		150	150		150	150		150	150		150	150		150	150		150	150		150	150		
Mat'l Balance		280	43230	43230	546091	546169		506971	503854		86244	83775		43085	43069		120741	117285		120741	117285		172340	172340		120741	117285		172340	172340		
				1.0000		1.0038			0.9968			0.9714			0.9986			0.9714			0.9986			1.0000				1.0000			1.0000	
Solid/Gas	(wt ratio)	200	2096	269	912	263		163	2003		33	40		2,819	16		0	0		33	40		2,819	16		0	0		33	40		
Pipe/Reactor Diameter	(ft)	0.069	0.87	0.87	0.87	0.87		0.87	0.87		0.87	0.87		0.87	1.50		0.87	0.87		0.87	0.87		2.20	2.20		0.87	0.87		2.20	2.20		
Pipe/Reactor X-Sect	(ft ²)	0.004	0.6	0.6	0.6	0.6		0.6	0.6		0.6	0.6		0.6	1.8		0.6	0.6		0.6	0.6		3.8	3.8		0.6	0.6		3.8	3.8		
Reactor Length	(ft)	15	5	5	20	20		35	35		60	60		5	5		60	60		60	60		5	5		60	60		5	5		
Reactor Volume	(ft ³)	0.096	2.9	2.9	11.8	11.8		20.6	20.6		35.3	35.3		5.6	5.6		35.3	35.3		35.3	35.3		19.0	19.0		35.3	35.3		19.0	19.0		
Solids Slip Factor	(solids/gas time)	1	1	2	1	1		1	1		1	1		1	1		1	1		1	1		1	1		1	1		1	1		
Void Frac	(vol frac)	0.99	0.57	0.84	0.83	0.95		0.97	0.96		1.00	1.00		0.9692	0.9992		1.00	1.00		1.00	1.00		0.8692	0.8692		1.00	1.00		0.8692	0.8692		
Gas/Solids Mixture Density	(lb/ft ³)	1.2646	64.1	24.2	25.2	6.9		4.0	6.5		0.5	0.6		19.6	0.1		0.5	0.6		0.5	0.6		19.6	0.1		0.5	0.6		19.6	0.1		
		1.2646	64.1	24.2	25.2	6.9		4.0	6.5		0.5	0.6		19.6	0.1		0.5	0.6		0.5	0.6		19.6	0.1		0.5	0.6		19.6	0.1		
Gas Residence Time (Acct'd for Solids Vol)	(sec)	0.903	16	3	9	2.0	0.5	1.2	0.6	1.0	0.8	0.8	1.0	0.9	9.2	0.1	4.6	0.6	0.7	0.6	7.8	7.8	7.8	0.6	0.7	0.6	7.8	7.8	7.8	0.6	0.7	0.6
Solids Residence Time (Acct'd for Solids Vol)	(sec)	0.903	16	6	11	2.0	0.5	1.2	0.6	1.0	0.8	0.8	1.0	0.9	9.2	0.1	4.6	0.6	0.7	0.6	7.8	7.8	7.8	0.6	0.7	0.6	7.8	7.8	7.8	0.6	0.7	0.6
Superficial Velocity (Gas-only)	(ft/s)	16	0.18	1.41	0.80	9	36	22	58	35	46	74	61	68	0.90	50	26	104	86	95	0.56	0.56	0.56	104	86	95	0.56	0.56	0.56	104	86	95
Superficial Velocity (Acct'd for Solids Vol)	(ft/s)	17	0.32	1.68	1.001	10	38	23.932	59	37	47.910	75	61	67.969	1	51	26	104	86	95	1	1	1	104	86	95	1	1	1	104	86	95
Solids in Reactor	(lb)	0.070	188.8	71.0	129.9	296.5	80.6	188.6	82.4	134.1	108.3	18.7	22.2	20.5	110.4	0.7	55.5	18.7	22.2	20.5	372.8	372.8	372.8	18.7	22.2	20.5	372.8	372.8	372.8	18.7	22.2	20.5
Solids loading	(lb/ft ³ of space)	1	64	24	44.1	25	7	16.0	4	7	5.3	1	1	0.6	20	0	9.9	1	1	0.6	20	20	19.6	1	1	0.6	20	20	19.6	1	1	0.6
Solids Static Head	(psia)	0.13	2.23	0.84	1.53	3.50	0.95	2.22	0.97	1.58	1.28	0.22	0.26	0.24	0.68	0.00	0.34	0.22	0.26	0.24	0.68	0.68	0.68	0.22	0.26	0.24	0.68	0.68	0.68	0.22	0.26	0.24
Solids Static Head	(in H ₂ O)	3.6	61.6	23.2	42.4	96.8	26.3	61.5	26.9	43.8	35.3	6.1	7.2	6.7	18.9	0.1	9.5	6.1	7.2	6.7	18.9	18.9	18.9	6.1	7.2	6.7	18.9	18.9	18.9	6.1	7.2	6.7

Three primary reactors are included, the Oxidizer, Reducer, and Calciner. For Options 1 & 2, the Prototype will have Oxidizer and Reducer reactors only. For Option 3 the Prototype will have two Calciners to allow for some process optimization. Additionally, there are two primary chemical loops within this process. One loop indirectly supplies oxygen to the Reducer for the gasification of the coal. The second loop captures CO₂ from the fuel gas and then releases the captured CO₂ as a second product gas stream, which is compressed and liquefied for sequestration or use. Heat is supplied as required throughout the processes by the sensible heat in the solids streams mainly from the Oxidizer. The chemical loops will be described first followed by the reactors and other major process equipment and systems.

Oxygen Transport:

The oxygen transport loop is shown in **Figure 5-1**. The solids separated from the gas/solids mixture leaving the Oxidizer (Stream O) are rich in hot CaSO₄ and are split into two streams. One stream is transported to the Reducer (Stream 8A) and the other stream (Stream P) is recirculated back to the Oxidizer. The CaSO₄ contained in Stream 8A supplies oxygen to the Reducer, where it is reduced to CaS. The solids in stream 20, which are rich in CaS, are returned to the Oxidizer in stream 6A after release of the CO₂ to complete the oxygen transport loop.

Limestone (Stream 2) is added to the system to react with sulfur contained in the coal and eventually capture CO₂ produced in the Reducer. Calcium, in the form of CaO and the sulfur, in the form of H₂S, combine to form CaS in the Reducer, as shown below, which is used as the oxygen carrier in the chemical looping reactions described above. Solids are removed from the system in the Oxidizer to avoid a buildup of CaS and to remove the captured sulfur by the following reaction:



Sulfur is removed by a solids drain in the Oxidizer as stated. The solids contain only CaSO₄, when drained from the Oxidizer exit stream. Sulfur is removed from the coal as indicated in the chemical reaction listed and then the sulfur travels around the system in the form of CaS and CaSO₄. Eventually the Sulfur is removed as CaSO₄ in the solids drain.

CO₂ Capture:

In Option 3 mode, the CO₂ is captured in the Reducer (**Figure 5-1**). Entering the Reducer, Stream 4 is a regenerated CaO rich stream that is provided to capture the CO₂ gas that is produced in the Reducer. The medium-Btu fuel gas and entrained solids stream leaving the Reducer enter a particulate removal device, where the solids (Stream A), now rich in CaCO₃, are separated from the gas. Stream A is then split into three parts with Stream 7 flowing to Calciner 2. Calciner 2 regenerates CaO from the CaCO₃ contained in Stream 7. The gas solids mixture leaving Calciner 2 (Stream P6A) contains the captured CO₂ gas released in Calciner 2 and solids that are rich in CaO. This stream enters a particulate removal device where the solids (Stream 4) are

separated from the gas. Stream 4 returns to the Reducer to complete the CO₂ capture loop. The captured CO₂ product stream is cooled and then supplied to the Gas Processing System.

For the Prototype, two calciners are supplied for testing flexibility. A primary Calciner (Calciner 1) is supplied to provide final calcination prior to burning the CaS (which is contained in the stream) to CaSO₄ in the Oxidizer. Calciner 1 is fed by a stream of solids from the bottom of the Reducer where carbon is minimized (Stream 20). The solids collected by the Calciner 1 cyclone are mixed with the Oxidizer recycle solids and return to the Oxidizer in stream 6A.

Oxidizer:

The Oxidizer also receives solids containing CaS from the Reducer via Calciner 1. The Oxidizer is designed to capture oxygen from air utilizing a stream of recirculated bed solids. The bed solids are used as a chemical looping oxygen carrier, whereby the oxygen is picked up by the solids from air in the Oxidizer vessel. The Oxidizer operates at about 1,900 °F and 1.0 ata. About 90 percent of the oxygen contained in the incoming air is captured by the solids. The basic chemistry in the Oxidizer is shown in the following reaction.



Therefore, the purpose of the Oxidizer is to react the oxygen contained in the air with CaS to form hot CaSO₄ with a minimal amount of excess air utilized in the Oxidizer. The hot CaSO₄ represents a very effective oxygen carrier due to its high oxygen loading in addition to carrying heat to the appropriate locations.

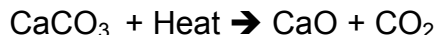
Leaving the Oxidizer there is a mostly nitrogen gas stream (Stream G1) with excess oxygen, which is cleaned of solids, cooled and finally exhausted to the atmosphere through the stack after passing through the Induced Draft (ID) fan. The NO_x leaving the Oxidizer is expected to be negligible based on previous pilot plant testing.

Hot solids (Stream 3), are removed from the Oxidizer through water-cooled bed ash coolers, controls solids inventory in the system while removing heat from the hot ash.

Calciner:

The calciner, which is used in conjunction with Option 3 only, is designed to separate the captured CO₂ from the entering solids stream that are rich in CaCO₃ (Stream 7), thereby regenerating the CaO for additional CO₂ capture. After the calciner there is a cyclone. Two streams leave the calciner cyclone: (1) a solids stream, containing regenerated CaO, which is returned to the Oxidizer and (2) the off gas (Stream P6A), containing captured CO₂ product.

The calciner is a fluidized bed reactor controlled to operate at about 1,600 °F. The hot solids stream entering the calciner from the Reducer, at about 1,700 °F, provides the heat required for regeneration of the CaO. Under these conditions the following reaction occurs.



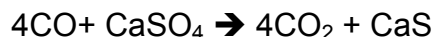
Calciner Particulate Removal:

The CO₂ gas which is released in the Calciner (Stream P6A) flows through a particulate removal device that separates the entrained solids from the gas stream. The CO₂ product then is cooled by a heat exchanger.

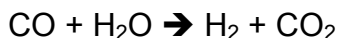
The solids leaving the Calciner particulate removal device, at about 1,600 °F, are rich in CaO and are piped to the Reducer (Stream 4). This completes the CO₂ capture solids loop, and the CaO is available to capture more CO₂.

Reducer:

The Reducer operates at a temperature range of 1600 to 1800 °F and approximately 2.5 ata. The Reducer can be operated in three different modes or options and has several functions to perform. It can be described as a multiple zone reactor. When the Reducer is operated in the "excess air" mode, i.e., Option 1, where there is an excess of available reactive oxygen, the gas leaving the Reducer is mainly CO₂ and H₂O. In Option 2, one function of the Reducer is to reduce the CaSO₄ in the presence of coal, thereby producing a medium-Btu gas. The oxygen carried by the solids (CaSO₄ in Stream 14) is reacted sub-stoichiometrically with the carbon and hydrogen contained in the coal (Stream 1) and recycle solids in the lower Reducer vessel to form a medium-Btu fuel gas. Fuel gas comprised of primarily H₂ with smaller amounts of CO, CO₂, NH₃ and H₂O vapor, flows through a particulate removal device, where hot solids are removed and recirculated. The principal overall reactions, which are overall endothermic, are shown below:



A second process (Option 3) occurring in the Reducer is the shift reaction whereby the following reaction occurs.



This is done to shift most of the carbon into CO₂ for subsequent capture.

A third, Option 3, the function of the Reducer is to capture CO₂. The CO₂ is captured in the Reducer according to the following reaction.



The medium-Btu fuel gas leaving the Reducer, which is mostly hydrogen, is cleaned of solids, cooled and sent to be disposed of in the product gas burner.

Process steam is introduced into the Reducer vessel and the Sorbent Activation Heat Exchanger (SAHE) for purposes of solids activation and to promote the shift reaction. Sorbents, in this process, are the solids containing calcium that react to collect the Oxygen, CO₂ and Sulfur.

The temperature in the Reducer is controlled to the proper level by splitting the flow of hot re-circulated solids leaving the particulate removal system between an un-cooled stream that flows directly back to the Reducer and the SAHE, where the solids are cooled before returning to the Reducer (Stream C).

High Temperature Coolers:

The fuel gas from the prototype is cooled to 100°F to knockout (condense) most of the water. The captured CO₂ stream leaving the prototype is cooled. In the prototype, the CO₂ is discharged to atmosphere. The cooling of the gas streams leaving the Oxidizer, Reducer and calciner vessels is done in a high temperature cooler where the sensible heat of the streams is transferred to a cooling water stream.

Material and Balance

Table 5-2 shows the material balance for Option 2. The stream numbers shown at the top of each column of the table refer to stream numbers shown in the simplified PFD for the Chemical Looping Island (**Figure 5-1**). This performance was calculated at full load conditions for this unit.

5.1.2 Cost Issues

The support structure in the original estimated budget was based on a modification in which the Chemical Looping Prototype equipment would be added to the existing Multi-Use Test Facility (MTF) structure. Once the Phase IVA project was underway, an outside architect was hired to better define the support structure costs. The outside architect advised Alstom that Alstom's assumption to tie in a support structure to the existing building was more costly than originally estimated. They provided an initial budget estimate for a standalone structure, as described above, and for integrating the prototype into the existing MTF structure. However, it was determined the integrated option is still less expensive, faster and therefore it became the basis for the revised Budget Period 2 estimate. The integrated option, as priced for the BP 2 estimate, was higher than the original estimated budget and the continuation request reflected the new cost in the Budget Period 2 budget.

The integrated option uses the MTF and virtually all of its associated equipment in the prototype. The MTF vessel itself is used as the Oxidizer. In this option, the existing feed system, gas handling and cleanup system, and all of the MTF instrumentation are used to reduce the amount of new equipment added.

Alstom continued with the integrated option as the basis for the Revised Budget Estimate. Alstom continued to work to find lower cost options and ways to reduce costs within the integrated option.

5.1.3 Prototype Design Using the MTF

A revised prototype design was developed using the existing MTF facility. In this concept the existing MTF vessel is used as the Oxidizer in the Chemical Looping system. All of the existing MTF equipment is used and all of the new equipment for the Reducer and crossover lines is fit into the existing structure that houses the MTF.

The following modifications were made to the standalone prototype design. The existing MTF vessel was used as the Oxidizer. The MTF has an inside refractory diameter of 40 inches. A new refractory liner was installed inside the old one to reduce the inner diameter of the MTF to the diameter needed by the Oxidizer (approximately 15 inches). This method of modifying the MTF has been successfully used before. The MTF will have the ability to be returned to its original condition if needed in the future.

All of the MTF equipment was retained and used as much as possible. The MTF cyclone, feed system, heat exchangers, fans and gas cleanup system were used.

The first Calciner (Calciner 1) was designed into the system to leave room in the arrangement. Calciner 1 will not be installed until Phase IV B, since the hot testing in Phase IVA only includes the auto-thermal test run of 40 hours in Option 1 mode. If the project proceeds to Phase IVB, Calciner 1 will be installed. In place of Calciner 1, a crossover line from the Reducer bottom to the Oxidizer was used. The second calciner will not be installed in this configuration because the space around the MTF is tight.

The new Chemical Looping equipment is supported at the 22-foot elevation. The existing MTF equipment is primarily supported at this level.

The support structure and foundation for the MTF, as originally designed, can handle the extra weight of the new Chemical Looping vessels, however the structural review recommended that four additional small columns be added inside the existing MTF structure to spread the additional load more evenly on the existing foundation pad. The four new columns will run from the foundation to the steel at the 22-foot level.

Revised Process Flow Diagram

A revised process flow diagram is shown in **Figure 5-2**. The PFD is color coded to indicate which equipment exists and which will be added to the existing MTF. The equipment drawn in blue represents existing MTF equipment and the equipment drawn

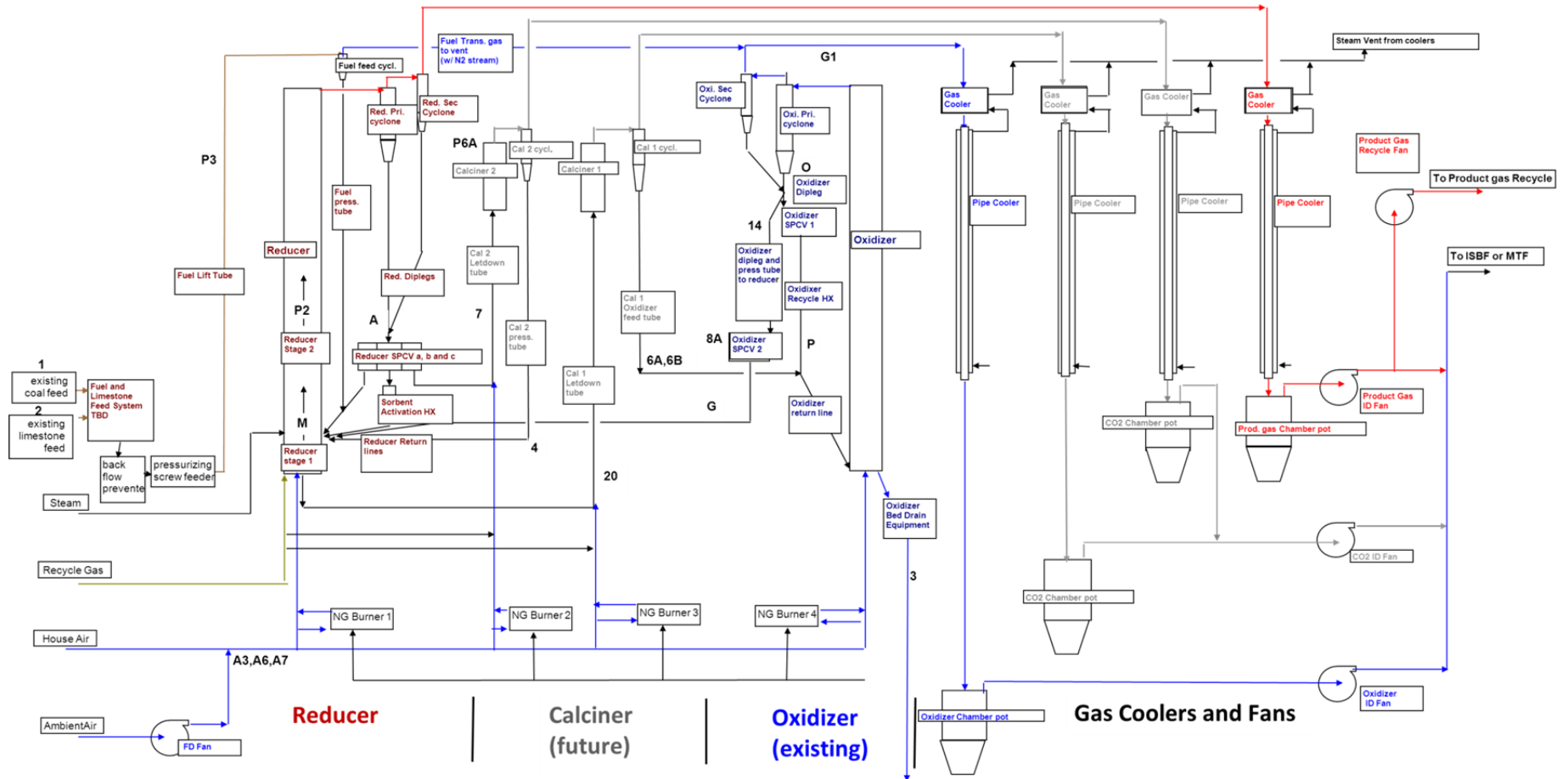
in red indicates the new equipment. A green box is drawn around the Calciner 1 equipment to indicate that this will be installed later. For Phase IVA, Calciner 1 will be replaced by a crossover line directly from the Reducer to the Oxidizer.

Revised Prototype arrangement

The revised prototype arrangement is shown in **Figures 5-3, 5-4 and 5-5**. **Figure 5-3** shows how the new equipment will fit into the existing MTF structure. The arrangements presented here include the future addition of Calciner 1 and its associated equipment. The equipment is a tight fit but manageable. The equipment is packed close together for another reason. Crossover pipes needed to be minimized in length. The further apart the equipment is, the smaller the angle the crossover lines can be. Crossover solids flow is enhanced by steep crossover lines. **Figure 5-4** shows the equipment arrangement without the steel structure and identifies the components. **Figure 5-5** shows the equipment arrangement in a top view.

Table 5-3 Lists the revised Prototype equipment and weights.

Figure 5-2 - Revised Prototype Process Flow Diagram using MTF



CHEMICAL LOOPING
PROTOTYPE PLANT
STRUCTURAL STEEL
ARRANGEMENT

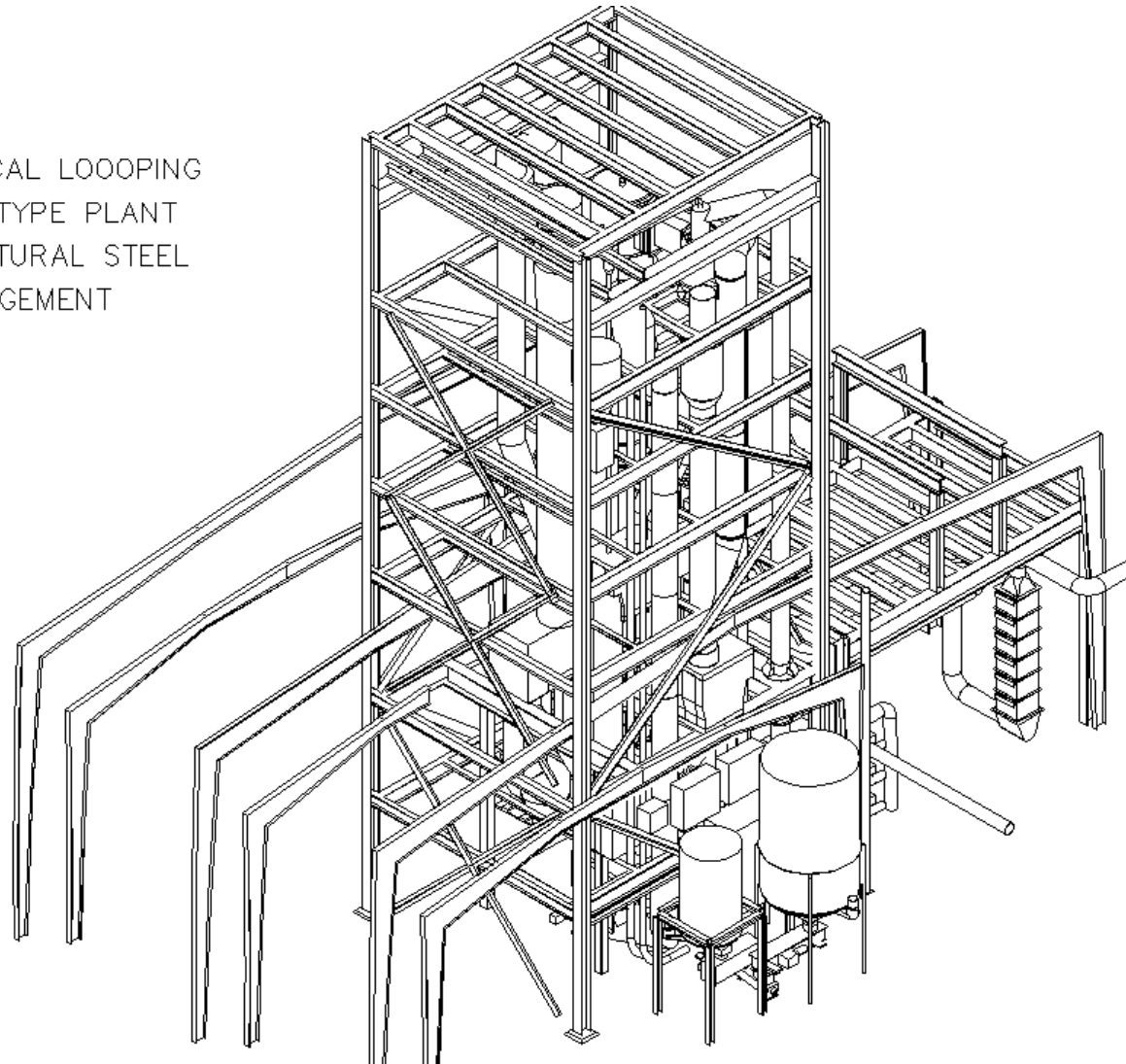


Figure 5-3 – Revised Prototype – Isometric View in Existing Steel

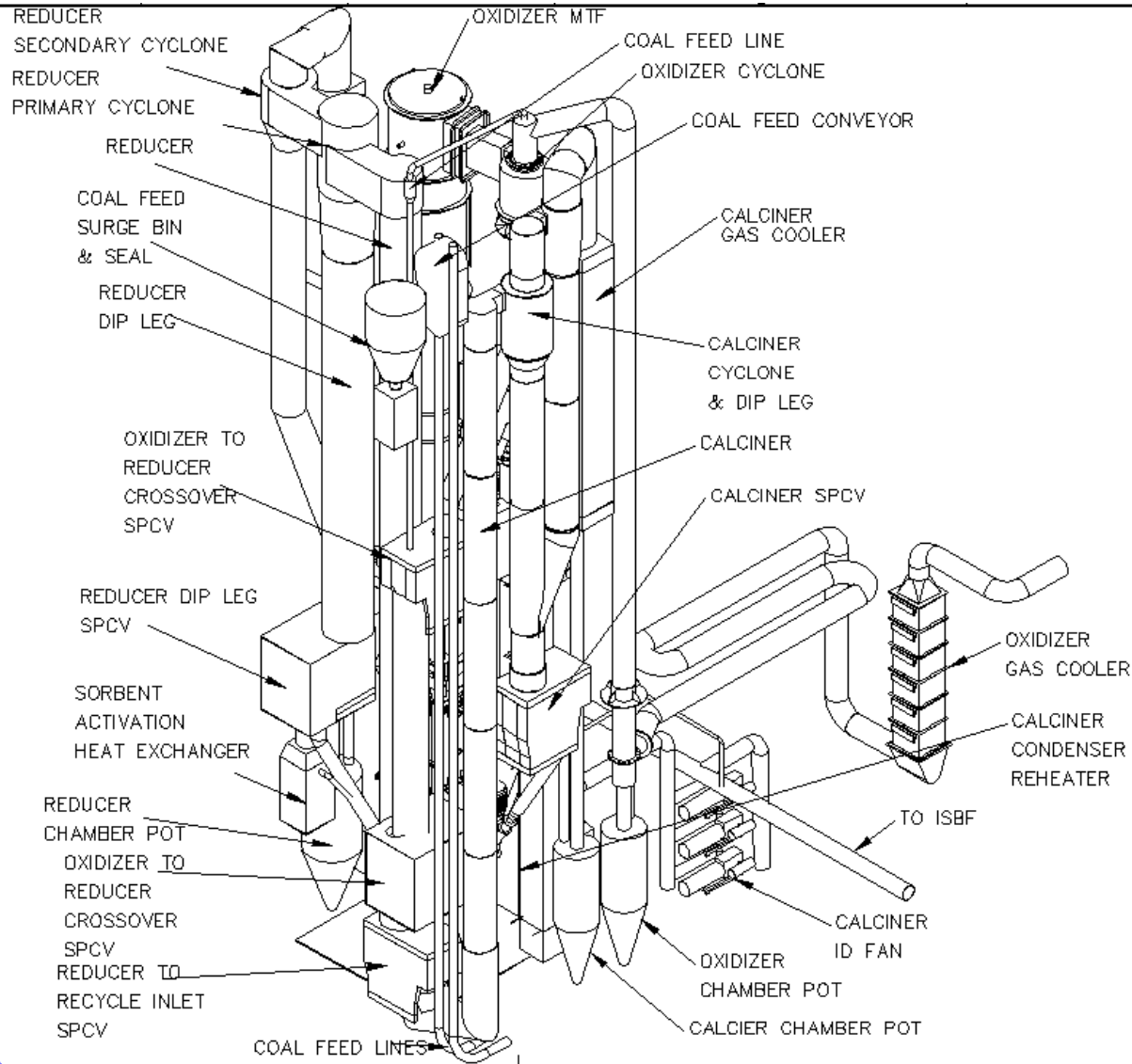


Figure 5-4 – Revised Prototype – Isometric View – Components

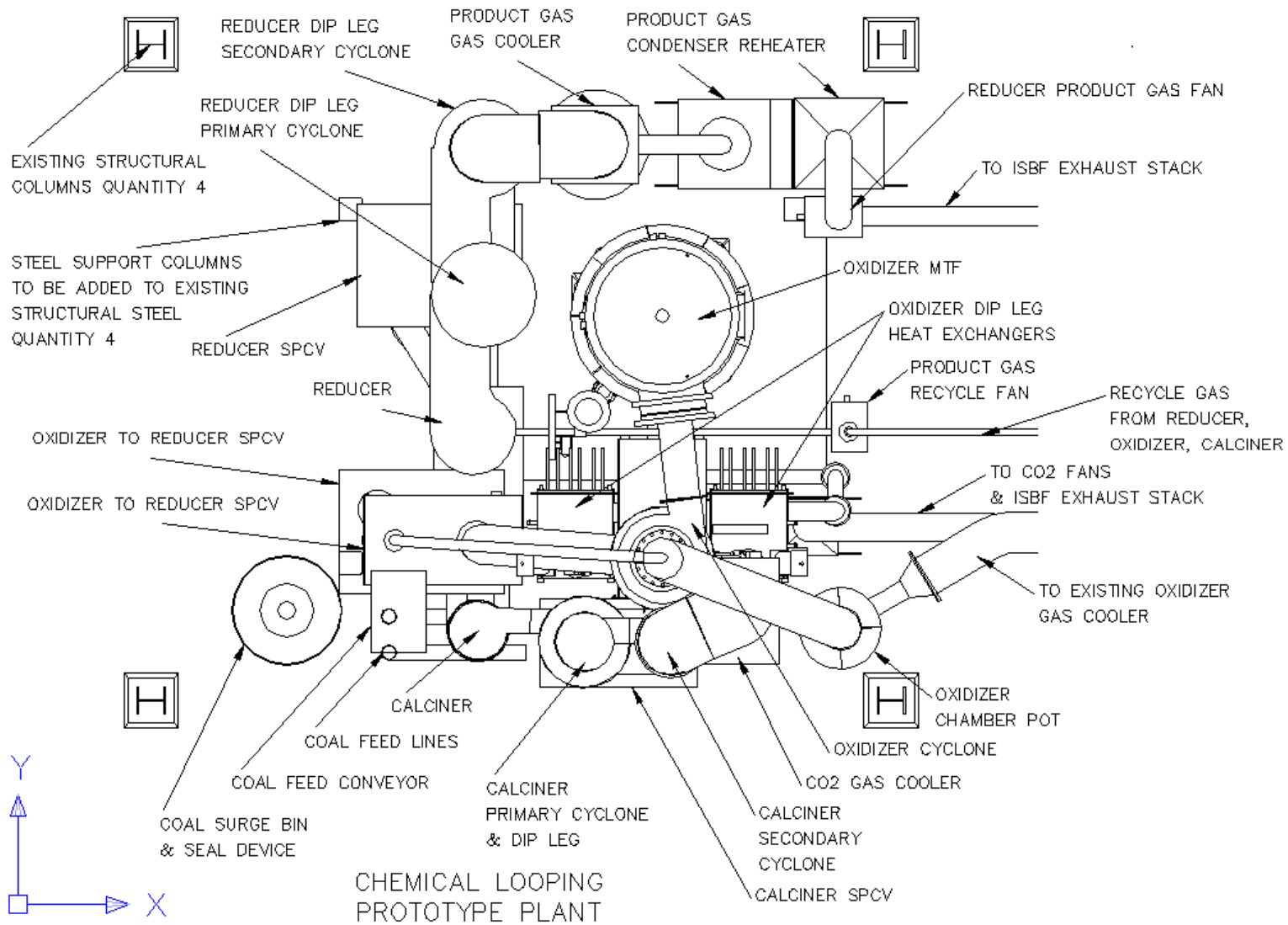


Figure 5-5 – Revised Prototype Design Using MTF – Top View

Table 5-3 - Revised Prototype Equipment List

Design "3"	Weights			
	EQUIPMENT			
	pounds	tons	pounds	tons
Reducer Reactor Vessel :				
120 Reducer Stage 1	2,081.96	1.04		
Nozzles				
bottom discharge to xover	368.85	0.18		
solids inlet	583.53	0.29		
ignitor	368.85	0.18		
121 Reducer Stage 2	8,327.83	4.16		
Reducer Stage 3	14,573.70	7.29		
steam inlet	167.66	0.08		
outlet to Pri-cyl -inlet duct	338.17	0.17	26,810.56	13.41
Reducer Pri-cycl -barrel	4,879.94	2.44		
Reducer Pri-cycl -exp	1,253.59	0.63		
110 Reducer Pri-cycl -inlet duct	1,474.87	0.74		
111 Reducer Pri-cycl -discharge	14,449.69	7.22		
112 Pri-cycl-outlet to Sec cycl inlet duct	1,106.56	0.55		
Reducer Sec-cycl -barrel	972.69	0.49		
Reducer Sec-cycl -inlet duct	1,334.24	0.67		
113 Reducer Sec-cycl -discharge	4,836.36	2.42	30,307.95	15.15
Oxidizer Vessel MTF	101,459.33	50.73		
Nozzles (included in vessel)				
Bottom Discharge to ash drain	368.85	0.18		
ignitor	368.85	0.18		
Inlet from SPCV 1	217.97	0.11		
Inlet air (-20 degree)	19.98	0.01		
Outlet to Pri-cyl -inlet duct	311.69	0.16	102,746.68	51.37
MTF cycl -Total equiv weight	3,639.88	1.82		
Oxidizer -Pri-cycl -exp	1,282.11	0.64		
305 Oxidizer -Pri-cycl -inlet-duct	1,157.77	0.58		
306-8 Oxidizer -Pri-cycl - SPCV and HX discharg	10,757.56	5.38	16,837.32	8.42
Calciner 1	2,339.13	1.17		
207 Outlet to Cal 1 cyclone	1,106.56	0.55		
Calciner 1 cyclone inlet duct	1,334.24	0.67	4,779.93	2.39
not used:				
Calciner 2				
Calciner 2 cyclone inlet duct				
208 Outlet to Cal 2 cyclone				
109 Reducer Feed Tube	22,169.76	11.08		
201 Calciner 1 lift tube	21,953.22	10.98		
Calciner 1 -cycl -barrel	1,343.03	0.67		
Calciner 1 -cycl -exp	540.21	0.27	46,006.22	23.00
not used:				
Calciner 2 lift tube				
Calciner 2 -cycl -barrel	1,343.03	0.67		
Calciner 2 -cycl -exp	540.21	0.27		
301 Oxidizer feed tube	11,941.46	5.97	11,941.46	5.97
Steam activation vessel	2,214.27	1.11		
Nozzles				
Solids Inlet from Reducer SPCV	167.66	0.08		
Solids outlet to Red stage 3	167.66	0.08		
SA Tubes	27.43	0.01	2,577.01	1.29
Reducer SPCV 1	8,320.59	4.16		
Nozzles				
Inlet from MBHE 2 overflow	737.83	0.37		
Outlet to Calciner 2	335.31	0.17		
Outlet to Reducer Stage 3	570.11	0.29	9,963.84	4.98
Oxidizer SPCV 1 (Use MTF Seal pot)	3,888.62	1.94		
Nozzles				
Inlet from Oxidizer cyclones	637.20	0.32		
Outlet to Reducer	251.51	0.13		
Outlet to recycle	251.51	0.13	5,028.84	2.51
Oxidizer SPCV 2(use MTF Seal Pot)	3,131.09	1.57		
Nozzles				
Inlet from Oxidizer cyclones	637.20	0.32		
Outlet to Reducer	251.51	0.13		
Outlet to recycle	251.51	0.13	4,271.32	2.14

Table 5-3 –Continued -Revised Prototype Equipment List

	H/X - Reducer tubes	5,523.89	2.76	5,523.89	2.76
	H/X #1- Calciner tubes	453.07	0.23	453.07	0.23
	H/X #1- Calciner tubes	6,802.22	3.40	6,802.22	3.40
		776.69	0.39	776.69	0.39
not used:	H/X#2 - Calciner tubes				
	Calciner Condenser tubes	1,119.32	0.56		
	Calciner Reheater tubes	776.69	0.39		
		1,119.32	0.56		
		776.69	0.39	3,792.02	1.90
Chamber Pots					
	Oxidizer Barrel	1,080.03	0.54		
	Oxidizer Cone	594.97	0.30		
	Reducer Barrel	1,080.03	0.54		
	Reducer Cone	594.97	0.30		
	Calciner -1 Barrel	1,080.03	0.54		
	Calciner -1 Cone	594.97	0.30	5,025.01	2.51
not used:	Calciner - 2 Barrel				
	Calciner - 2 Cone				
Fans Blowers and (
	FD Fan				
	Oxidizer ID Fan				
	Reducer ID Fan				
	Calciner Vacuum Pump.	2,850.00	1.43		
Piping					
	103 Steam Inlet	5,029.65	2.51		
	123 Solids Supply	388.21	0.19		
	110 Outlet to Pri-cyl -inlet duct	586.70	0.29		
	104 Reducer recycle gas	7,545.39	3.77		
	105 Reducer air	668.22	0.33		
	106 Reducer Start up burner air	87.75	0.04		
	107 Reducer start up gas	87.75	0.04		
	108 Fuel, Limestone Feed	688.47	0.34		
	108 Feed Cyclone	152.21	0.08		
	114 Feed dipleg	7,545.39	3.77		
	115 Reducer sorbent activation HX inlet	1,073.14	0.54		
	116 Steam activation solids	1,257.56	0.63		
	117 Reducer SPCU return line	1,257.56	0.63		
	118 Calciner 2 dipleg	3,772.69	1.89		
	119 Reducer feedline	1,662.73	0.83		
	122 Oxidizer crossover dipleg	7,545.39	3.77		
	202 Calciner 1 recycle gas	7,545.39	3.77		
	204 Calciner 2 recycle gas	7,545.39	3.77		
	205 Calciner 1 air	334.11	0.17		
	206 Calciner 2 air	334.11	0.17		
	302 Oxidizer return	1,344.70	0.67		
	303 Oxidizer air	222.74	0.11		
	304 Oxidizer start up gas	87.75	0.04		
	309 Oxidizer start up burner air	222.74	0.11		
	401 Recycle gas	6,287.82	3.14		
	501 Fuel transport gas	890.96	0.45		
	502 Oxidizer cyclone outlet	1,257.56	0.63		
	505 Calciner 1 ID fan inlet	1,625.42	0.81		
	506 Calciner 2 ID fan inlet	1,625.42	0.81		
	507 Oxidizer ID Fan inlet	2,982.98	1.49		
	508 Calciner 1 CO2 condenser inlet	5,868.09	2.93		
	509 Calciner 2 CO2 condenser inlet	5,881.59	2.94		
	510 CO2 reheater inlet	5,895.09	2.95		
	511 CO2 ID Fan inlet	165.37	0.08		
	512 product gas ID fan inlet	313.86	0.16		
	504 Product ID gas fan inlet	668.22	0.33		
	503 N2 ID fan inlet	3,831.12	1.92		
	513 Combined ID Fan outlet	1,983.06	0.99		
	514 Oxidizer bed drain	668.22	0.33		
	403 FD Fan Outlet	6,979.67	3.49		
	600 non-contact cooling water	4,786.02	2.39	111,546.21	55.77
					142

5.2 Construction

The Prototype configuration for BP2 is shown schematically in **Figure 5-2**.

The 3 MWt Chemical Looping Prototype was constructed by making use of Alstom's existing multi-use test facility (MTF) which was originally configured as a circulating fluidized bed (CFB) boiler pilot plant. The existing CFB pilot (shown as blue in **Figure 5-2**) was modified to serve as the Chemical Looping Prototype's Oxidizer. A Reducer system (shown in Red in **Figure 5-2**) and additional auxiliary equipment were added to constitute the remainder of the Chemical Looping Prototype. A Calciner was planned for a future test program pending a successful outcome of Phase IVA testing and funding availability.

The equipment arrangement drawings, process flow diagrams and the design engineered equipment and auxiliary systems were completed. Equipment configurations were updated to match process requirements. Plans for auxiliary systems such as cooling water, air supply, recycled product gas, startup natural gas and other systems were completed. Equipment used in the auxiliary systems was selected. Weights and heat loss calculations were updated. Final cost studies and design tradeoffs were completed to ensure that the Prototype could meet the budget and experimental objectives.

Detailed drafting of the fabricated process equipment was completed and procurement was done. Structural steel design was completed and design of the equipment support and reinforcement system was completed. Controls engineering proceeded in parallel with installation of controls and instrumentation.

Prototype Procurement and Installation

The MTF's circulating fluid bed (CFB) was modified to serve as the Oxidizer (**Figure 5-2**) of Chemical Looping Prototype. A drawing showing the current MTF configuration and the Prototype is shown in **Figure 5-6**.

Procurement and installation of the Prototype was completed in December 2010. A schematic showing the current MTF configuration and the constructed Prototype is shown in **Figure 5-7**.

The MTF modification involved reducing the inside diameter of the CFB from 40 inches to 15 inches. **Figure 5-8** shows the lower sections of the Oxidizer before modification and **Figure 5-9** shows the same nearing completion at LVR, the refractory fabricator.

Figure 5-10 shows the Reducer main SPCV under construction. To the left in **Figure 5-11** is the Main seal pot control valve (SPCV) prior to being lifted into place on Elevation 22 of the steel. To the right is the top of the Oxidizer after installation of the new refractory lining.

Figure 5-12a on the left shows the cactus and Reducer gas injection nozzles ('Octopus') before lifting into the steel. On the right **Figure 5-12b** shows the Main SPCV, the lower Reducer section and the pressurizing column lower SPCV after installation on Elevation 22.

Figure 5-13 shows the nearly completed Primary and Secondary Cyclones under construction. **Figure 5-14a** (left) shows the upper Seal Pot Control Valve (USPCV) being installed. **Figure 5-14b** (right) shows the Reducer Bottom Outlet (RBO) after installation. The RBO transfers solids to the Oxidizer. **Figure 5-15** shows the Reducer primary and secondary cyclones installed on Elevation 61 of the steel. **Figure 5-16** shows the product gas condenser (left) and Reducer chamber pot (right)- during installation.

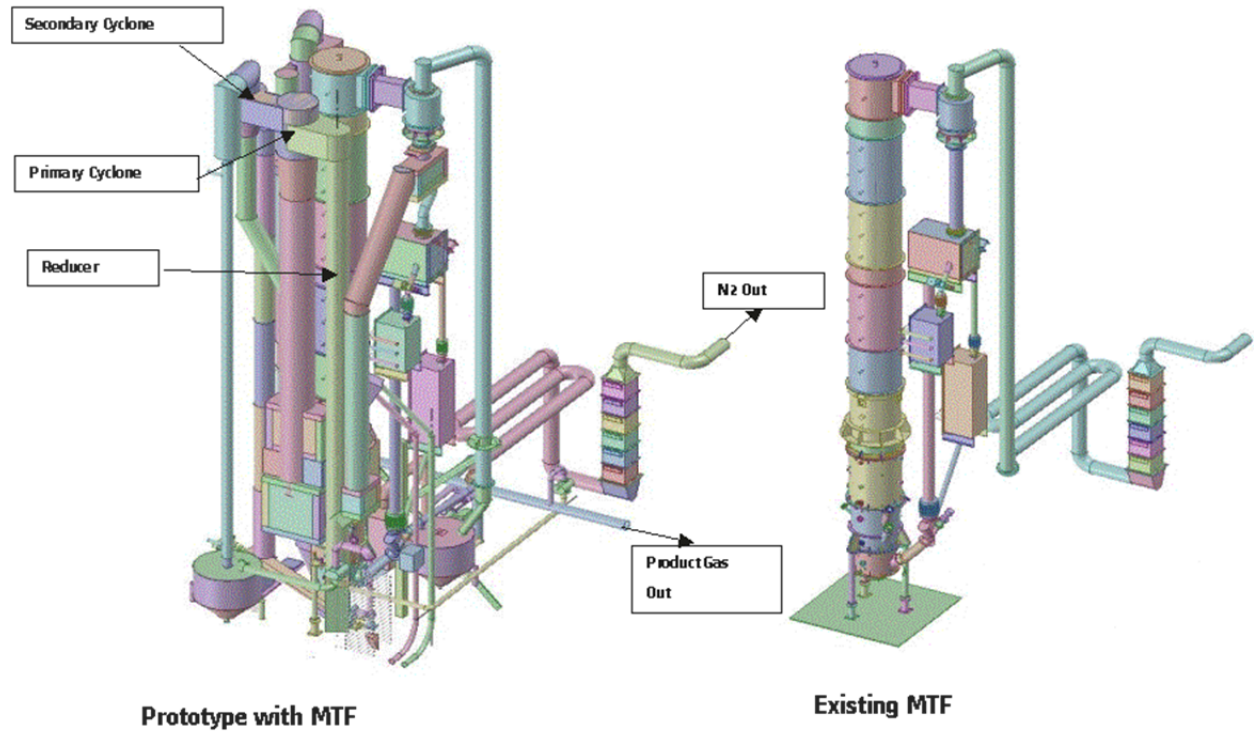


Figure 5-6 - MTF Modification to Chemical Looping Prototype

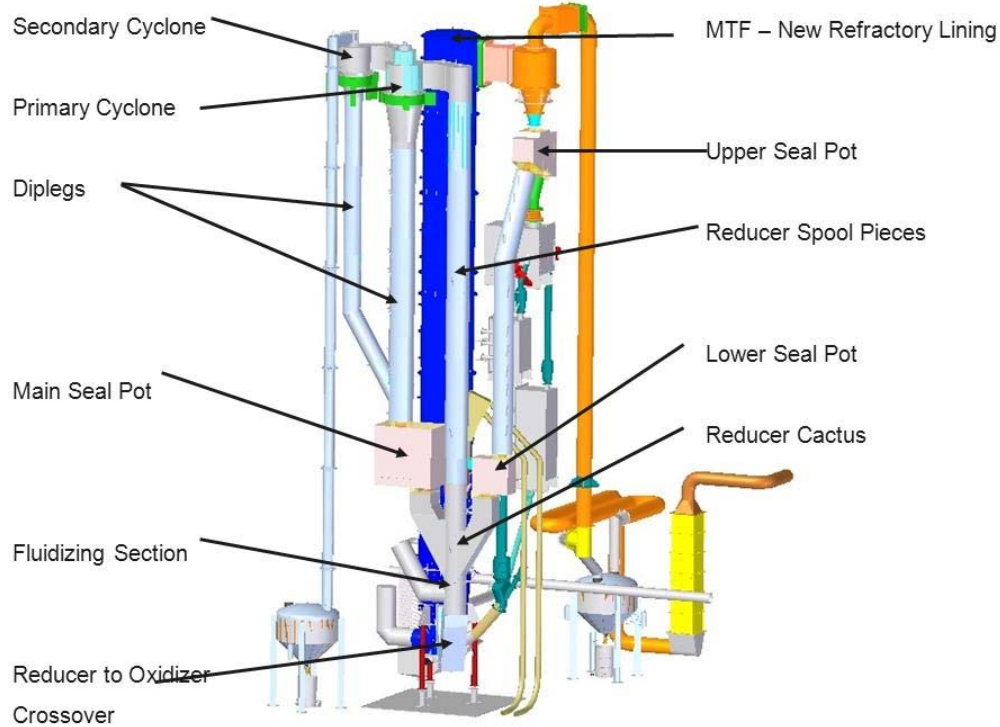


Figure 5-7 - 3-D Perspective View of the Prototype Facility



Figure 5-8 – Oxidizer before modification with refractory removed



Figure 5-9 – Lower Oxidizer refractory installation by LVR



Figure 5-10 – Reducer main SPCV under construction



**Figure 5-11a (left) – Modified Oxidizer Lower Section Installed and Main SPCV before lift
Figure 5-11b (right) - Top of Oxidizer after new refractory installation**



Figure 5-12a (left) – Cactus and Lower Reducer
Figure 5-12b (right) – SPCVs and lower Reducer installed



Figure 5-13 – Primary and Secondary Cyclones during fabrication

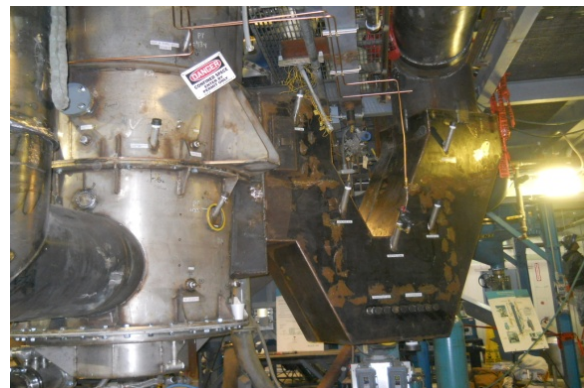


Figure 5-14a (left) – USPCV being installed
Figure 5-14b (right) – Reducer Bottom Outlet



Figure 5-15 – Reducer Primary and Secondary Cyclone



Figure 5-16 – Product Gas Condenser (left) and Reducer Chamber Pot (right)

Modifications made to the Prototype after Testing

As testing proceeded, several modifications were made to the prototype based on operating results, as described in Section 7. The major equipment changes were made to make operation of the prototype easier. No major process changes had to be made. The equipment changes made were:

- The fuel feed system was changed to give a higher length to the fuel feed pipe. The changes included:
 - raising the height of the coal conveyor discharge,
 - increasing the size of the rotary valves,
 - increasing the distance between the rotary valves and
 - designing a water cooled inlet pipe with a silicon carbide liner for the final coal chute into the reactor.

The old and the revised configuration of the fuel feed system is shown in **Figure 5-17**.

- The Oxidizer Cyclone was moved to be directly over the Lower SPCV. This made the RPC into a straight vertical drop for the solids from the Oxidizer Cyclone to the Lower SPCV. Originally the RPC had a short 60 degree slanted section from where the Oxidizer cyclone was located. The bend in the RPC seemed to cause solids to stop flowing so it was replaced by a straight section. This is shown in **Figure 5-18**.

The current arrangement of the Prototype is shown in **Figure 5-19**. A composite picture of the prototype is shown in **Figure 5-10**. This composite picture was comprised of individual photographs taken at each level in the building structure with blacked-out sections where the prototype was obscured by steel.

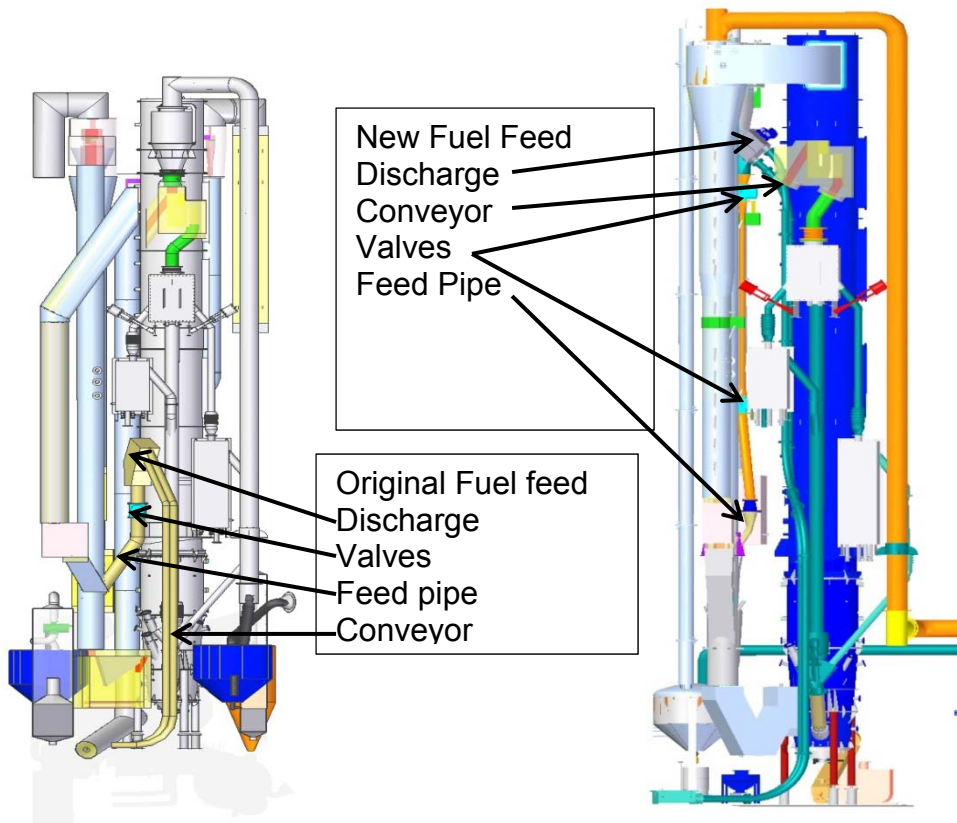


Figure 5-17 - Old and New Fuel Feed systems.

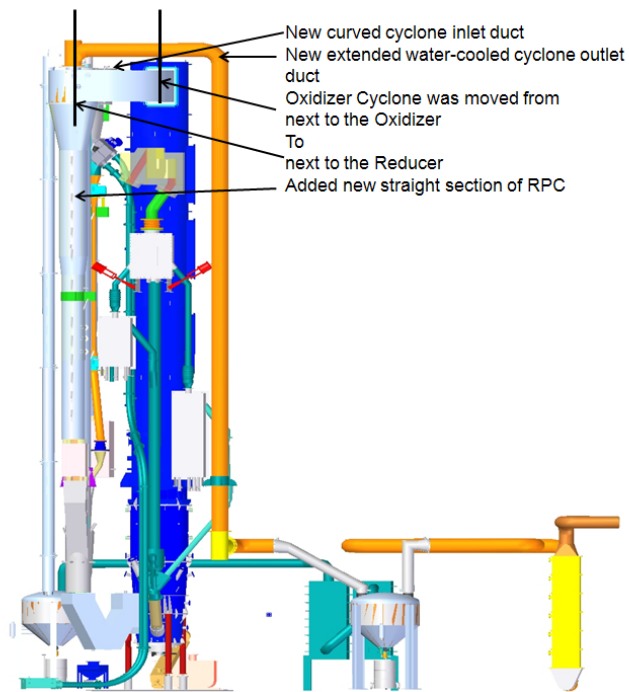


Figure 5-18 - 3-D Arrangement of the Prototype with Modifications

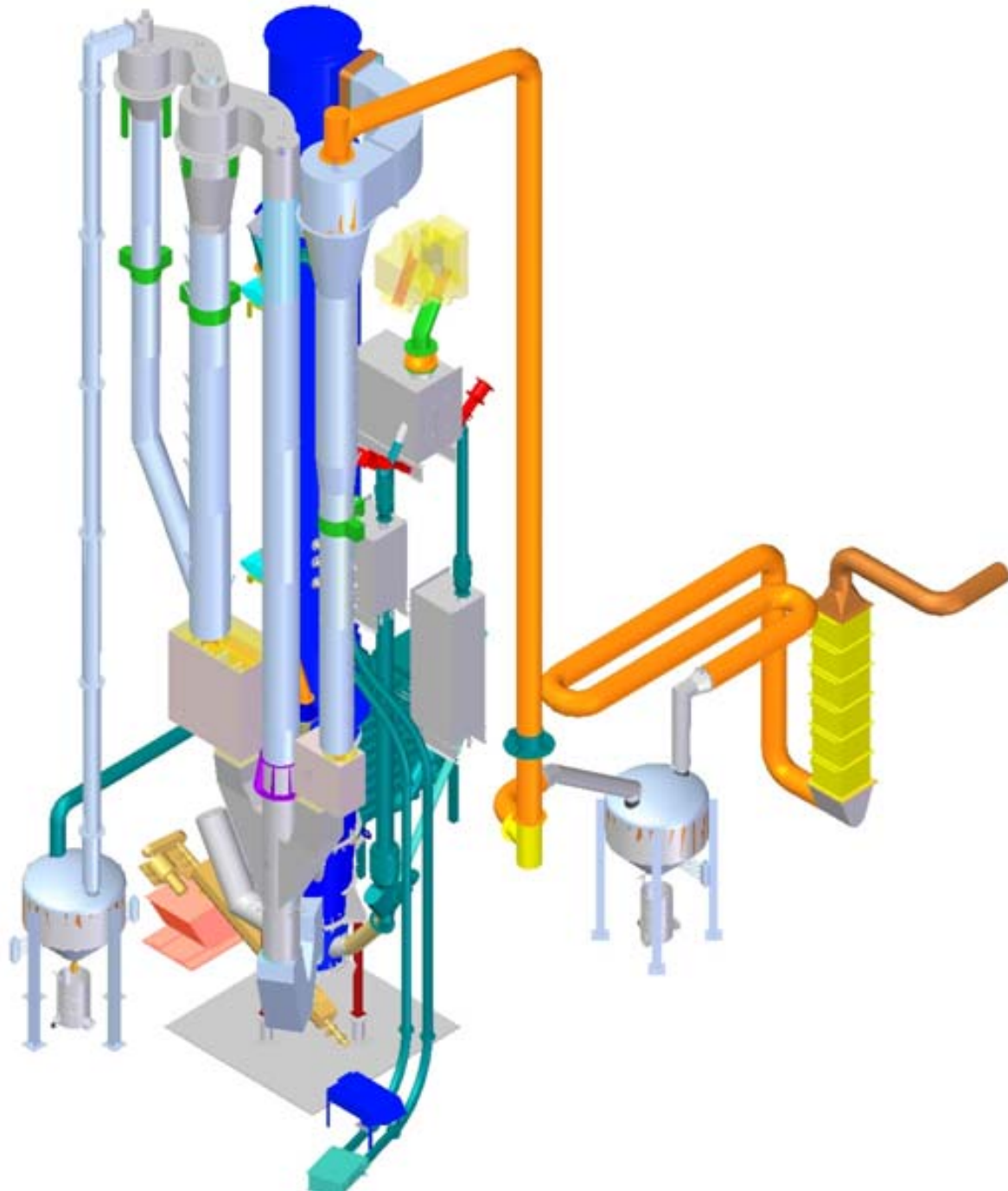


Figure 5-19 – Current Arrangement of the Prototype



Figure 5-20 – Composite Picture of the Prototype

6. Cold Flow Testing

6.1 Cold Flow Modeling Goal

The goals of the Cold Flow Modeling (CFM) are to analyze and visualize solids transport in Alstom's chemical looping process, and to develop methods to transport, distribute and control solids flow for the operating loops. The specific needs are to establish a controllable and stable performance in the operating range, maximize solids flow control range for the given pressure system and minimize pressure drop for each looping system.

In Phase IVA, the cold flow models were developed to serve as tools for:

- Integrating the new Oxidizer loop into the existing cold flow model Reducer loop to form a complete solids circulation loop similar to the prototype unit,
- Trouble shooting for the prototype unit,
- Verifying the conceptual design of the prototype for the solids transport in multi-loop operation,
- Demonstrating the operation methodology in multi-loop CFM operation including the start-up, shut-down and control stability of the system,
- Establishing operating guidelines for the prototype unit multi-loop operation as a training tool and as a trouble-shooting device.

6.2 Cold Flow Model Design and Construction

The original 40 ft. CFM is shown in **Figure 6-1**. This version of the 40 ft. CFM had a single loop solids circulation and two cyclone stages in series for gas/solid separation. The Prototype version of the CFM is based on the existing 40 ft. loop CFM. It includes a complete multi-loop solids circulation system, including Reducer riser and dip-leg, Oxidizer riser and dip-leg, a pressure seal pot control valve (SPCV) between the Oxidizer return and Reducer (called the Reducer Pressurizing Column (RPC)), a Reducer Bottom Outlet (RBO) to the Oxidizer and a Reducer section connecting all vessels together (called the cactus for the shape of junction). These connections include the Reducer return from the main SPCV, and the Oxidizer return from the RPC SPCV. Solids split into two streams in the cactus, the up-ward solids flow to the Reducer riser, and the down flow to the Oxidizer through the RBO SPCV. The complete system is shown schematically in **Figure 6-2**.

The existing 40 ft. CFM loop served as the Reducer loop with two cyclones in series for separating product gas and solids. These two high efficiency cyclones were used to capture fine particles from the Reducer riser. Separated solids from cyclone was collected in the cyclone dip-leg, which moves downward like a fixed bed and also serves as pressure seal. Solids flow in the dip-leg is controlled by an SPCV before returning to the cactus. A new Oxidizer loop, 3.5 inches in diameter, was added. A single cyclone is used in the Oxidizer loop. The Oxidizer was designed to include an internal circulation loop. An upper SPCV is used to control solid flow between the

Oxidizer's own solids circulation and the solids return flow through the RPC. Solids flow returning to the cactus is controlled by an SPCV at the bottom of RPC. An extended pipe section under the cactus consists of the Reducer riser gas inlet (Octopus) and the passage for solids transferred to the RBO and Oxidizer. The shape of cold flow model RBO exactly simulates the prototype RBO, which was tailored to the available space in the MTF.

Figure 6-3 shows components of the Oxidizer loop and the rest of the connecting vessels arranged on the floor before construction. The completed assembly of the CFM test facility for the chemical looping prototype is shown in **Figure 6-4** with key components identified.



Figure 6-1 - 40 Foot Cold Flow Model with a 4" Riser

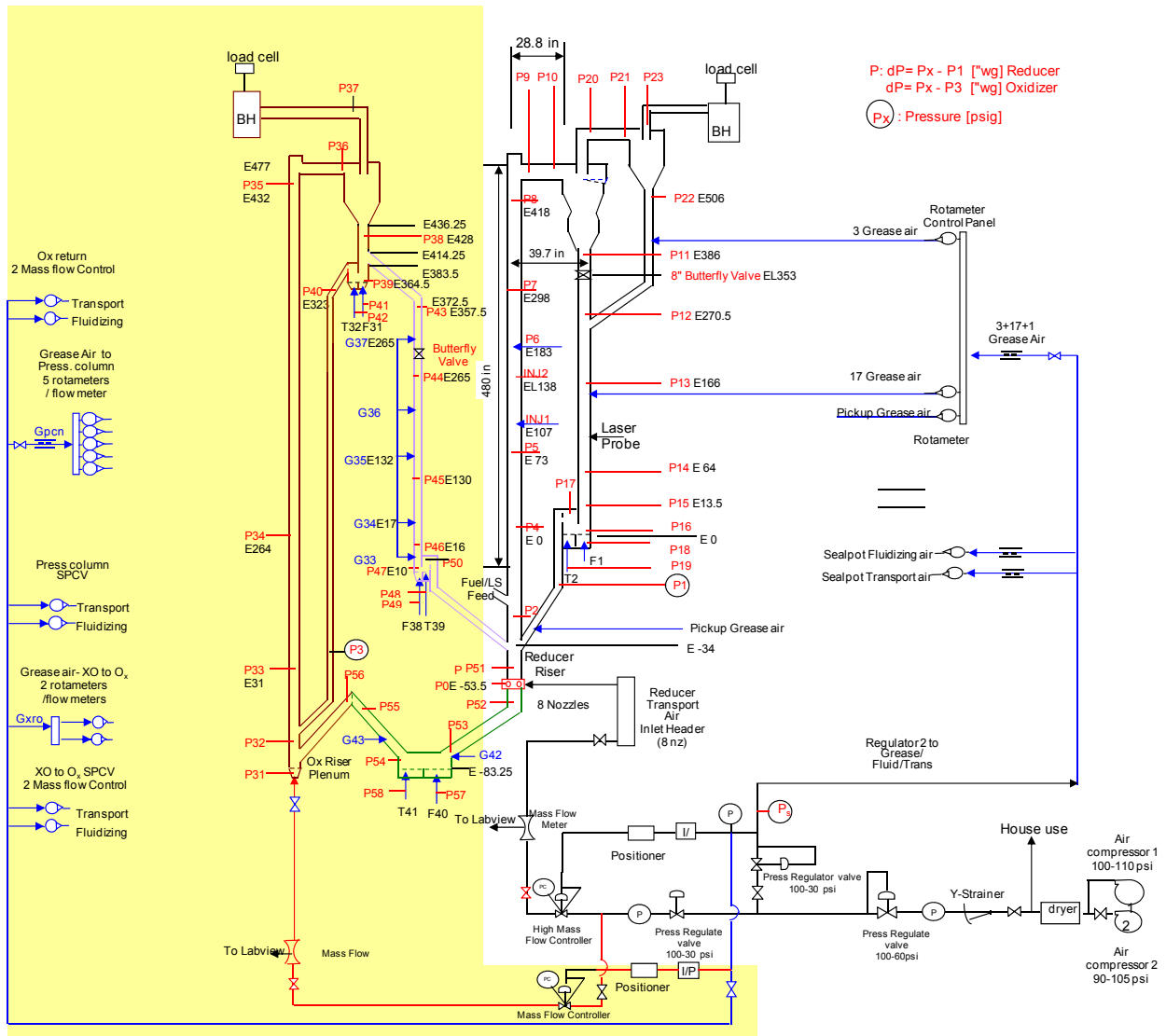


Figure 6-2 - Process Diagram of the 40 Foot Cold Flow Model of the Prototype

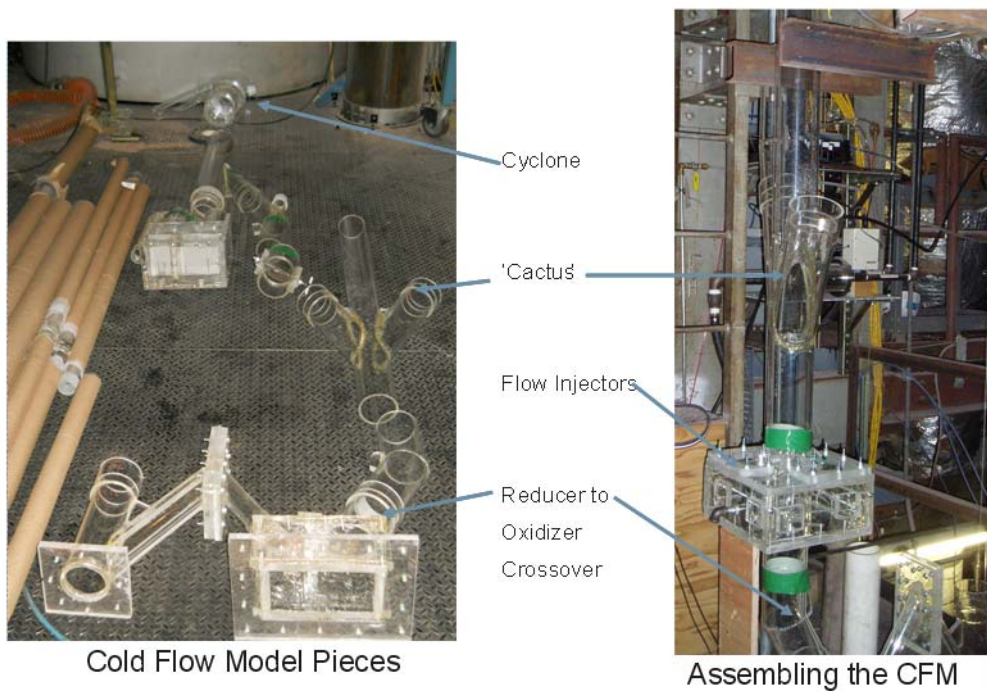


Figure 6-3 - Layout of CFM Components before Construction

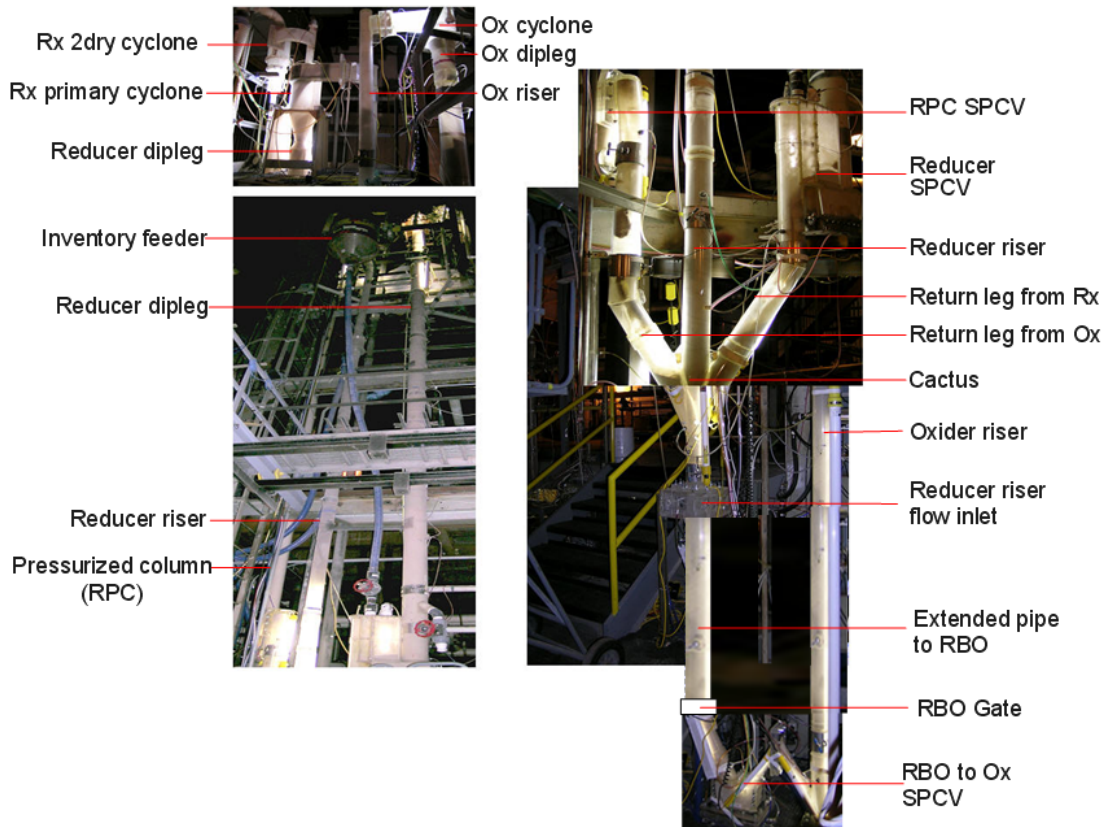


Figure 6-4 - Multi-loop CFM for the Chemical Looping Prototype

6.3 Cold Flow Tests and Training

All test data was automatically logged in a computer server for a selected time period. Typical data logging is set for 1 second for recording one complete set of data. The chemical looping CFM was first calibrated and zeroed before the first test, including measurements of pressure, temperature, and flow rate. The control station including one PC, one server, and four cameras recording the system is shown in **Figure 6-5**. Because of the natural strength of plexi-glass, the total inventory remained constant during the test.



Figure 6-5 - Control Console for the CFM

The CFM was used to train the operators of the prototype unit to familiarize themselves with operation, control of gas and solids flow, and response of solid movement relating to pressure.

6.4 CFM used as trouble shooting tool for prototype operation

6.4.1 Coal feed into pressurized reactor

The CFM was used to analyze a coal feed problem at the prototype. During the prototype testing in November 2010, coal was lifted by the conveyor into a transition bin before entering the 4-inch feed pipe. Coal flow was controlled by two sequential arranged rotary valves before entering the 60 degree slope feed pipe into the Reducer. The bottom rotary valve had significant wear resulting in enlarged clearances and hot gas leaking to the fuel feed pipe. Because of the high temperature, coal was clogged up at the entrance to the Reducer. **Figure 6-6** shows the coal feed pipe at the prototype during a hot test when the pipe became hot enough to glow red.

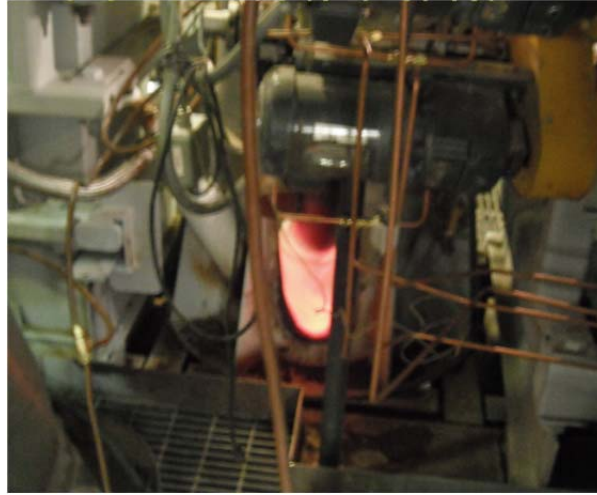


Figure 6-6 - Coal Feed Pipe Overheating due to Failed Solids Seal

To simulate the prototype feeding, the CFM unit was set up to run high circulation solids flow in the Reducer at about 200 inch water gage at the cactus near the bottom of the Reducer riser. Solids were fed continuously into the main solid control valve (SPCV) exit port from the bin feeder. The height for the solids feed hose, as shown in **Figure 6-7** was adjusted for the feed-pipe connecting feeding bin and SPCV. It was found that about 10 ft. to 15 ft. net pipe height would sufficiently seal the required pressure in the cactus region, depending on the solid bulk density tested.

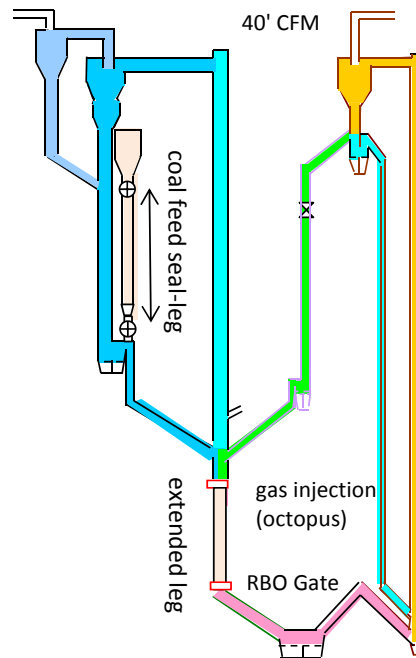


Figure 6-7 - CFM with Extended RBO Entrance leg and Coal feed Seal Leg

The result of this testing was subsequently applied to the Prototype. With the entrance section cooled by water and sufficient solids height maintained between new rotary valves, the new feeding system in the Prototype successfully fed solids into the Reducer under pressure.

6.4.2 Gas permeating from the cactus through the RBO to the Oxidizer

The solids control valve at the exit of Reducer riser bottom is called the Reducer bottom outlet (RBO) which controls the solids flow to the Oxidizer. With the original CFM layout, the distance between the octopus and the RBO is less than 3 ft., due to space limitations of the test-bay. The CFM test with the 3 ft. long pipe showed that once the cactus pressure reaches about 80"wg, the down-stream pressure in the RBO inlet showed a cyclic pattern as shown in **Figure 6-8**. This implies that gas entering from the octopus for the riser transport media may have permeated downward through the RBO to the Oxidizer. The cyclic pattern may result from the pressure impact at the RBO exit and Oxidizer riser bottom. The solids flow tries to balance two forces from different directions. Eventually the higher pressure in the Reducer cactus forced solids flow to the Oxidizer. This then resulted in a substantial pressure increase – the “runaway” shown at the end of the period shown in **Figure 6-8**. Under this condition, solids continue to circulation at a rather limited flow, controlled only by the opening of the orifice at the SPCV outlet. Although the solids circulation remained relative steady, the solids controllable range is greatly reduced.

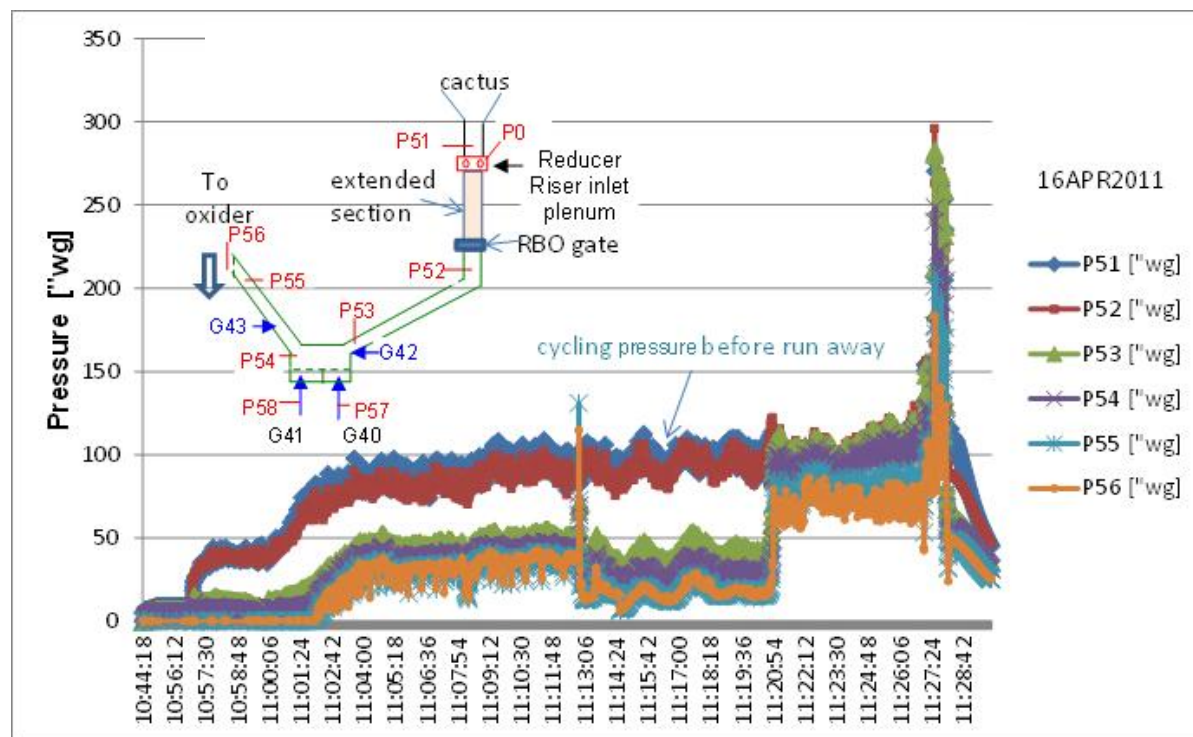


Figure 6-8 - Pressure Change Characteristics before RBO Runaway

To prove that the prototype unit actually has the same characteristics as shown in the CFM test, the section under the octopus at the CFM was extended to be at the same distance as the prototype unit for a length about 9 ft., as shown in **Figure 6-7**. Test results from the modified CFM indicated that the same characteristics were actually duplicated.

To simplify the control of solid circulation and extend the operational range of the prototype unit it was decided to add an RBO gate at the bottom of the cactus extension for minimizing or eliminating the permeation of cactus gas to the Oxidizer. The reacting gas will go up the Reducer riser and part of the solids will go down to the Oxidizer through the RBO in a counter-current flow. This should also enhance the separation of unburned carbon. The RBO gate concept was tested independently. This was shown to be very effective in separating char or coal particles from the circulating solids. The integrated RBO gate from the cold flow model will be tested later in the CFM.

6.4.3 Dip-leg Seal capability

Figure 6-9 shows a typical pressure distribution along the loops of CFM. In this example, solids circulation is very stable as demonstrated by the balanced pressure at each loop.

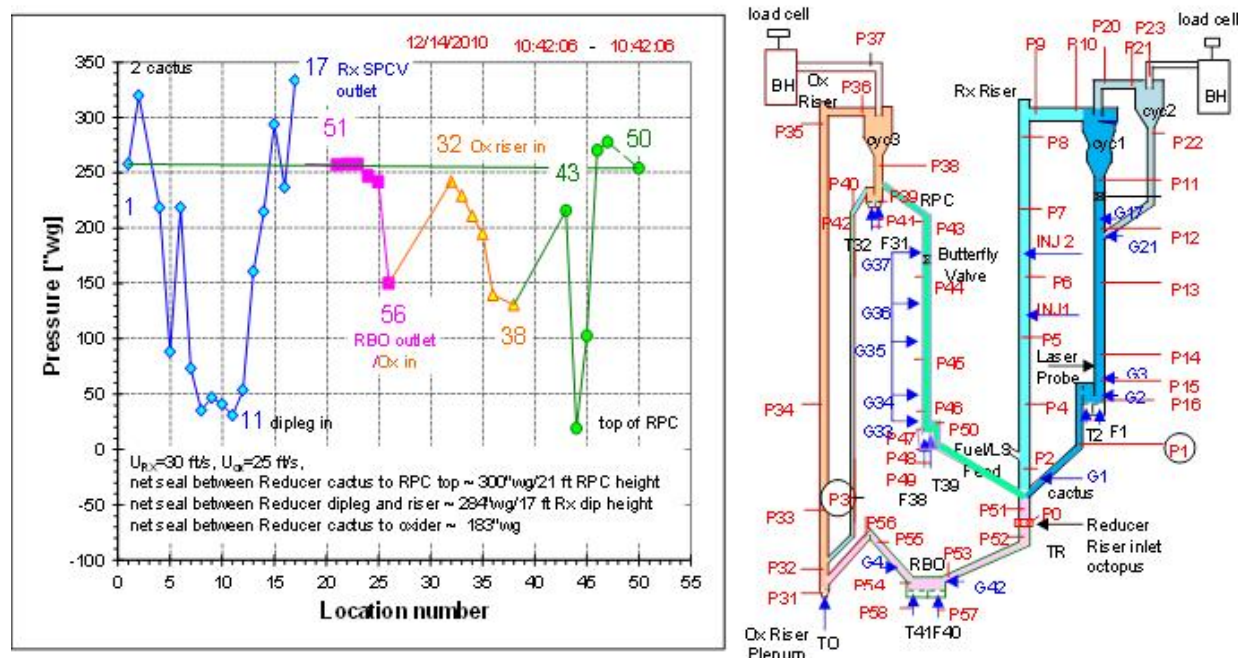


Figure 6-9 - Typical Pressure Distribution Along the Solids Loops

Notably, in **Figure 6-9**, the net pressure seal between the Reducer cactus and the RPC top is about 300''wg for a RPC height of about 21 ft. The net pressure drop between the Reducer dip-leg and riser is about 284''wg for a 17 ft. dip-leg height. The

net seal between the Reducer cactus bottom and the Oxidizer inlet is about 183"wg. The maximum capability of the pressure seal was not tested in the CFM because of the concern for lower strength of the plexi-glass, especially at the junctions bounded together by glue. Nonetheless, this test demonstrated that it is possible to seal pressure by a solids column. In this example, it is capable to seal a pressure of at least 16.7 inches water gage per foot of seal height. The practical seal capability is much higher in the prototype, which is constructed of steel.

6.4.4 Simulating the Dip-leg Seal as a Moving Fixed Bed

The total pressure drop along the dip-leg is not exactly equal to the weight of the solids column in the dip-leg, like a typical correlation by Ergun. Further analysis found that the frictional pressure drop is rather small along the dip-leg wall, but is sensitive to the frictional pressure drop created by gas passing through the densely packed fixed bed particles. The calibrated frictional factor, as shown in **Figure 6-10** is very similar to the pressure drop summarized by Zenz from data of Carman, Barkmeteff and Fesdoroff and Orman and Watson (**Reference 5**). Test data shows that for a given particle size, as gas velocity increases the Reynolds number of the particles increases. This will increase the solids circulation rate because of the decrease of frictional pressure drop through the bed. Once the gas velocity reaches the particle minimum fluidization velocity, the frictional pressure drop will be diminished, and the total pressure drop will be close to the static pressure drop as a function of bed height and gas void presented.

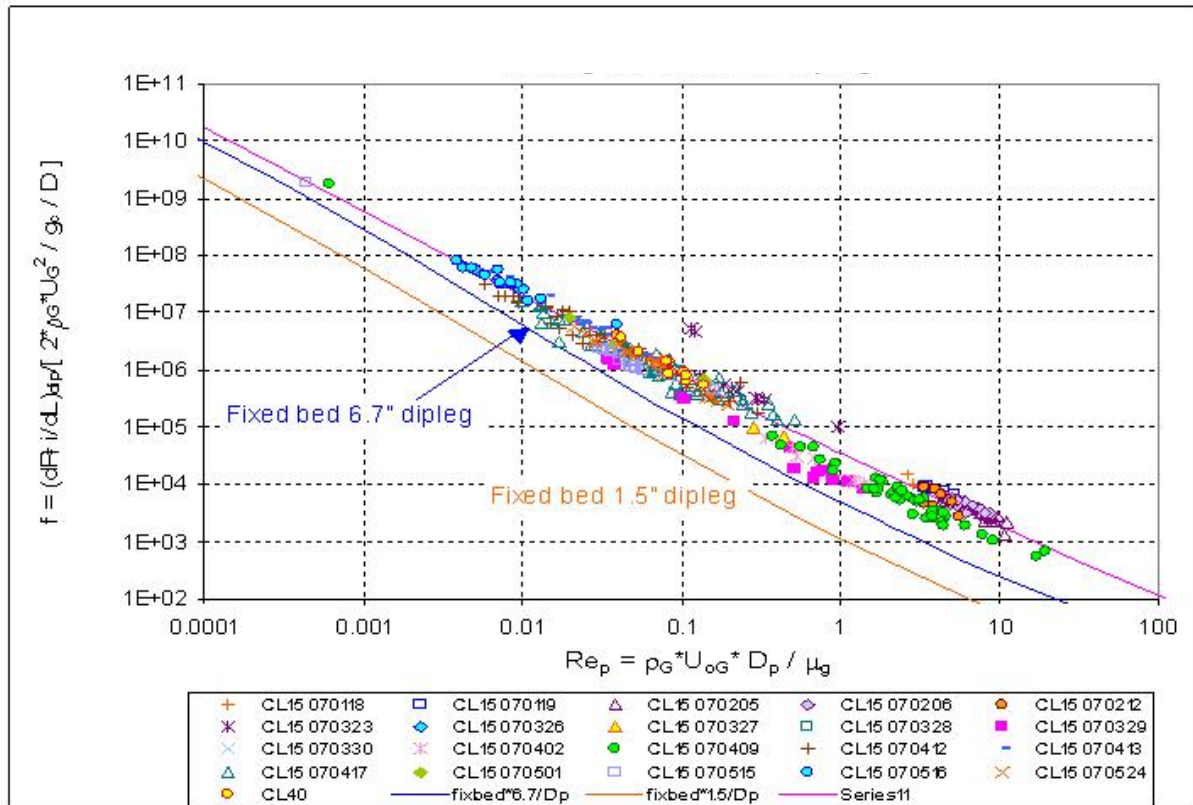


Figure 6-10 - Friction Factor versus Reynolds Number of Particles with Solids Moving as a Fixed Bed in the Dip-leg

Equation (1) to Equation (11) summarize the over-all correlation for the pressure drop in the dip-leg.

- (1) $dP_{f_bed} = dP_{dip_total} - (dP_a + dP_s - dP_{f_wall})$
- (2) $dP_a = \rho_{b_dip} * U_{s_dip}^2 / (2 * g_c) / 144 * 27.7$
- (3) $dP_s = \rho_{b_dip} * g / g_c * H_{dip} / 144 * 27.7$
- (4) $dP_{f_wall} = f_{Fanning} * H_{dip} / D_{ft} * Z_w * 144 / 27.7$
- (5) $dP_{f_bed} = f_{fxb} * H_{dip} * Z_{bed} / 144 * 27.7$
- (6) $Z_w = 2 * \rho_{g_G_dip} * (U_{g_G_dip} + U_{s_dip})^2 / g_c$
- (7) $Z_{bed} = 2 * \rho_{g_G_dip} * U_{g_G_dip}^2 / g_c / D_p$
- (8) $f_{Fanning} = f(\text{wall roughness}, Re_D)$
- (9) $f_{fxb} = (dP_{f_bed} / H_{dip}) / Z_{bed} = f(Re_p)$
- (10) $Re_D = \rho_{g_G_dip} * U_{g_G_dip} * D_{dip} / \mu_g$
- (11) $Re_p = \rho_{g_G_dip} * U_{g_G_dip} * D_p / \mu_g$

dP_{dip_total} = total pressure drop in dip-leg ["wg]

dP_a = pressure drop in dip-leg due to acceleration of solid ["wg]

dP_s = pressure drop in dip-leg due to static weight of solid ["wg]

dP_{f_wall} = pressure drop in dip-leg due to wall friction ["wg]

dP_{f_bed} = pressure drop in dip-leg due to gas through particles in the bed ["wg]

ρ_{b_dip} = bulk density of solids in dip-leg [lb_m/ft³]

$\rho_{g_G_dip}$ = maximum density of gas from grease gas [lb_m/ft³]

ρ_g = viscosity of gas [lb_m/ft-s]

$U_{g_G_dip}$ = gas superficial velocity in the dip-leg from grease air [ft/s]

U_{s_dip} = solids velocity in dip-leg [ft/s]

6.4.5 Measurement of solids flow rate by thermocouples and chilled ash

Solids velocity was originally measured with two laser beams. With the increase in vibration physically for the dip-leg, the laser measurement was found to be less robust in practical applications. A butterfly valve was used in the dip-leg to measure solids velocity with a known solids built-up time and volume. Other methods were also tried.

Typically, pressure along the dip-leg fluctuates with cycling, as shown in **Figure 6-11**.

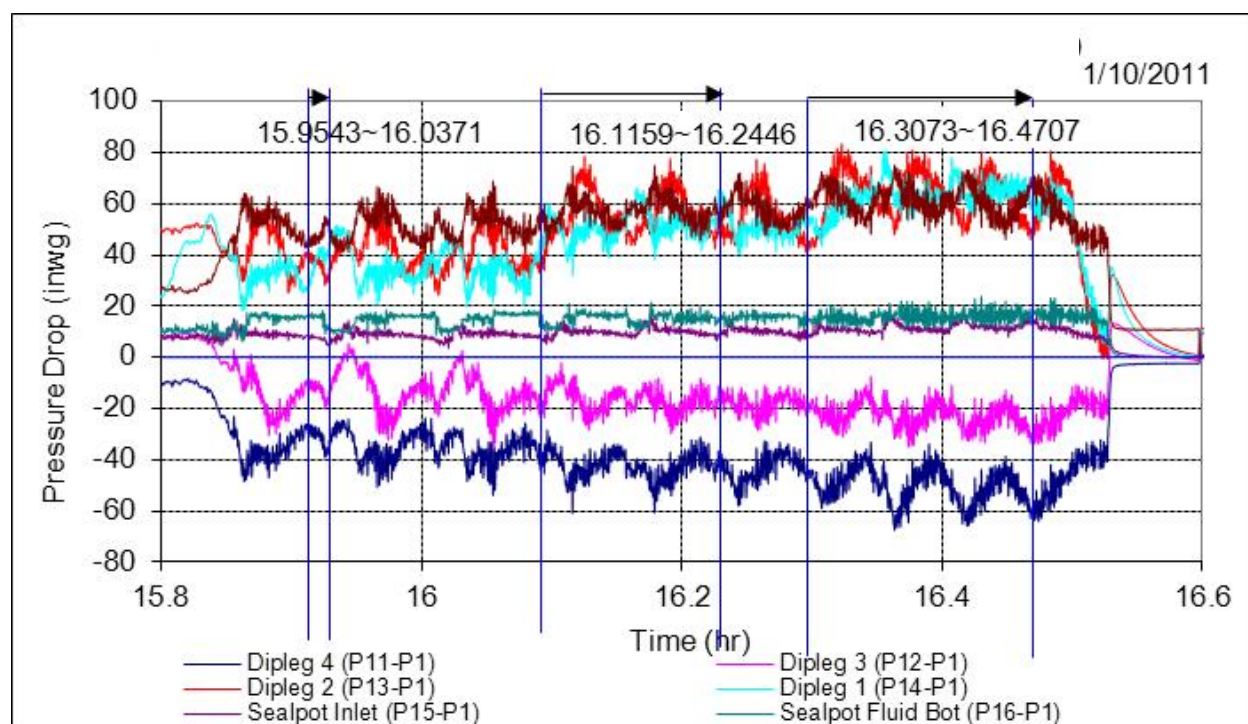


Figure 6-11 - Pressure Distribution along the Reducer Dip-leg

These cycling characteristics, reflecting solids built up in the dip-leg from cyclone separation resulted in rising pressure. Solids fluidized locally in the SPCV at the bottom of the dip-leg resulted in a pressure drop. The period of time between cycles may be used to estimate solids velocity once the dip-leg height is known. The average solids velocity calculated is about 0.09 ft/s to 0.13 ft/s in this case for number of peak of 1, 2, and 3. The pressure cycling becomes smooth as grease air along the dip-leg is increased.

An alternative way to determine solids velocity downward in the dip-leg was tried. Dry ice was tried by injecting it at top of the dip-leg during solids circulation. Temperatures were recorded as the cold gas passes through the thermocouples in different elevations. Solids velocity can be calculated by knowing the distance between thermocouples installed and the time traveled by the cold gas between thermocouples. In the test, dry ice was sublimed into the gas phase, which complicated local solid flow characteristics with the additional gas flow created.

Subsequently, solid particles were pre-mixed with the dry ice to cool the overall mixture temperature. The chilled ash particles were differentiable from the temperature of the major circulation solids. Chilled ash was then injected into the top dip-leg. The temperature change between the thermocouples indicated the timing for the front of the solids flow passing through the temperature measuring points. **Figure 6-12** shows the

typical ash temperature measured during the test. For example, in **Figure 6-12**, the time that the minimum temperature passed through the thermocouples at elevations of 200", 120", and 40" were detected at 13.5304h, 13.5882h, 13.6546h. The calculated velocity would be 0.034 ft/s between the 200" and 120" elevation, and 0.028 ft/s between the 120" and 40" elevation.

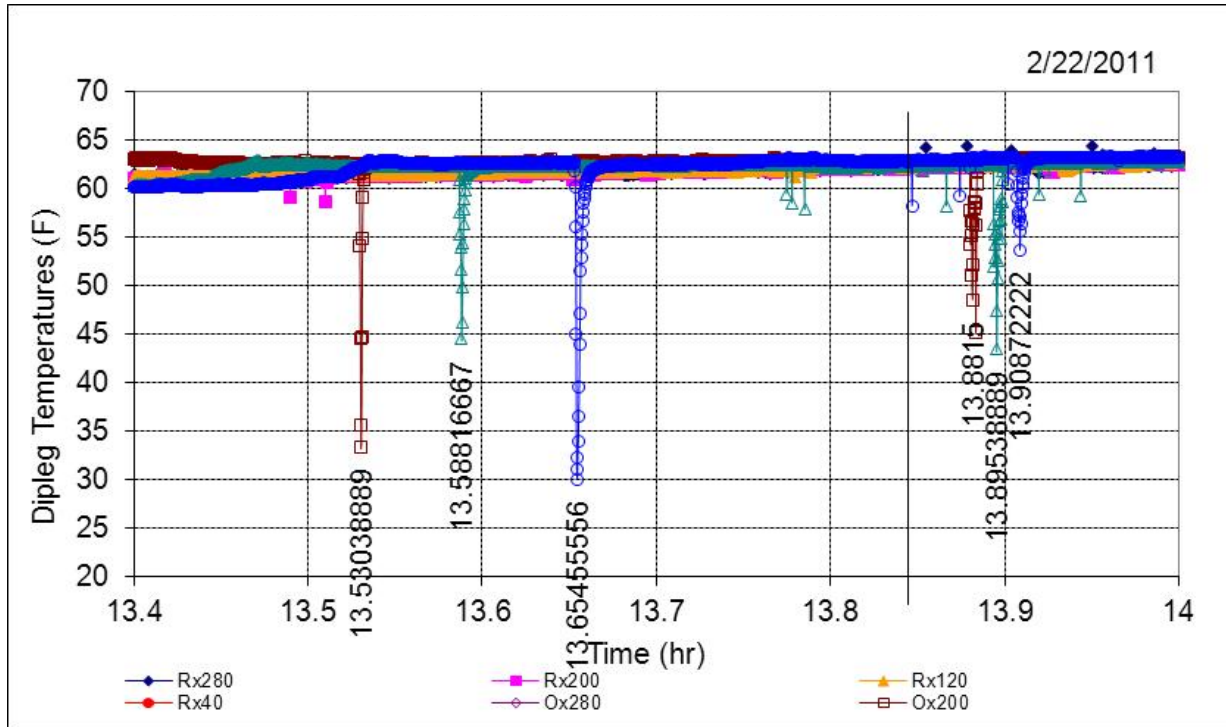


Figure 6-12 - Dip-leg Velocity Trace in the CFM

7. Prototype Testing

A Total of five test campaigns have been conducted as part of the Prototype task. Highlights of the test campaigns include:

- 12 hours of auto-thermal operation on two coals (Pittsburgh Seam 8) and Adaro (an Indonesian sub-bituminous);
- All chemical looping reactions working in a fully integrated manner;
- Total unburned carbon (UBC) consistently < 1% of the carbon in the coal
- Up to 96% carbon capture achieved at some conditions;
- Sulfur controllable to near zero for some conditions;
- Stable operation for long periods;
- Operation on 5 fuels (Pittsburgh Seam 8, Adaro, Illinois #6, wood charcoal and natural gas): and
- No major changes from Alstom's original concept or to the Prototype as originally designed and constructed were required to achieve successful auto-thermal operation.

7.1 Prototype Operation

Highlights from the operation of the Prototype are described below. A chronology of the Prototype testing is given in Appendix A, and additional details of the operation are described in Appendix B.

Shakedown of the Prototype unit commenced in October, 2010 with the commissioning of the gas analysis systems for the Oxidizer, Reducer and Reducer outlet gas flare. Shakedown proceeded in a systematic fashion, checking each component to ensure proper and complete installation as well as testing core functionality against specified design criteria. Purchased equipment such as fans, pumps, heaters, etc. were checked for operation and control. Instrumentation (Thermocouples, Pressure Cells, Mass Flow Controllers/Meters, Control Valves, etc.) were verified as to correct placement, calibration, range and communication to the DCS. Controls implemented in the DCS were vetted for performance and safety logic implementation. Fabricated components (solids control lances, riser flow nozzles and other equipment) were characterized.

Upon completion of component level shakedown, the facility was prepared to be run through a series of Air Tests. These tests were intended to demonstrate integrity of the facility flow paths, characterize the facility flow and pressure drops, as well as to define limits of operation for support equipment. These tests were also to incorporate and verify operation of additional equipment such as:

Start-up Fans - Define flow and stall characteristics
Electric Heaters - Verify operation and controllability, determine max heat input
Orifice Flow Measurements - Verify feedback, cross-check calculated flows
Recycle Gas System - Check compressor operation, control, limits, and stability

Chiller System - Check operation and control
Condensate System - Check pressure isolation, pH neutralization
Steaming Heat Exchangers – Check water flow measurements, control valves
Oxidizer / Reducer Reactors - Determine flow vs. pressure drop, limits of operation

During these tests, the natural gas warm-up burners were fired for the first time, defining their maximum heat input and operational envelope.

Following the Air Tests, several tests were initiated to validate solids preparation and handling equipment. These tests verified operation of the outside material feed system (feed hopper, roll-crushers, incline screw, bucket elevator, etc.) that would be used for both coal and ash supply to the unit. These operations included successful tests to demonstrate successful size-grading and transport of the CFB solids to the storage hopper.

In March 2011, tests were run to warm up the main loop refractory for the first time with sustained electric heater and burner operation. The solids pneumatic fill-up system was also tested and successfully used to load CFB solids into the Prototype for anticipated cold flow solids transport testing. These tests established solids fill-up procedures. Once equipment was successfully loaded with solids, tests commenced to characterize Seal Pot Control Valve (SPCV) lance flow and fluidizing performance. Once all SPCVs were full, the Oxidizer and Reducer loops could be isolated and tested independently for the first time.

Cold flow solids transport testing began in April 2011 with the goal of achieving stable dual-loop operation prior to hot testing. Initial attempts resulted in high solids loss as operators had to become familiar with the characteristics of the system. Using SPCV and air flow settings suggested by the cold flow model, operators were able to progress to a stable operating mode.

Stable dual-loop solids circulation in the Prototype was achieved on April 5, 2011 which represented a major milestone in the commissioning process.

The next series of tests was performed in mid April 2011, and was targeted at achieving stable dual-loop solids circulation in a warm-up mode, with both electric heaters and gas burners in operation to demonstrate a complete warm-up cycle of the Prototype. Solids circulation was started and run for a 24-hour period during which the process was heated slowly, starting with electric heaters and progressing through the load range of the gas burners. Overall, these tests achieved a significant amount of operator training and generated operational data which was logged for subsequent analysis.

The unit was restarted in May 2011. The unit was again run for over 24 hours with improved natural gas flow to the burners. For the first time, main natural gas injection in the Reducer was successful while circulating solids. The solid fuel feed system was commissioned and coal was fed to the process for the first time. Coal feed

rate was restricted to 100 pounds per hour with supplemental natural gas and the unit briefly reached 1450 degrees F. Syngas was made in the Reducer for the first time.

In early June 2011, the prototype was restarted. The riser temperatures were able to be raised high enough to sustain main natural gas ignition in both the Oxidizer and Reducer risers while maintaining solids circulation. The Oxidizer was heated up to full operating temperature. Coal was fired along with natural gas in the Reducer.

In mid June 2011, the prototype was restarted. Previous modifications and acquired operator experience allowed rapid warm-up to operating temperatures. Coal was fired for about an hour at rates up to 360 pounds per hour. **Chemical looping reactions were achieved on June 11, 2011.** Reducer riser air was eliminated as the recycle gas compressors were switched to recycle mode to provide transport gas for solids transport in the Reducer.

Preparations were made for a new series of test runs in August 2011. A new batch of solids was obtained from the Warrior Run CFB. The solids used in the previous tests were replaced because the extended startup testing caused size degradation and contamination.

A cryogenic CO₂ gas system was installed on the Prototype and the piping system was modified to allow selection of air or CO₂ for the Reducer riser air, Grease Fluidizing and Transport air (GFT), SAHE fluidizing air, and the coal feed chute cooling air.

The prototype was then tested in hot operation mode during the week of September 26, 2011.

The unit was restarted on October 3, 2011, achieving a full warm-up and transition to coal.

In April 2012 a new coal feed system was tested. A series of tests were performed using pulverized Illinois #6 coal to determine coal feed versus elevated rotary valve discharge pressure. The tests showed that the new coal feed system could feed coal from atmospheric pressures into a back pressure similar to the maximum Reducer operating pressure.

In May and June 2012, the 'Reducer Test' was executed, which meant running the Prototype in a "decoupled" mode. Decoupling means that the Reducer heat was supplied by supplemental natural gas firing in the Oxidizer, instead of relying solely on the Oxidizer exothermic chemical reactions to supply heat as would be the case in the auto-thermal mode of operation. In this mode the Oxidizer is being used predominantly as a heat source to maintain temperature in the Reducer. Testing and sampling were targeted at just the Reducer without having to characterize the Oxidizer at the same time. The objectives of the Reducer test were to show the Reducer chemical looping reactions and to evaluate the Reducer performance. The data produced was the coal and CaSO₄ conversions, solids recycle rate and the Reducer solids loading.

The Reducer tests were very successful. The results showed that, 1) all chemical looping reactions were realized, 2) there was a high carbon burn-up efficiency of greater than 98% and 3) there was low carbon carryover to the Oxidizer. Oxygen demand was 15 to 20%. SO₂ release can be controlled by varying the excess air to fuel ratio.

In July 2012 the Prototype was prepared for the 'Oxidizer Test' and characterization. The purpose of this test was to verify the Oxidizer reactions. The intent was to use fuels of varying reactivity in the Reducer and determine carbon carryover and CaS conversion in the Oxidizer. Various sources of calcium were used as a CaSO₄ source.

The unit was started for Oxidizer testing on July 23, 2012. During this test run, all test matrix conditions were executed, and **Auto-thermal Operation was achieved on July 26, 2012**. Auto-thermal operation was sustained for a combined total of 12 hours before the unit was intentionally shut-down.

7.2 Prototype Performance

7.2.1 Prototype Description

A schematic of the Prototype is shown in **Figure 7-1**.

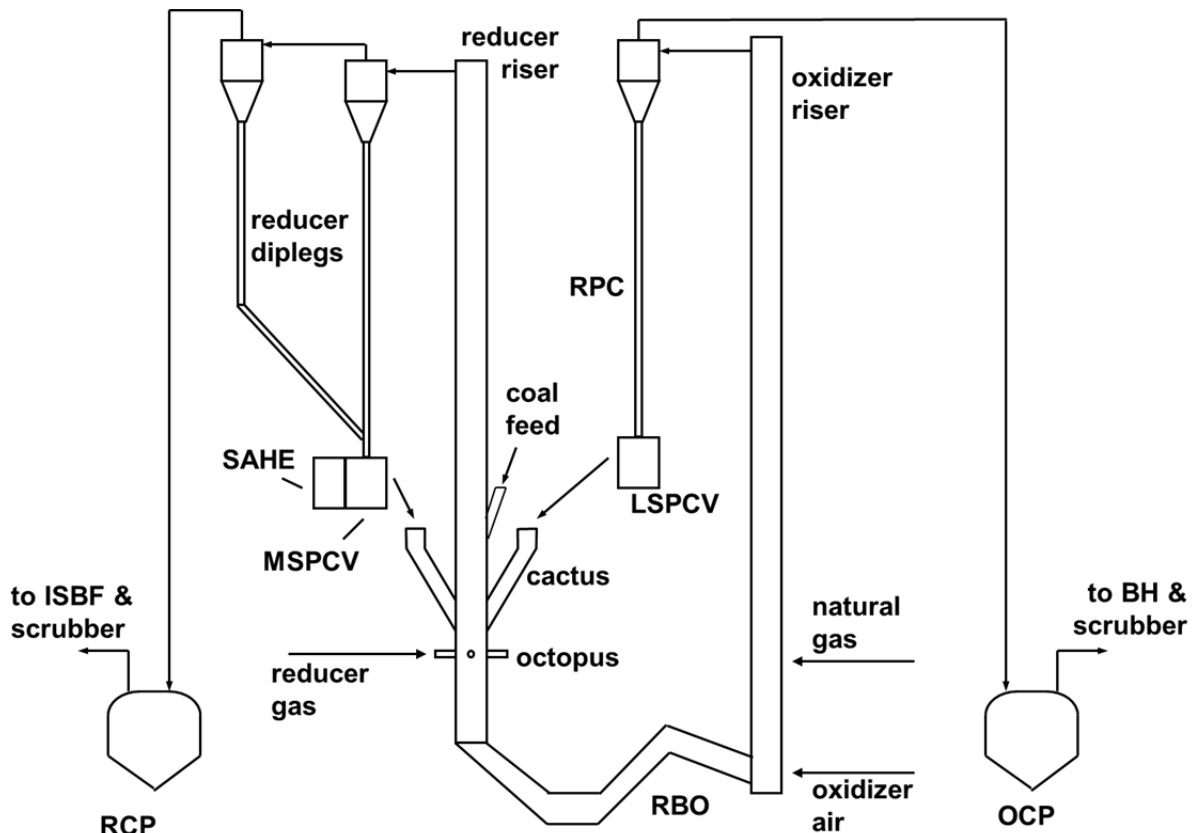


Figure 7-1 - Schematic of CLC Prototype Facility

Coal is fed into the Reducer riser along with any makeup ash or limestone. Replenished CaSO₄ from the Oxidizer enters in one leg of the cactus (named for its shape). Gas which enters the Reducer in the octopus (named for its 8 ports around the riser) transports the solids up the Reducer where the reactions take place; the main reactions being the gasification of carbon with CO₂ (Reaction 1) and the oxidation of CO by CaSO₄ (Reaction 2).



Similarly, the hydrogen and sulfur in the fuel is combusted in a multi-step process: forming reduced species (e. g., H₂, CH₄, H₂S) which may be further oxidized. Sulfur in the coal can be captured by lime from the added ash or limestone, for example, by:



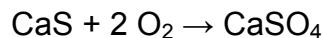
Most of the solids are separated from the gas in the cyclones and recycled to the Reducer via the main dip leg to maintain Reducer solids inventory. The Main Seal pot Control Valve (MSPCV) establishes a seal in the dip leg against the higher pressure in the Reducer. Adjacent to the seal pot is the sorbent activation heat exchanger (SAHE), which can be brought on line for heat removal and reactivation of the calcium sorbent.

A small portion of the solids entering the cyclone are lost from the system; some are caught in a down-stream knockout drum called the Reducer Chamber Pot (RCP) to protect downstream piping. Because at some test conditions the Reducer gas may contain significant amounts of reduced species (mainly CO, H₂, CH₄, H₂S), this gas is incinerated in Alstom's Industrial Scale Burner Facility (ISBF) before going to the site scrubber.

Some of the circulating solids which return through the cactus are not re-entrained, but rather fall downward into the Reducer Bottom Outlet (RBO). This rate is controlled by the seal pot control valve at the bottom of the RBO.

The Reducer regions below and above the octopus are designated Zone I and Zone II, respectively. Most of the reactions occur in Zone II. The riser is designed to take advantage of the lower density of unburned carbon compared to the bulk of the calcium solids to decant the carbon from the mixing region just above the octopus and minimize its carryover to the RBO and Oxidizer. Unburned carbon which does drop into Zone I can continue to oxidize in the RBO according to Reactions 1 and 2.

Solids entering the Oxidizer through the RBO are entrained upward by air fed to the bottom of the Oxidizer riser. Solids may be drained from the bottom of the Oxidizer to maintain solids inventory. The entrained CaS in the solids are combusted with the Oxidizer air via the following reaction:



Reaction 4

Unburned carbon not reacted in Reducer Zone II or Zone I is mostly burned in the Oxidizer.

After leaving the Oxidizer riser, the solids flow through the Oxidizer cyclone where most are separated from the gas and recycled to the Reducer via the Reducer Pressurizing Column (RPC) to supply heat and CaSO₄. A small portion of the solids entering the Oxidizer cyclone are lost from the system and are mostly caught in a downstream knockout drum called the Oxidizer Chamber Pot (OCP) to protect downstream piping. The flue gas goes to the facility's bag house fabric filter to remove fly ash that gets through the Chamber Pot before going to the site scrubber.

The prototype facility is controlled by an ABB Advant DCS with different screens available for the operators to control the systems on the facility.

Startup Procedure

The unit is filled with an initial charge of spent ash from a commercial circulating fluid bed (CFB) boiler – currently ash from the Alstom supplied Warrior Run CFB (W-R ash). The CFB ash contains spent CaSO₄, CaO and coal ash and is indistinguishable from the product created by the chemical looping process. Although the ash is inactive for CFB purposes, the CaO and CaSO₄ in the ash provide the chemical species necessary for the chemical looping reactions.

Once the unit is filled, solids circulation is started by adding air to the Oxidizer bottom and to the Reducer octopus. Two natural gas warm-up burners are started to heat each of these air streams. When the Oxidizer temperature reaches about 1300 °F, natural gas is injected directly to the Oxidizer to continue warm-up and eventually both warm-up burners are shut off. Heat up in the Reducer continues by circulating the solids heated in the Oxidizer. When the Reducer is up to operating temperature (typically 1600 – 1700°F), coal is fed to the Reducer. As the coal reacts with the CaSO₄ in the startup inventory, CaS is formed. This CaS is circulated to the Oxidizer, where it is burned to form CaSO₄. Since this reaction is exothermic, natural gas firing in the Oxidizer must be reduced to control the temperature. Coal feed is increased and natural gas injection correspondingly decreased to reach a desired condition.

At this point, the air to the Reducer is switched over to nitrogen or a mix of nitrogen and CO₂ to simulate recycle gas. Nitrogen is introduced as a tracer, as discussed in the section below.

Data Collection

Several LabView programs pull data from the Advant control system to present longer term current trends of the data for the operators and to archive the data for future analysis. Two separate archives are made: with data recorded every 5 seconds and every 1 minute. Either can be used depending on the needs of the particular analysis. Each archive is written to at least 2 locations on our network.

The archived data includes, among others,

- gas flow rates at many locations
- feed rates of coal and makeup ash
- system pressures, pressure drops, and temperatures
- cooling water flows and temperatures
- various valve positions and motor speeds
- six gas analyzer systems:
 - Oxidizer outlet (O₂, CO₂, CO, NO_x, SO₂, and in-situ, wet O₂)
 - Reducer outlet (O₂, CO₂, CO, H₂, CH₄, and SO₂)
 - Reducer outlet (O₂ and SO₂ after complete oxidation for total sulfur)
 - Reducer outlet (gas chromatograph for N₂ and Argon)
 - after burnout of the Reducer gas (O₂, CO₂, CO)
 - continuous emission monitor (CEM) at the stack (CO₂ and SO₂)

Throughout the testing, samples of solids are collected at these locations:

- feed streams – coal and makeup ash
- lower seal pot control valve (LSPCV)
- RBO inlet and outlet
- Oxidizer bottom
- Reducer and Oxidizer Chamber Pots

Not every location is sampled each time. The coal samples are analyzed for proximate and ultimate analyses and higher heating value. The other solids are usually analyzed for unburned carbon and for calcium and forms of sulfur.

To close the mass balances around the Oxidizer, Reducer, and the whole system, it is necessary to know the gas flow rate leaving each reactor. Although we have mass flow meters on each outlet stream and an orifice on the Reducer outlet, these measurements are used as checks. We determine the molar gas flow rate leaving each reactor by the nitrogen tracer method. The amount of nitrogen, N₂, leaving in the outlet gases should be the same as the measured inlet feed rates in air and/or pure nitrogen. We ignore the very small conversion of N₂ to NO_x, and either ignore or estimate the contribution of fuel nitrogen and the movement of nitrogen between the two reactors (entrained in the circulating solids).

The total dry gas molar flow leaving a reactor is calculated by the molar flow of nitrogen into the reactor divided by the fraction of N₂ measured in the dry flue gas.

For the Oxidizer, the input nitrogen comes from the measured air flow and the nitrogen content of the exit gas is determined by difference:

$$\%N_2 = 100 - \%O_2 - \%CO_2 - \%SO_2$$

For the Reducer, except during startup, we exclude air and add either nitrogen or

a N₂/CO₂ mixture. (In order to be able to do the tracer gas calculation, pure CO₂ is not used.) The nitrogen content of the exit gas is also determined by difference.

$$\%N_2 = 100 - \%O_2 - \%CO_2 - \%CO - \%H_2 - \%CH_4 - \text{Total Sulfur}$$

There is also a gas chromatograph to give a direct measurement of the nitrogen content.

The gases to the Reducer are shown in **Figure 7-2**. Air is used for startup; some tests are done with all nitrogen. For CO₂ tests, there is still a supply of nitrogen for pressurizing the fuel feed chute, for various grease, fluidizing, and transport flows (GFT), for fluidizing the sorbent activation heat exchanger (SAHE) if operating, and any additional tracer flow directly to the Reducer through the octopus.

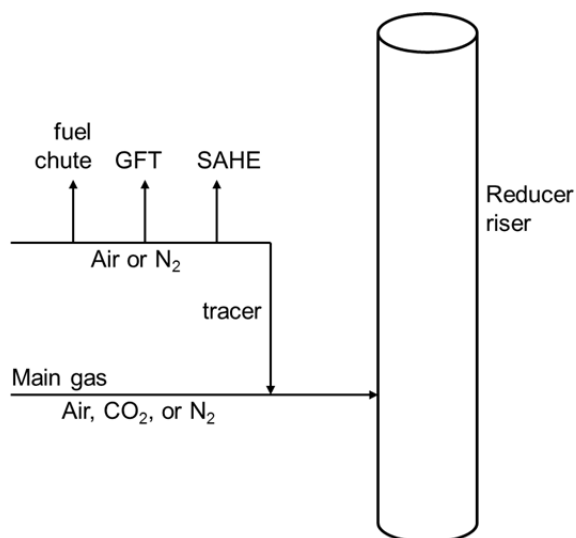


Figure 7-2 - Gas flows to the Reducer riser

7.2.2 Performance Objectives

The objectives for commercial units are shown in **Table 7-1** and described below.

Table 7-1 - Performance objectives for the LCL-C™ prototype facility

Item	PERFORMANCE ITEM	UNITS	Performance Target
1	Unburned carbon loss	% of carbon in coal	0.5
2	Reducer carbon capture	% of carbon in coal	>95
3	Carbon carryover to Oxidizer	% of carbon in coal	<5
	Sorbent reactivity:		
4	sorbent cycles since coal start (Reducer-to-Oxidizer)		~3000
5	CO ₂ content	% of carbon in Product Gas	>99.5
6	CaS burned-to-CaSO ₄ in	% required	100

	Oxidizer	CaSO ₄	
7	Oxidizer sulfur loss	ppmv	0
	Reducer gas composition:		
8	tar / hydrocarbons	ppmv	negligible
9	total sulfur (all forms)	ppmv	<10
10	CH ₄	% of carbon in Product Gas	<1
11	CO content	% of carbon in Product Gas	<0.5
12	Load	%	100
13	Reducer Cactus gas velocity	ft/sec	≤15
14	Reducer RTO gas velocity	ft/sec	≥100
15	Oxidizer gas velocity	ft/sec	≥100
16	Dip Leg solids flush coal flow limit (pc coal)	% full load	100

Item 1 - Unburned carbon loss

This is the percentage of total carbon in the coal which is uncombusted and lost either as fly ash or a bed drain stream. Meeting this goal is a prerequisite to achieving high carbon capture performance, high electrical efficiency and low cost of electricity.

Item 2 – Carbon capture

Carbon Capture measures the percentage of total carbon in the coal that ends up captured in the gas leaving the Reducer. This represents the total carbon which can be recovered for sequestration or other utilization.

Item 3 – Carbon Carryover to the Oxidizer (CCO)

This represents the percentage of the total carbon in the coal that gets carried over to the Oxidizer through the RBO. In the Oxidizer it is assumed to be combusted and leave as CO₂ in the exit gas – CO₂ which will not be captured. The Zone I / Zone II interface described above is designed to minimize the amount of carbon carryover.

The next three items refer to Sorbent Reactivity – the general ability of the CaS/CaSO₄ to accomplish its required chemical conversions.

Item 4 – Number of Sorbent Duty Cycles

Without some form of sorbent replacement or reactivation, the oxygen carrying sorbent (in our case CaS/CaSO₄) loses its reactivity with continued cyclical use.

In the case of the LCL-C™ process, fresh lime or limestone will be added to capture the sulfur in the fuel and solids will be drained to remove this captured sulfur and ash from the fuel. Thus there is a natural makeup and purge of the oxygen carrier. For example, with a typical Pittsburgh #8 coal with 2.5% sulfur and limestone added at a Ca:S molar ratio of about 2.5, most of the solids are estimated to spend less than 3000 cycles (between the Reducer and Oxidizer) before being drained.

If needed, Alstom's proprietary on-line sorbent activation process can be used to restore the reactivity of the circulating sorbent.

Item 5 – CO₂ Content of the Dry Reducer Product Gas

The intent of the LCL-C™ process is to completely oxidize the carbon in the coal to CO₂. If there is insufficient active CaSO₄, there may be unreacted CO and CH₄. The target is that more than 99.5% of the total carbon in the gas be as CO₂.

Item 6 – CaS Burned to CaSO₄ in the Oxidizer

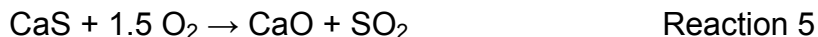
In Alstom's LCL-C™, all of the oxygen required to consume the coal in the Reducer comes from reducing hot CaSO₄ to form CaS via Reaction 2. Ideally, all of the CaS formed in the Reducer should be burned in the Oxidizer to form hot CaSO₄ for re-use in the Reducer. If the rate of CaSO₄ replenishing cannot keep up with the coal requirement, the inventory will deplete and the oxidation of carbon in the Reducer will decrease.

Item 7 – Oxidizer Sulfur Loss

The desired reaction for burning CaS in the Oxidizer is Reaction 4:



However, when insufficient oxygen is locally available, the following CaS reaction can occur which releases sulfur as SO₂ from the circulating solids:



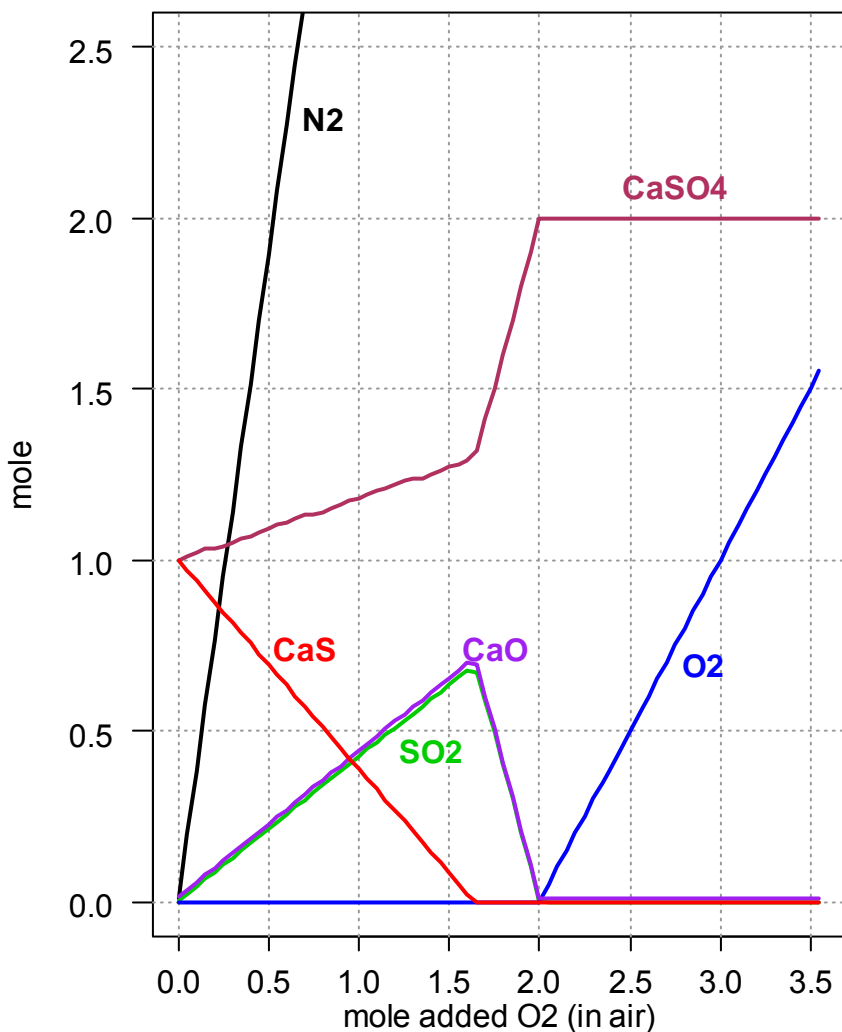


Figure 7-3 - Equilibrium predictions for the Oxidizer

Figure 7-3 shows equilibrium predictions (from the HSC Chemistry program) for 1 mole each of CaS and CaSO₄ and increasing amount of oxygen at 1903°F. Above the stoichiometric amount of 2 mole, all the sulfur is stable in the form of CaSO₄. But if there are substoichiometric regions in the Oxidizer, some CaO and SO₂ can form according to Reaction 5. Even with overall excess air in the Oxidizer, substoichiometric regions might be found in the lower riser, where the circulating solids containing CaS and unburned carbon enter. The upper reactor should be uniformly above stoichiometric conditions and some of the CaO and SO₂ could recombine to form CaSO₄.

Low levels of sulfur loss in the Oxidizer exit gas would need to be handled by flue gas sulfur removal equipment. High sulfur losses, especially above the rate of sulfur fed

with the coal, would deplete the CaSO₄ carrier and require sulfur makeup. The commercial target is for no measurable sulfur loss from the Oxidizer.

Reducer Gas Composition – Ideally, the gas leaving the LCL-C™ Reducer would contain all the carbon in the fuel as CO₂, water vapor, some fuel nitrogen, and no other contaminants. After drying, and perhaps venting the nitrogen, this nearly pure CO₂ can be compressed for sequestration. If there are additional trace quantities of contaminants, the gas processing requirements are more stringent. Significant amounts of sulfur loss in the gas are undesirable as discussed above in Item 7. High levels of fuel gases – CO, CH₄, and H₂ – will represent energy losses from the power cycle. Specific targets for the Reducer product gas composition are discussed in the following Items 8 – 11.

Item 8 – Tar and Hydrocarbon Content of the Reducer Product Gas

Tars in the Reducer gas outlet could cause problems as they condense in the downstream equipment. Any high level of higher hydrocarbons represents an energy loss from the power cycle. The target is for negligible tar and higher hydrocarbon in the Reducer gas.

Item 9 – Total Sulfur Loss

As with sulfur loss from the Oxidizer, sulfur in the Reducer gas – as SO₂ or as reduced sulfur species – will require downstream removal, and large losses will deplete the CaSO₄ carrier and require sulfur makeup.

Although our goal is to achieve as low a sulfur loss as possible, our current economic studies do include sulfur control on both the Oxidizer and Reducer outlets.

Item 10 – CH₄ in the Reducer gas

The target is less than 1% of the total carbon in the gas as methane.

Item 11 – CO in the Reducer gas

The target is less than 0.5% of the total carbon in the gas as CO.

Item 12 – Load (% of Design Coal Flow)

The Prototype is designed to operate at a coal heat input of 10 MMBtu/hr. The target is to operate the prototype at the full design load.

Item 13 – Reducer Cactus Gas Velocity

It is desirable to operate with a minimum of lift gas added to the Reducer Octopus nozzles that are placed just below the Cactus mixing zone (see **Figure 7-1**). The lower the cactus gas velocity, the less recycle CO₂ and/or steam is required – the bulk of the riser transport gas is generated from the coal combustion, thereby improving performance and economics. The target for the velocity at the Cactus – based only on the added gas – is 15 ft/sec.

Item 14 – Reducer Top Outlet (RTO) Gas Velocity

In order to have a compact design, there is a target for the Prototype to operate

at 100 ft/sec at the top of the Reducer riser while still maintaining the required solids inventory in the Reducer riser.

The velocity determines the gas residence time in the Reducer – it will be on the order of 1 to 2 seconds. This must be sufficient to allow reaction of reduced species, such as CO, H₂, and CH₄, to react with the CaSO₄ in the riser. The single pass solids residence time in the Reducer riser will also depend on the gas velocity, but will be several times larger than the gas residence time because of slip between the particles and the gas. One pass through the Reducer will not be sufficient to burn out the carbon from the coal. The carbon conversion depends on a sufficient solids inventory in the entire Reducer loop and retaining the carbon in the loop for multiple cycles.

Item 15 – Oxidizer Top Outlet (OTO) Gas Velocity

In order to have a compact design, there is a target for the Prototype to operate at 100 ft/sec at the top of the Oxidizer riser while still maintaining the required solids inventory in the Oxidizer riser.

Item 16 – Reducer Main Dip Leg Solids Flushing Coal Flow Limit

Circulating solids captured by the Reducer cyclones are returned to the Reducer at the cactus. Since the Reducer at the cactus is at a higher pressure than the cyclone, it is necessary to establish a seal. This is done in the main seal pot control valve (MSPCV) to maintain a head of solids in the dip leg. Since the circulating solids contain CaSO₄ and some unburned carbon, gasification continues to occur in the dip leg, generating additional gas. As the coal feed rate increases, the amount of unburned carbon and generated gas may also increase. As a result, the amount of fluidizing gas in the MSPCV should decrease. If the gas flow is too high, a column of solids cannot be supported – they flush right out of the dip leg. It is possible that at some coal feed rate, the generated gas alone may be high enough to flush the dip leg. The target is to be able to operate the prototype at full load without dip leg flushing.

7.2.3 Prototype Testing Plans and Chronology

7.2.3.1 2011 Testing and results

Test plans for 2011 involved commissioning of all systems to enable coal firing, initial coal firing tests aimed at gaining operating experience and determining chemical looping performance. These objectives were successfully completed. Plans for 2011 called for operating the Prototype auto-thermally. However, due to equipment limitations previously described, auto-thermal operation was not achieved until 2012.

Three coal test campaigns were carried out during 2011. The first coal test (May 2011) showed that natural gas flow to the warm-up burners was below design levels, impeding coal-fired startup. With burners fixed, the June 2011 coal test showed that the chemical looping reactions were taking place (with support of natural gas firing in the Oxidizer). This test indicated reaction rate performance similar to that observed during testing of the 65 kWt process development unit (PDU), **Reference 1**, Phase I Report.

As described earlier, the third coal test series (September-October 2011) revealed deficiencies in the coal feed system (which caused coal feed interruptions) and the Reducer pressurizing column (which caused solids re-circulation interruptions). Although troublesome, this test series provided valuable operator training, improved data acquisition and analysis capabilities and provided data important to future test design.

7.2.3.2 2012 Testing

The goals for 2012 were to

- verify the Reducer reactions
- verify the Oxidizer reactions
- operate with fuels of different sizes and reactivity's
- achieve auto-thermal operation

Several systematic tests were planned, to concentrate separately on the Reducer performance, the Oxidizer performance, and finally to achieve auto-thermal operation. It turned out that auto-thermal operation was achieved early, so the last test was used to study sulfur capture and retention which is critical to the success of the process.

Five different fuels were fired in the 2012 tests:

- crushed charcoal,
- crushed Adaro coal,
- crushed Pittsburgh #8,
- pulverized Adaro coal, and
- pulverized Pittsburgh #8

The crushed fuels were sized to 1/8" top size (1/8x0). Analyses of several fuel samples taken during the tests are given in **Table 7-2**

Table 7-2 - Analysis of fuels samples in 2012

Date	Coal	Size	C	H	O	N	S	Ash	Moist	VM	FC	HHV Btu/lb
					as-fired							
5/22/2012	Adaro	crushed	54.9	3.8	14.9	0.9	0.2	5.7	19.6	37.8	36.9	9389
5/23/2012	charcoal	crushed	81.9	3.5	8.9	0.1	0.1	2.2	3.3	14.5	80.0	13031
6/5/2012	Adaro	pulv.	53.8	3.9	14.7	0.7	0.1	2.4	24.5	35.7	37.4	9173
6/5/2012	Adaro	pulv.	53.8	3.9	14.7	0.7	0.1	2.4	24.5	35.7	37.4	9173
7/24/2012	Adaro	pulv.	53.8	3.9	14.7	0.7	0.1	2.4	24.5	35.7	37.4	9173
7/25/2012	Adaro	crushed	52.2	3.7	14.1	0.7	0.2	3.8	25.3	35.3	35.6	8865
7/26/2012	pitt8	crushed	69.8	4.7	5.7	1.2	3.0	13.1	2.5	36.5	47.9	12577
7/26/2012	Adaro	pulv.	53.8	3.9	14.7	0.7	0.1	2.4	24.5	35.7	37.4	9173
8/14/2012	Adaro	crushed	53.1	3.7	14.1	0.8	0.1	3.2	25.0	36.2	35.7	9042
8/15/2012	Adaro	crushed	53.1	3.7	14.1	0.8	0.1	3.2	25.0	36.2	35.7	9042
8/15/2012	Adaro	pulv.	58.0	3.8	14.4	0.9	0.3	6.2	16.4	39.3	38.0	9814
8/16/2012	pitt8	pulv.	74.0	4.8	7.1	1.4	2.7	8.4	1.7	38.5	51.5	13434
8/16/2012	Adaro	crushed	53.1	3.7	14.1	0.8	0.1	4.3	23.9	35.5	36.3	8978

After making the required modifications identified during 2011, testing resumed in May 2012. The testing took place from May 21 through May 23, with short periods of firing crushed Adaro coal on May 22 and charcoal on May 23 as shown in **Figure 7-4**.

In this and following figures, the shaded regions indicate periods of coal (or charcoal) firing. **Figure 7-4** and the following three figures contain three plots to give an overview of each test week:

- the top plot shows the feed rate of coal to the Reducer and natural gas to the Oxidizer
- the second plot shows the temperatures at the top of the two risers
- the third plot shows the % CO₂ and CO in the dry Reducer outlet gas

Most of the testing on May 21 and 22 was shaking down the modified systems. Late on the May 22, crushed Adaro coal was fired. Until about 22:55 hours, there was some air fed to the Reducer and some excess O₂ in the flue gas. For the last 10 minutes of the test, only nitrogen was used. At this point the temperature dropped and we did not achieve a steady operating point.

At 01:20 hours on May 23, crushed charcoal was fired along with 100% nitrogen gas to the Reducer. These tests clearly demonstrated self-sustaining chemical looping reactions in the Reducer. With the higher charcoal flow at the end of the test, the CO increased, consistent with the lower stoichiometry.

Testing ended later on the 23rd when a water leak was discovered at the outlet of

the Oxidizer cyclone.

Note in the third plot, that prior to the coal firing, the CO and CO₂ levels were high – these are analyzer calibrations. For the most part, we avoid calibrating the analyzers during the coal firing periods. Note also that during the charcoal firing, the CO and CO₂ dipped to zero a couple of times; this is from a purge of the gas analyzers to clean the filters. It was not always possible to avoid purging during the coal firing periods.

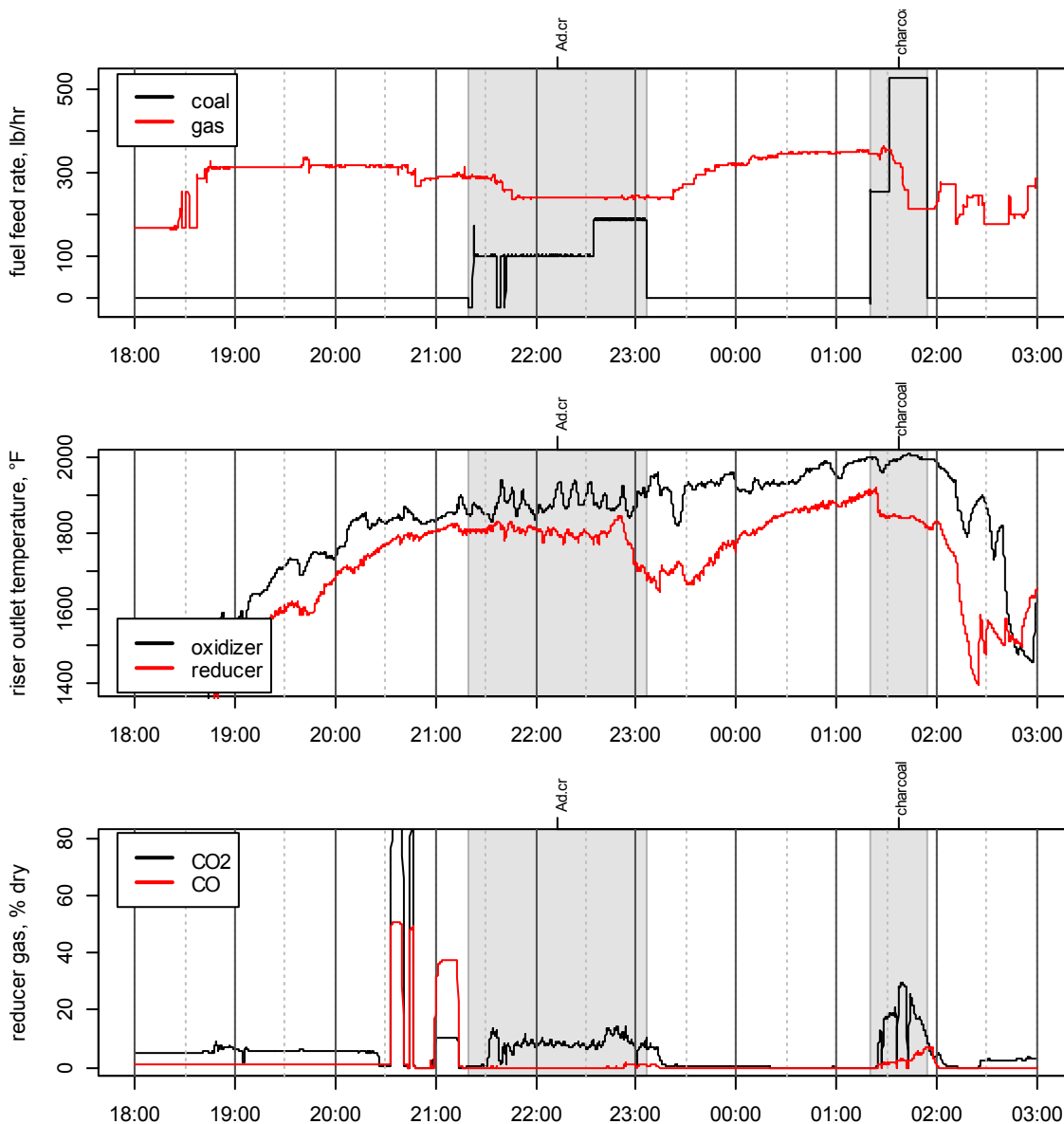


Figure 7-4 - Coal and charcoal firing on May 22 – 23, 2012

The second test was done on June 5, 2012 with pulverized Adaro coal at increasing feed rates. **Figure 7-5** shows some of the summary data. At about 05:40,

we switched from all nitrogen to a CO₂/N₂ mixture to the Reducer: this is seen by the large increase in CO₂ in the outlet gas in the third plot of **Figure 7-5**.

Again, as the coal flow increased, the Reducer CO increased, indicating a shift in the stoichiometry.

As the coal feed rate increased, the temperatures leaving the risers also increased, until the Reducer temperature suddenly dropped off. A blockage had formed in the RPC, shutting off the circulation and supply of regenerated CaSO₄ to the Reducer. The blockage could not be cleared out without opening up the cyclone, thus the test ended.

The blockage may have been related to the high temperature, but inspection of the blockage showed that the solids were tightly compacted and not fused together. Chunks of these compacted solids were removed for examination. As air slowly diffused into the chunks they would crumble back to their original size distribution. It turns out the solids can be compacted and locked in place in the dipleg and RPC by process pressure excursions. In later tests, we made process and operating changes to avoid locking up the solids and made sure to back off the natural gas firing rate to the Oxidizer as the fuel feed increased in order to keep the Oxidizer outlet temperature under control. We had no further pluggages of this type.

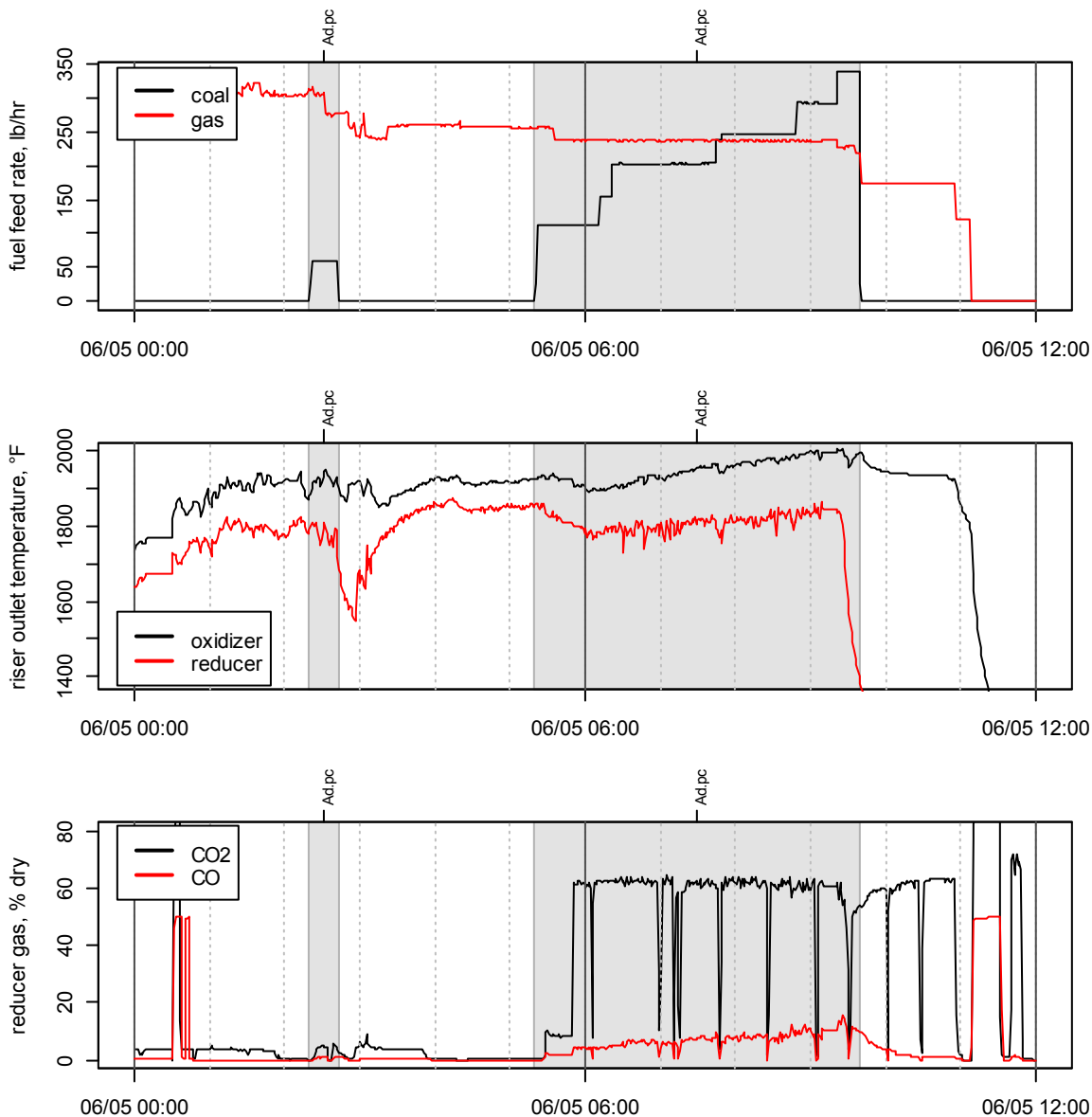


Figure 7-5 - Coal firing during June 5, 2012 test

Testing resumed on July 23, 2012 with firing pulverized and crushed Adaro coal and crushed Pittsburgh #8 coal as shown in **Figure 7-6**. At the beginning of the testing, 100% nitrogen was fed to the Reducer. A mixture of CO₂ and N₂ was used from about 14:30 hours on the 24th until midnight July 26 – this is seen in the CO₂ content of the Reducer gas in **Figure 7-6**. The gas was switched back to all nitrogen for the end of the test because of concerns about CO₂ delivery to refill our tanks.

On the afternoon of July 25, we began ramping up the coal feed rate and reducing the natural gas injection to the Oxidizer, until at about 18:00 hours the natural gas was turned off completely. As seen in **Figure 7-6**, the temperatures started to drop – there was insufficient CaS being oxidized to maintain the temperature in the Oxidizer

(and therefore the Reducer as well). The natural gas was turned on again to maintain the temperatures as the coal was further increased. Finally at about 01:30 on the 26th, the gas was shut off for good and the temperatures were maintained – i. e., self-sustained auto-thermal operation.

This was followed by auto-thermal operation with crushed Pittsburgh #8 coal. The Pittsburgh #8 started at a feed rate of about 530 lb/hr, but the Oxidizer air firing rate was higher than we wanted, so it was reduced to 300 lb/hr.

Finally we tested again with pulverized Adaro coal, but it appears that the sulfur inventory had dropped off and could not sustain the chemical looping reactions – see the temperature drop in **Figure 7-6**. At this point the testing ended for the week.

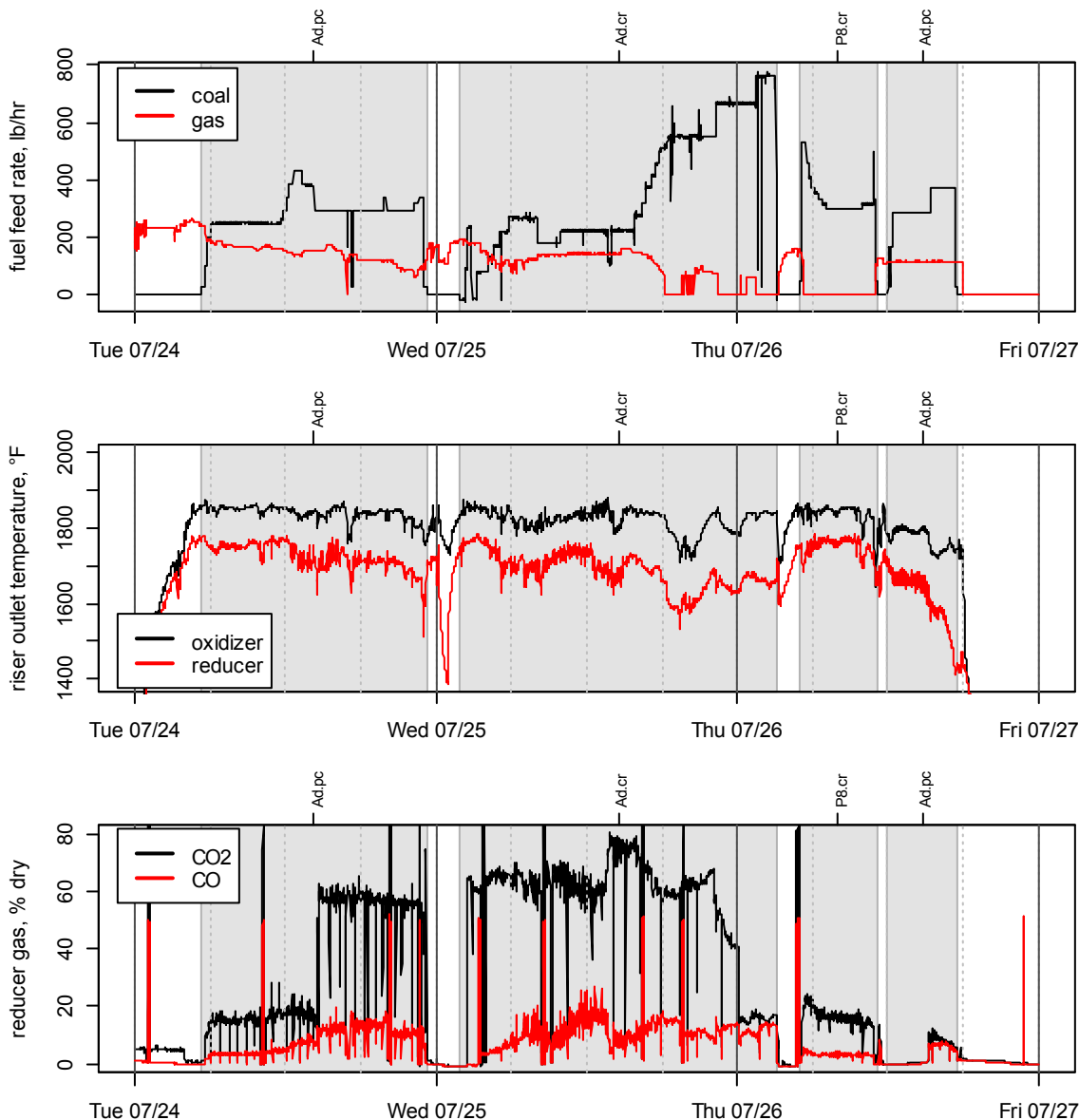


Figure 7-6 - Coal firing periods during the July 2012 test

The August 2012 test began with a low coal feed rate of about 100 lb/hr of crushed Adaro and varying the Reducer temperature. See **Figure 7-7**. Temperature control was achieved by adjusting the natural gas firing rate to the Oxidizer. In the later part of the test, the pulverized fuels were fired as well as crushed Adaro at higher feed rates.

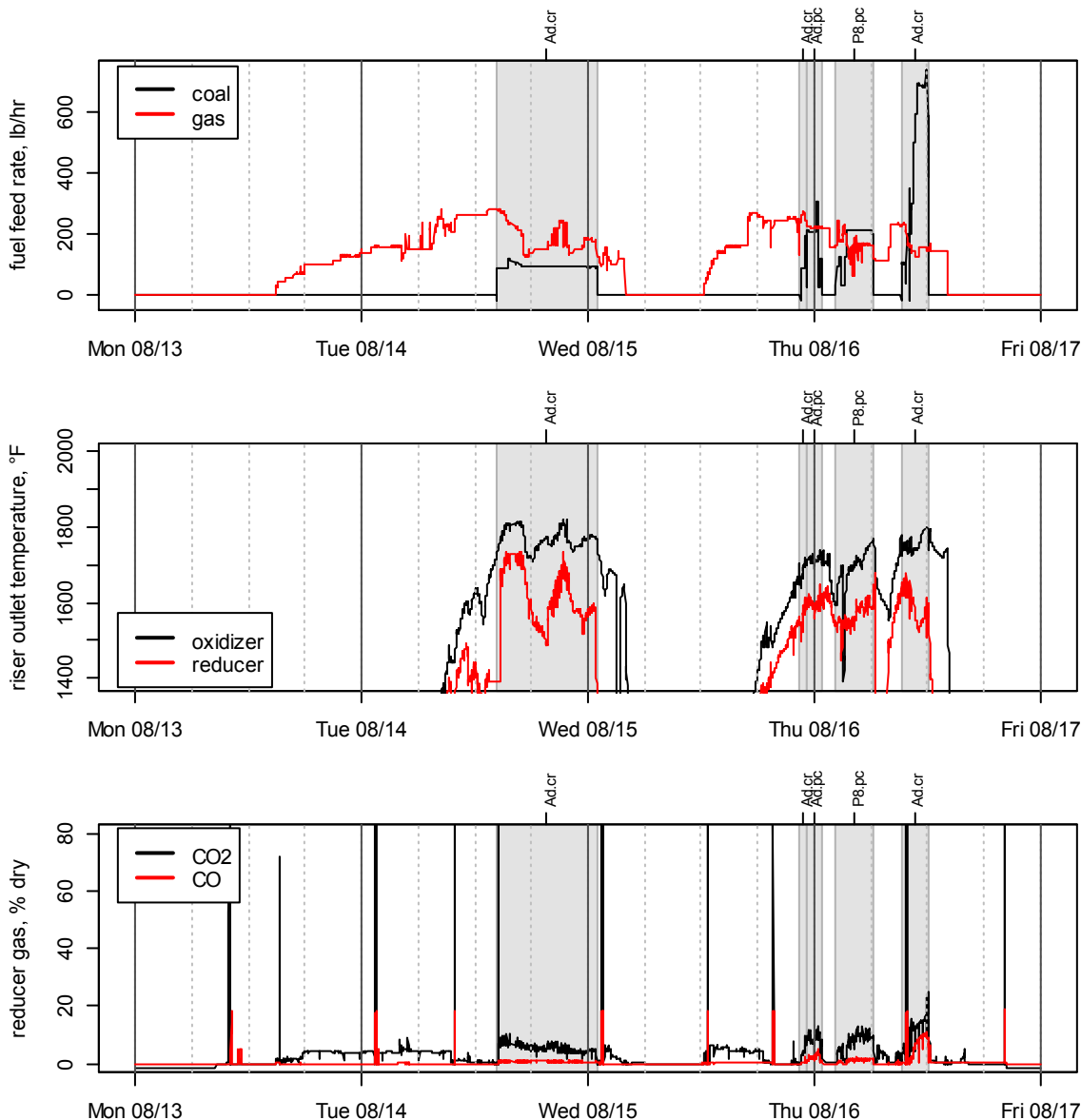


Figure 7-7 - Coal firing periods during the August 2012 test

7.2.4 Test Results

Significance of Auto-thermal Prototype Operation and Test Highlights

Auto-thermal operation is a critical step to demonstrate the viability of the LCL-C™ technology. Alstom achieved stable, auto-thermal, coal-only operation with the 3 MWt Prototype in July 2012 for 12 hours on two different coals (Pittsburgh #8 and Adaro). Prior to this successful operation, all previous chemical looping tests had required the use of supplemental energy to drive the chemical looping reactions. Previous bench and 65 kWt PDU tests were electrically heated. All of the non-auto-thermal 3 MWt Prototype tests were heated with supplemental natural gas which was fired in the Oxidizer to help drive the chemical looping reactions.

During the successful auto-thermal tests, the 3 MWt Prototype was operated exclusively on coal which was fed to the Reducer with air fed only to the Oxidizer. No supplemental fuel of any kind was required. Nearly full design coal flow was attained. Attaining auto-thermal performance necessarily required that all of the following factors are occurring:

1. Coal is combusted in the Reducer to CO₂ via hot CaSO₄, forming CaS;
2. CaS is burned in the Oxidizer forming hot CaSO₄ for the Reducer;
3. LCL-C™ chemical looping reactions are self-sustaining;
4. Long-term, stable solids circulation and
5. These results justify further testing which can be reasonably expected to provide a firm basis for a successful LCL-C™ demonstration plant.

Although noteworthy as a first effort, the auto-thermal test performance is not perfect and there is plenty of work left to do towards optimizing the Prototype. However, these initial results are sufficient to show that Alstom's LCL-C™ concept is viable and that the Prototype is correctly sized and configured. The results also indicate directions for improvement.

The significance of the achievements during the recent prototype test campaigns is that most of the critical technical assumptions and potential technical issues for the LCL process have been confirmed, and potential solutions to these issues demonstrated at a pilot scale.

During the July 2012 test campaign we were able to achieve autothermal operation on coal only without natural gas firing. The prototype operated autothermally for several hours each firing crushed Adaro sub-bituminous and crushed Pittsburgh #8 bituminous coals – see **Figure 7-8**.

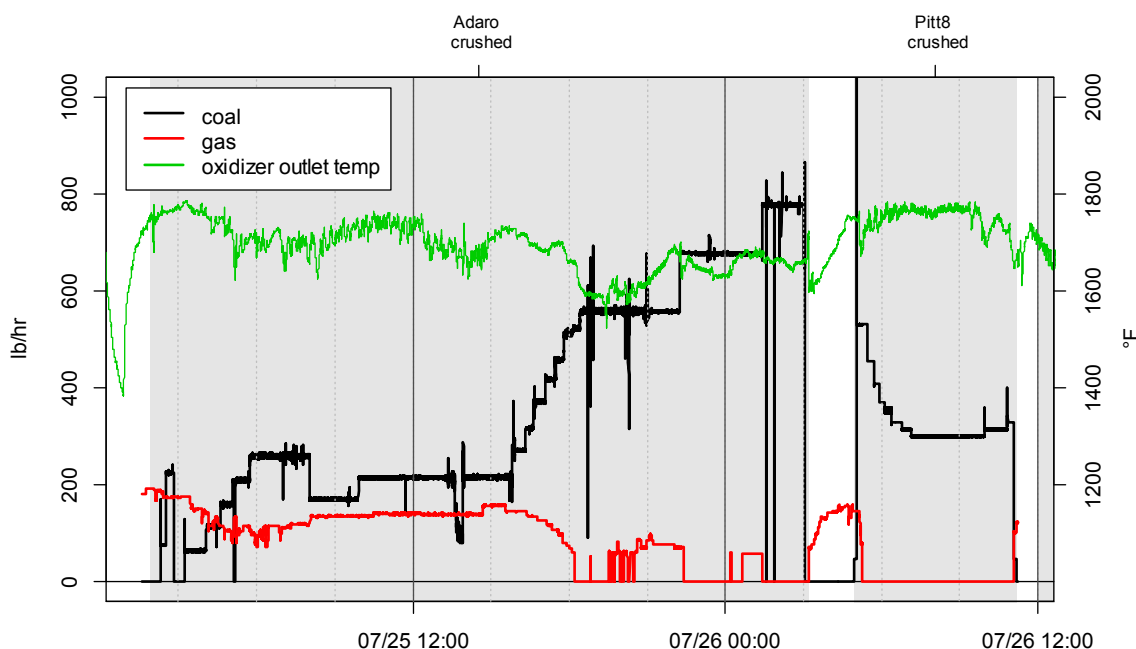


Figure 7-8 – Autothermal testing during July 2012 campaign

On the afternoon of July 25, we began ramping up the coal feed rate and reducing the natural gas injection to the Oxidizer, until at about 18:00 hours the natural gas was turned off completely. As seen in **Figure 7-8**, the temperatures started to drop – there was insufficient CaS being oxidized to maintain the temperature in the Oxidizer (and therefore the Reducer as well). The natural gas was turned on again to maintain the temperatures as the coal was further increased. Finally at about 01:30 on the 26th, the gas was shut off for good and the temperatures were maintained – i. e., self-sustained autothermal operation.

The Adaro autothermal test was followed by autothermal operation with crushed Pittsburgh #8 coal. The Pittsburgh #8 started at a feed rate of about 530 lb/hr, but the Oxidizer air firing rate was higher than we wanted, so it was reduced to 300 lb/hr – see **Figure 7-8**.

Although noteworthy as a first effort, the auto-thermal test performance is not perfect and there is plenty of work left to do towards optimizing the Prototype. However, these initial results are sufficient to show that Alstom's LCL-C™ concept is viable and that the Prototype is correctly sized and configured. The results also indicate directions for improvement. A goal of future longer-term autothermal testing will be to establish

steady conditions and take more solids samples over the longer term to establish reliable mass and energy balances.

7.2.5 Data Gaps

Performance data collected during the Reducer and Oxidizer characterization test campaigns have shown that most of the performance objectives in **Table 7-1** can be achieved. **Table 7-3**, are the performance gaps in our current understanding.

Table 7-3 - Data Gap Summary

<u>Problem</u>	<u>Solution</u>
Carbon carryover to Oxidizer	RBO Gate
Dip leg flush, from C + CaSO ₄	Dip leg gas drain
Reducer & Oxidizer sulfur loss	Temp & Solids control; Bench studies
SAHE Commissioning and Testing	Hot solids testing planned
Material Balance	On-going data acquisition and analysis improvement

The necessary improvements are summarized as follows:

RBO Gate

The RBO Gate will be a type of grid plate with fluidizing gas and a drain to pass the solids. The purpose of the RBO Gate is to:

1. maintain as much carbon as possible from entering Reducer Zone I by decanting the entering lighter carbon from the heavier calcium and ash solids;
2. react the carbon entering Zone I via Reaction 1;
3. maintain countercurrent gas and solids flow with upward moving CO₂ and downward moving solids. Alstom's proprietary carbon/ash separation technology will be employed for these purposes.

Retaining the carbon and CO₂ in Zone II will improve carbon capture in the Reducer and decrease carbon carryover to the Oxidizer. Cold flow testing followed by Prototype testing is planned to complete this work.

Main Dip leg Gas Drain

Alstom has long had contingency plans for a Dip leg gas drain to bleed off the gas produced by carbon in the Main Dip leg and venting to a lower pressure region in the reducer. Such equipment has been successfully used for similar purposes in Alstom's Chemical Looping Product Development Unit (PDU). This modification will allow the use of control gas to control solids transport and inventory in the dip leg. Cold flow modeling and Prototype testing are required.

Reducer and Oxidizer Sulfur Loss Prevention

Understanding and preventing Reducer sulfur loss involves completing the Prototype sulfur performance data analysis that is underway to determine what bench tests and/or cold flow model tests may be required to develop remedies to be tested on the Prototype.

Oxidizer sulfur loss is more easily understood. Smooth flow through the RBO and good mixing in the Oxidizer are required. The RBO Gate and eliminating dipleg flushing should help smooth the solids flow rate. Modifications to the air and solids inlets in the Oxidizer may be tested to control the local stoichiometry in the lower Oxidizer region.

Sorbent Activation Heat Exchanger (SAHE) Commissioning

Based on results from PDU testing (**Reference 2** Phase II Report) and Alstom CFB testing, commissioning the SAHE is expected to solve several Prototype performance problems. First, since the SAHE removes excess process heat, the Prototype will be able to be operated at full design load (10 MMBtu/hr). Second, an operational SAHE will enable the on-line sorbent activation system to be operated. This proprietary system increases sorbent reactivity at high levels for the entire time that the sorbent is retained within the system. The improved sorbent reactivity improves sulfur capture, CaSO₄ reduction, CO₂ formation, CO and CH₄ oxidation, Water-Gas Shift reaction rate, carbon capture and CaS oxidation, thereby making the achievements of many of the commercial performance targets easier to attain.

7.2.6 Prototype Operation and Performance Summary

Summaries of the operating and performance highlights successfully achieved during the Phase IVA project are given in **Table 7-7** and **Table 7-8**.

Table 7-7 - Summary of Prototype Operating Achievements

- Controlled Reducer & Oxidizer streams independently without losing gas seals.
- Developed procedures to circulate Solids with hands-off stability (1st cold, then hot).
- Verified unique warm-up burner operation able to operate with outlet submerged in solids.
- Developed procedures to light off Oxidizer/Reducer auxiliary natural gas without slagging up the burners or reactors.
- Developed de-slagging method to use when temperature limits are widely exceeded during testing.
- Verified that the ash/sorbent has no agglomerating tendencies in operating range even when ID and FT are within 100 °F.
- Determined that the ash/sorbent can be “locked-up” if solids flow and pressures are improperly managed (solids management procedure development is on-going).
- Developed and improved material balances and performance analysis procedures (on-going).
- Developed system operating procedures and exercised emergency procedures.
- Developed remote inspection and maintenance procedures necessary for all-welded construction.
- Developed on-line solids feed procedures.
- Successfully fired four crushed fuels (1/8” x 0”) charcoal, Adaro (Indonesian sub-bituminous), Illinois #6 and Pittsburgh Seam 8 coal
- Successfully fired two pulverized coals (Adaro & Pitt 8)
- Achieved 1st auto-thermal operation (11 hours total) on two widely different crushed fuels (Adaro and Pitt 8)

Table 7-8 - Summary of Prototype Performance Achievements

- Completion of auto-thermal operation
 - Reducer and Oxidizer characterization test campaigns
 - Integrated auto-thermal operation with Pittsburgh #8 and Adaro (1/8" x 0")
- High carbon conversion:
 - Over 95% of fuel conversion efficiency to gaseous products were achieved while firing Adaro coal.
 - CO level could be maintained low by changing fuel-to-oxygen carrier ratio (i.e., fuel-to-air ratio) – Result: low CO means high CO₂ purity.
 - Integrated operation
- Moderate sulfur emissions:
 - Moderate levels of sulfur release observed from Reducer and Oxidizer;
 - Sulfur release correlates with CO content and temperature
 - Reducer sulfur release could be lowered to close to zero
- Stable solids transport
 - Long periods of stable operation were maintained
 - Carbon carryover from Reducer to Oxidizer could be maintained at low levels

8. Lessons Learned

8.1 Operation

- Controlled Reducer & Oxidizer streams independently without losing gas seals.
- Developed procedures to circulate Solids with hands-off stability (1st cold, then hot).
- Verified unique warm-up burner operation able to operate with outlet submerged in solids.
- Developed procedures to light off Oxidizer/Reducer Aux Natural Gas without slagging up the burners or reactors.
- Developed de-slagging method to use when temperature limits are widely exceeded during testing.
- Verified that the ash/sorbent has no agglomerating tendencies in operating range even when ID and FT are within 100 deg. F.
- Determined that the ash/sorbent can be “locked-up” if solids flow & pressures are improperly managed (solids management procedure development is on-going).
- Developed and improved material balances and performance analysis procedures (on-going).
- Developed System operating procedures and exercised emergency procedures.
- Developed remote inspection and maintenance procedures necessary for all-welded construction.
- Developed on-line solids feed procedures.
- Developed on-line solids sampling of important streams
- Successfully fired four crushed fuels (1/8 X 0) Charcoal, Adaro (Indonesian lignite), Illinois #6 and Pittsburgh Seam 8 coal
- Successfully fired two pulverized coals (Adaro & Pitt 8)
- Achieved 1st auto-thermal operation (12 hours total) on two widely different crushed fuels (Adaro and Pitt 8)

8.2 Performance

- **Completion of auto-thermal operation**
 - Reducer and Oxidizer characterization test campaigns
 - Integrated auto-thermal operation with Pittsburgh Seam 8 and Adaro (1/8” X 0”)
- **High carbon conversion:**
 - Over 95% of fuel conversion efficiency to gaseous products was achieved while firing Adaro coal.
 - CO level could be maintained low by changing fuel-to-oxygen carrier ratio (i.e., fuel-to-air ratio) – Result: low CO means high CO₂ purity.
 - Integrated operation
 - Reaction rates exceed requirements

- **Moderate sulfur emissions:**
 - Moderate levels of sulfur release observed from Reducer and Oxidizer;
 - Sulfur release correlates with CO content and temperature
 - Reducer sulfur release could be lowered to close to zero by lowering Reducer temperature and/or injecting limestone (or Ca(OH)₂)

- **Stable solids transport**
 - Long period of stable operation were maintained
Carbon carryover from Reducer to Oxidizer could be maintained at low levels

8.3 Design and Construction

- Refractory lined steel vessels worked effectively in the design of the Prototype.
- All welded construction of the process vessels and connections proved effective at reducing process leaks.
- Repairs were made by cutting into the vessels and welding the vessels after repairs.
- The refractory lined vessels survived the operation very well with two exceptions.
 - The hard-faced refractory that was used in the ceiling of the RBO horizontal section was difficult to support. It was supported by imbedded metal studs welded to the case and had to be braced with a metal plate. A better construction method would be to support any hard ceiling refractory on both sides of the span with wall tiles or other support.
 - The cylindrical tiles in the Oxidizer cracked and lost the loosely packed backing insulation. A new design for the Oxidizer refractory is being developed.
- The refractory construction including a hard-faced dense refractory on the process surface coupled with a soft insulating refractory behind the hard refractory, proved effective in limiting heat loss from the process to a level that allowed auto-thermal testing.
- Heat loss from the process was less than originally calculated, based on measurement of the skin temperature of the process vessels. Since the refractory and metal heat transfer characteristics are well known, the inside process film heat transfer coefficient was less than assumed and within 20% of the value used on an overall basis.

9. Economic Update

Prototype Performance

LCL-C™ commercial plant economics were re-examined in the light of the performance achieved during Phase IVA 3 MWth LCL-C™ Prototype testing. The Prototype performance is summarized in **Table 7-1**, reproduced here as **Table 9-1**, and is discussed in detail in Section 7 of this report and summarized here. Refer to **Figure 7-1** which shows the Prototype configuration and nomenclature.

Referring to **Table 9-1**, Column 2 lists the performance items that affect the ability of LCL-C™-based power plants to meet the Alstom/DOE performance goals for carbon capture (> 90%) and cost of electricity (< 35% more than today's best supercritical pulverized coal plants that do not capture carbon). Column 7 shows Alstom's performance targets. Columns 4 and 5 summarize the performance during autothermal operation.

Autothermal tests (Columns 4 and 5) are tests in which the Prototype is operated using coal as the only fuel. During autothermal testing no burning of supplemental fuel (i.e., natural gas) is necessary in the Oxidizer (or Reducer) in order to maintain system temperatures. Thus, in order to achieve autothermal operation, the main chemical looping reactions must be occurring to sustain the operation. Specifically, the following must occur to enable autothermal operation:

1. In the Reducer, carbon from the coal must be gasified by: $C + CO_2 \rightarrow 2CO$. Hot CaSO₄ must be reduced by: $CaSO_4 + 4CO \rightarrow CaS + 4CO_2$. These are endothermic reactions requiring heat. The heat must be supplied by reactions occurring in the Oxidizer.
2. In the Oxidizer, the CaS burned by: $CaS + 2 O_2 \rightarrow CaSO_4$. In order to sustain the Reducer reactions, this exothermic reaction must occur in sufficient quantity to supply the heat required for the Reducer reactions, to supply the heat required to heat all feed materials entering the system, to replace all of the heat carried off with the gasses and solids leaving the system and to replace all of the heat losses from the process vessels and heat exchangers.
3. The solids circulation rates must be sufficient to carry all of the heat and reactants necessary to maintain system temperatures and sustain the chemical looping reactions.
4. The coal feed rate must be sufficient to sustain all of the above operations.

Table 9-1 - Achievement of Performance Objectives for the CLC-C™ Prototype Facility

1	2	3	4	5	6	7	8	9
Item	PERFORMANCE ITEM	UNITS	Adaro auto-thermal	Pitt 8 auto-thermal	best performance	Performance Target	Cause of shortfall	Indicated modification
1	Unburned carbon loss	% of carbon in coal	~0.5	~1	~0.5	0.5		
2	Reducer carbon capture	% of carbon in coal	75-80	60	95-97	>95	carbon/CO ₂ to Oxidizer	RBO Gate: solids decanting & countercurrent gas. Solids flow
3	Carbon carryover to Oxidizer	% of carbon in coal	21	41	5	<5	insuff. decant; down flow of gas	same as 2
	Sorbent reactivity:							
4	sorbent cycles since coal start (Reducer-to-Oxidizer)				~ 700 avg.	~ 3000 max.		
5	CO ₂ content	% of carbon in Product Gas	60 80 w/ CO ₂	80	90	>99.5	insuff active CaSO ₄	incr. effective surface (SAHE), incr. circulation
6	CaS burned-to-CaSO ₄ in Oxidizer	% required CaSO ₄	52	85	95	100	insuff. CaS surface	same as 5
7	Oxidizer sulfur loss	ppmv	2000	1000	0	0	local solids holdup (Rxn 5)	improve solids/gas mixing
	Reducer gas Composition:							
8	tar / hydrocarbons	ppmv	--	--	<25 / ~150	negligible		
9	total sulfur (all forms)	ppmv	1000	2000	~0	<10	under investigation: prototype analysis & bench tests	SAHE, add lime(stone), temperature,
10	CH ₄	% of carbon in Product Gas	2.5	1 – 1.5	~0.2	<1		
11	CO content	% of carbon in Product Gas	14	3.5	<1	<0.5	same as 5	same as 5
12	Load	%	70	38	70	100	heat removal	SAHE
13	Reducer Cactus gas velocity	ft/sec	25	28	22	≤15		
14	Reducer RTO gas velocity	ft/sec	45	35	60	≥100		
15	Oxidizer gas velocity	ft/sec	45	50	85	≥100		
16	Dip Leg solids flush coal flow limit (pc coal)	% full load	--	--	30	100	reaction in dip leg with incr. coal flow	dip leg gas drain

Column 6 shows the best performance achieved during any of the Prototype tests conducted during 2012, whether during autothermal or non-autothermal operation. The lowest unburned carbon loss and the highest load (Performance Items 1 and 12, respectively) are from the Adaro autothermal tests while all other Column 6 performance items are from non-autothermal tests. In these non-autothermal tests, natural gas was fired in the Oxidizer to supply enough hot solids to test the Reducer and Oxidizer reactions at the desired temperature and reactant stoichiometry. Operating the Prototype in this non-autothermal mode allows testing at lower coal flows than would be possible under autothermal conditions. In general, the performance recorded in Column 6 corresponds to non-autothermal operation with Pittsburgh Seam 8 coal at about 200 to 250 lb/hr (about 25% load).

Conclusions Regarding Prototype Performance

The test results listed in **Table 9-1** are important for reasons that are discussed in the following paragraphs:

First, comparison of autothermal performance (Columns 4 and 5) with the performance targets (Column 7) shows a performance shortfall. The most important measure of the shortfall is the Reducer carbon capture (Item 2) which shows 60%-to-80% achieved compared to Alstom's performance target of 95% (DOE target, 90%). The other important shortfalls encountered during these initial autothermal tests include: 1) loss of Main DipLeg solids during coal firing above 30% load (Item 16); 2) high sulfur emissions from the Reducer and Oxidizer (Items 7 and 9); and 3) too much CO in the CO₂ stream (Item 11). All of the performance shortfalls uncovered during the initial autothermal testing appear to be resolvable with changes to the current configuration. Their probable causes and remedies are listed in Columns 8 and 9 which were discussed in Section 7.2.

Second, despite the performance shortfalls, autothermal operation (Columns 4 and 5) could be maintained over a wide load range, at loads as low as 30% and as high as 70%, with two widely varying fuels. Adaro is a low sulfur subbituminous coal with a relatively high reactive char, while Pittsburgh Seam 8 is a high sulfur bituminous coal with a relatively low reactive char. Operating at 100% load at the Prototype requires the use of a solids heat exchange to cool the circulating solids to prevent system temperatures from getting too high. This heat exchanger (the sorbent activation heat exchanger or SAHE) has not yet been fully commissioned, therefore limiting load to 70% or less. When the SAHE is commissioned, the Prototype will be capable of LCL-C™ operation over a wide load range from 30% to 100% load with a world-wide range of commercially significant coals. This flexibility makes the Prototype well suited to successfully eliminating the current performance shortfalls described in the previous paragraph.

Third, the non-autothermal test results (Column 6) give a better indication of achievable LCL-C™ performance than the autothermal tests (Columns 4 and 5). As stated, these tests were generally conducted at about 25% coal load where autothermal operation

was not feasible. However, firing some natural gas in the Oxidizer to sustain operating temperatures in normal ranges allowed testing at these lower coal flows (about 200 to 250 lb/hr or about 25% load). Operating the Reducer at these lower-than-design coal flows eliminated two major operating problems that were associated with autothermal operation at higher coal flows. Carbon carryover from the Reducer to the Oxidizer (Performance Item 3) was reduced to the target value (5%) and the Main DipLeg solids inventory could be maintained without the loss of solids due to excess gas production in the DipLeg experienced at higher autothermal coal flows. The non-autothermal operation allowed operating the Reducer at more favorable reaction stoichiometries. As a result, these tests showed that the Reducer carbon capture goal of >95% (Item 2) can be achieved. Additionally, the carbon carryover (Item 3), sulfur capture (Items 7 and 9), and CH₄ and CO content (Items 10 and 11) goals were achieved at these lower coal flows.

Modifications To Reach Design Performance At Full Load

Three main modifications to the Prototype have been identified to achieve the performance targets at full load are listed in **Table 9-1**. These are discussed in detail in Section 7 and are summarized in the following paragraphs.

RBO Gate

Recirculating solids in the Prototype can flow through the Reducer bottom outlet (RBO) to the Oxidizer at a rate that exceeds the flow capacity of the Reducer pressurizing column (RPC). The mismatched flow capacities can cause solids transport instabilities which allow excessive amounts of CO₂ and carbon to be carried from the Reducer through the RBO to the Oxidizer, increasing carbon carryover (Item 3, **Table 9-1**) and thereby reducing Reducer carbon capture (Item 2). The RBO Gate is intended to prevent the flow mismatch, preventing excessive carbon carryover and thereby improving Reducer carbon conversion. Column 7 of **Table 9-1** shows that when excessive carbon carryover (Item 3, carbon carryover is 5%) can be avoided, the carbon can be retained in the Reducer Zone 2 long enough to be captured in the Reducer gas (Item 2, Reducer carbon capture is 95% to 97%).

The RBO Gate is essentially a grid plate at the bottom of Reducer Zone 1 (i.e., the region above the cactus) which is fluidized with a small amount of recycled CO₂ and equipped with a bed drain system which allows Zone 1 solids to pass from the Reducer to the Oxidizer. The purpose of the RBO Gate is to make the gate the point of highest pressure in the Reducer and to establish a maximum solids flow through the gate. These effects, in turn, are anticipated to prevent solids flushing through the RBO to the Oxidizer which carries unwanted CO₂ and carbon from the Oxidizer to the Reducer. The gate is also expected to promote the upward flow of Zone 1 gas against the downward flow of solids which, in turn, is expected to improve the separation of carbon from the downward moving zone 1 solids, thereby retaining more carbon in Reducer Zone 2 (i.e., the Reducer riser). Recent cold flow tests of the concept support this

concept. Further Prototype tests are planned for this concept.

The RBO Gate is intended to help remedy several operating problems encountered during Prototype testing. Specifically, it is intended to eliminate excessive carbon carryover (Cco) to the Oxidizer (Performance Item 3). Reducing Cco allows carbon to remain in Reducer Zone 2, thus increasing Reducer carbon capture (Item 2). Overloading the RPC with circulating solids causes the solids to back up in the Oxidizer cyclone causing excessive loss of solids. Since the RBO gate is intended to prevent overloading the RPC and Oxidizer cyclone, it will retain solids inventory within the system thereby increasing the average retention time and number of operating cycles of sorbent (Item 4). The quantitative effect of the RBO Gate on these performance items is discussed further on in this section.

Main DipLeg Gas Drain

Cold flow tests have shown that if the Main DipLeg is supplied with too much grease gas, the solids will flush out of the DipLeg causing flow disruption throughout the entire LCL™ solids transport system causing flushing through the RBO and loss of solids through the cyclones. The same effect is experienced in the Prototype at coal flows greater than 30% load. In these situations, gas is generated in the Main DipLeg by the reaction of hot CaSO₄ and carbon which forms CO₂ in excess of the DipLeg grease gas requirements. As with cold flow model tests, the resulting DipLeg flush causes solids transport disruptions throughout the LCL-C™ system. The Main DipLeg Gas Drain is intended to drain the unwanted gas out of the DipLeg and vent the gas into a lower pressure area of the Reducer. Together with the RBO Gate, the Gas Drain is expected to provide smooth solids transport throughout the Prototype system at full load coal flow, eliminate excessive carbon carryover and CO₂ from the Reducer to the Oxidizer, and eliminate the attendant high solids loss caused by solids transport instability at coal flows above 30% load.

The Main DipLeg Gas Drain is a louvered device installed in the lower portion of the Main DipLeg. The drain provides a means to separate the excess gas generated by chemical looping reactions in the DipLeg from DipLeg solids. As the excess gas is separated from the solids, it is piped to a lower pressure area of the Reducer. The Main DipLeg Gas Drain is a small change to the current LCL-C™ concept which adds no discernible additional cost to the LCL-C™ system and causes no change to plant efficiency or cost of electricity (COE).

The Main DipLeg Gas Drain is intended to help remedy several operating problems encountered during Prototype testing. Specifically, it is intended to eliminate the flushing of DipLeg solids caused by gas generated at high coal flow rates by chemical looping reactions occurring in the DipLeg (Item 16). This improvement will have several related beneficial consequences. Since the Gas Drain is intended to prevent flushing DipLeg solids thereby overloading the Reducer cyclone, it will retain solids inventory within the system, increasing the average retention time and number of operating cycles of sorbent (Item 4). Eliminating the rapid overload of solids to the Reducer will also

prevent solids transport excursions throughout the LCL-C™ system leading to more consistent solids-to-gas stoichiometry control. In combination with the RBO Gate, this is expected to provide improved control over solids-to-gas stoichiometry and Reducer gas quality, especially with respect to sulfur control in both the Oxidizer and Reducer (Items 7 and 9) which is especially susceptible to changes in gas-to-solids stoichiometry at LCL-C™ stoichiometric conditions. Tighter control of solids recirculation between the Oxidizer and Reducer promotes the maintenance of stable temperatures within these reactors. The quantitative effect of the Main DipLeg Gas Drain on these performance items is discussed further on in this section.

Sorbent Activation Heat Exchanger

Sorbent activation (SA) is a proprietary Alstom process developed for Alstom's circulating fluidized bed (CFB) boilers to enhance sorbent reactivity. It has been shown to have similar effects in Alstom's LCL-C™ 65 kWth process development unit. The SA process causes an increase in the effective surface area of the CaSO₄/CaS/CaO laden particles. The increased effective surface, in turn, promotes both the speed and extent of the chemical looping reactions. The particles undergo periodic trips through the SA process to maintain reactivity.

Sorbent activation at the Prototype take place in the sorbent activation heat exchanger (SAHE) which, in addition to the SA function, serves to cool the circulating solids to prevent excessive system temperatures. This system was installed during the LCL-C™ Prototype installation. Due to testing schedule and budget constraints it has not yet been fully commissioned. SAHE tests are planned for the future. The SAHE system has always been a part of the original LCL-C™ concept so that the cost is already included in the previous and current economic evaluations.

The SAHE is intended to remedy several performance problems encountered during Prototype testing. Specifically, the SAHE is intended to serve two distinct purposes during Prototype operation. First, it is intended to cool the circulating solids in order to keep the temperatures from exceeding LCL-C™ process limits. (This function would provide steam for power generation in commercial LCL-C™-based power plants.) The SAHE system is installed in the Prototype, but has not yet been commissioned. As a consequence, loads had to be maintained below 70% during autothermal testing (Item 12, Column 4, Table 9-1). Prototype tests are planned for the SAHE. With the SAHE on line (and with the Main DipLeg Gas Drain installed to prevent Main DipLeg solids flushing), operation at 100% coal load (Item 12) will be easily achieved. Operating at 100% of design coal flow necessarily generates sufficient gas in the Reducer and requires enough air in the Oxidizer to reach the performance targets for the Reducer top outlet (RTO) gas velocity (Item 14) and the Oxidizer gas velocity (Item 15).

The second purpose for the SAHE is to increase the effective surface area of the circulating solids. This, in turn, promotes both the speed and extent of the major chemical looping reactions which depend on gas-solid interaction. The particles undergo periodic trips through the SA process to maintain reactivity. The major

reactions which benefit from SA are as follows:

- $\text{CaSO}_4 + 4 \text{CO} \rightarrow \text{CaS} + 4 \text{CO}_2$ (Performance Items 5 and 11),
- $\text{CaO} + \text{H}_2\text{S} \rightarrow \text{CaS} + \text{H}_2\text{O}$ (Performance Item 9),
- $\text{CaS} + 2 \text{O}_2 \rightarrow \text{CaSO}_4$ (Performance Item 6).

Summary of Equipment to Reach Performance Targets and Cost Implications

Both the previous and current LCL-C™-based power plant studies have been based on achieving the performance targets listed in **Table 9-1**. The previous discussions described the modifications expected to achieve these LCL-C™ performance targets. These are summarized below along with their cost impacts.

RBO Gate

The RBO Gate concept adds a grid plate, fluidizing nozzles, and solids drains to the Reducer Zone 1. This feature adds a minor amount of steel and refractory to the original design and causes no increase in auxiliary power. This feature is included in the most recent LCL-C™ economic study (**Reference 7**).

Main DipLeg Gas Drain

The Gas Drain is a simple louvered device which adds a small amount of refractory and some small bore piping to the original LCL-C™ concept. The concept has no effect on the auxiliary power of the LCL-C™-based power plant. Although included in the most recent study, the system is too small to affect the economics which are calculated on weight-based cost factors.

SAHE

The SAHE has always been a part of the LCL-C™ system and has been included in all of Alstom's LCL-C™ cost studies.

In addition to the three equipment items discussed above, two more systems are involved in meeting the targets.

Sulfur Removal System

Sulfur emissions may occur during startup or off-design operations. Accordingly, Alstom has included sulfur removal provisions for both the Reducer and Oxidizer

in all LCL-C™ cost studies.

Gas Processing Unit (GPU) Provisions

Alstom has included two provisions in the GPU in the most recent LCL-C™ economic study that differ from previous LCL-C™ economic studies.

First, the GPU compressor system is used to recycle the required CO₂ to the Reducer Cactus for solids transport. Previous economic studies used process steam or a separate CO₂ Recycle compressor to serve this function.

Second, the most recent LCL-C™ economic study included provisions to separate gaseous sulfur species, CO, and CH₄ from the CO₂ and provisions to recycle these minor constituents along with sufficient CO₂ to the Reducer for solids transport. This allows the sulfur to be captured by the CaO in the solids, the CO and CH₄ to be reprocessed to CO₂ in the Reducer, and the GPU product gas quality to be maintained at the 99.5% CO₂ specification. Prototype tests have shown that sulfur capture is affected by CO content. This feature allows the CO performance target (Item 11) and the Reducer performance target (Item 9) to be traded off as may be necessary for the best sulfur capture / CO content combination. Prototype tests are planned to determine whether such a tradeoff is necessary.

These provisions have been included in the current economic study (**Reference 7**)

At this point, other possible solutions to improve the LCL-C™ performance, such as those discussed in Section 7.2.5, have not been incorporated into the economic studies, but will be considered for the next Prototype tests.

Economic Study Results

Limestone Chemical Looping Economics

Previous Economic Studies

Based on the successful Prototype performance described earlier in this Section, Alstom's commercial plant concept and economics (**Reference 4**) remain unchanged. The commercial new plant concepts, expected performance and economics are described in **Reference 4** (Cases 7, 12 and 13) and **Reference 2**. The results of Phase I, II, and III have been reported in **References 1, 2, and 3**, respectively.

Alstom's Chemical Looping technology competes with other approaches to capturing CO₂ from existing and new coal-fired power plants (e.g. IGCC, Scrubbing, Oxy-Firing, which are near-term options compared to chemical looping) and with other approaches to chemical looping (e.g. metal-oxide chemical looping).

Developing practical, economical methods to capture CO₂ from coal-fired power plants is essential to Alstom's business success. Accordingly, Alstom continues to investigate alternative CO₂ capture technologies and develop those which show most promise. Alstom's interest in Chemical Looping stems from the fact that of all of the technologies investigated to-date, Chemical Looping provides the lowest cost alternative for capturing CO₂ from coal-fired power plants. The economics of various CO₂ technologies being studied at Alstom for new coal-fired power plants are shown in **Figure 9-1 (Reference 6)**. **Figure 9-1** also lists the economic assumptions.

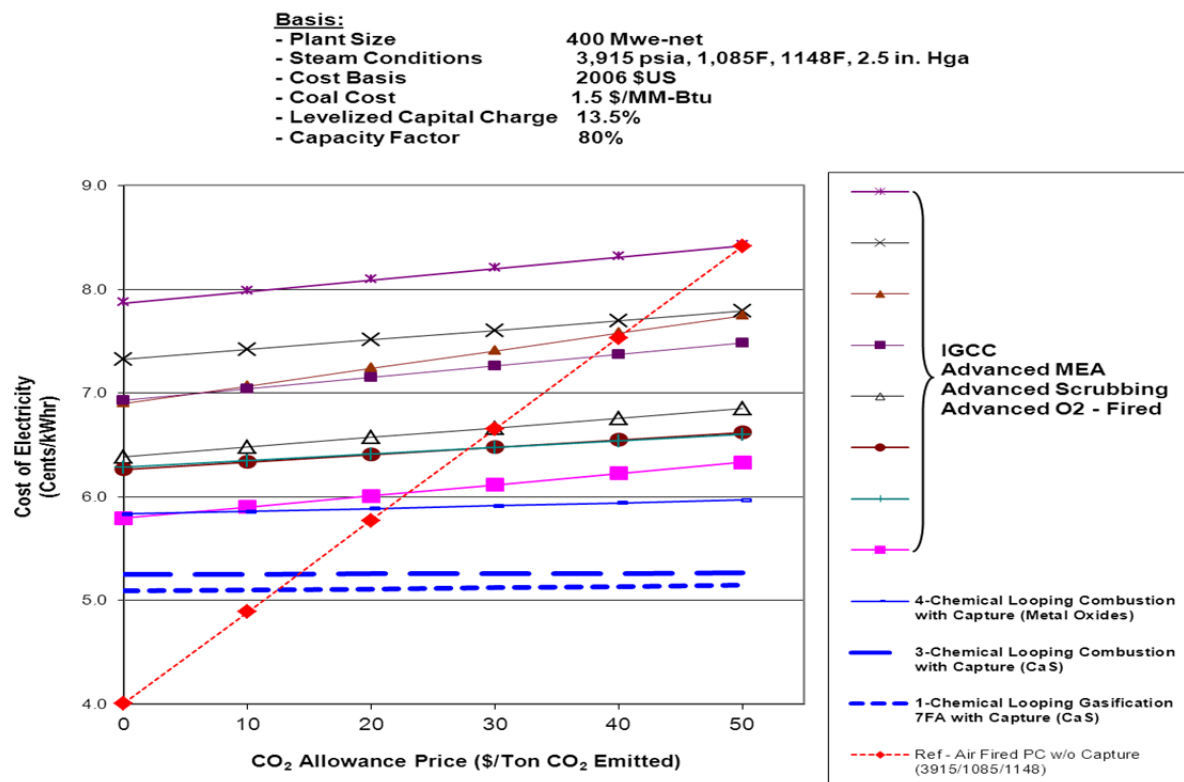


Figure 9-1 - New Capacity Economics – Alstom 2006 study

Figure 9-1 shows the cost of electricity of new capacity coal-fired power plants as a function of CO₂ allowance cost employing various CO₂ capture technologies including IGCC, Oxy-firing with advanced O₂ technology, advanced post-combustion CO₂ scrubbing technologies and chemical looping alternatives. All of the studies were on the same basis as shown in the figure. The three chemical looping cases have the lowest potential cost of electricity.

Current Economic Study Results

Alstom has recently completed a US DOE/NETL economic study of LCL-C™-based power plants (**Reference 7**) which compares Alstom's LCL-C™ to a supercritical pulverized coal power plants without CO₂ capture and to a supercritical oxy-fired

pulverized coal fired power plant with 90% CO₂ capture. All three plants are designed to produce 550 MWnet.

Figure 9-2 provides the process flow diagram of the LCL-C™-based power plant.

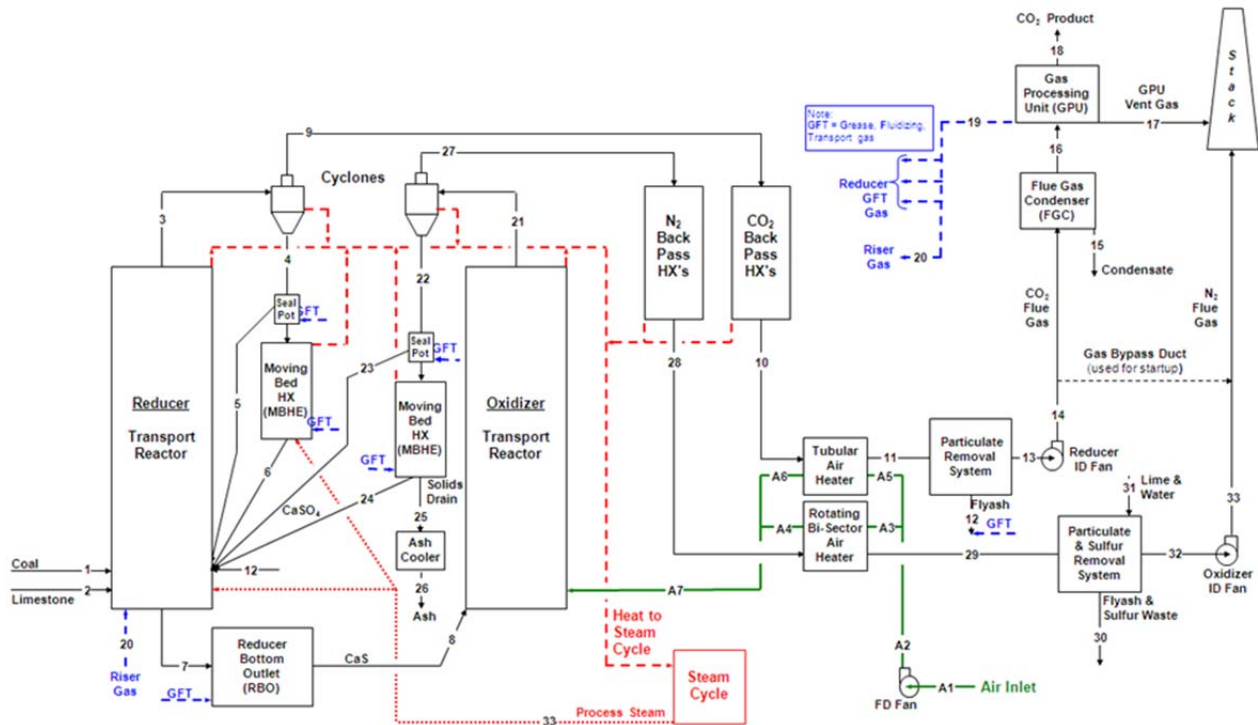


Figure 9-2 – Simplified Process Flow Diagram for a LCL-C™ Power Plant – Case 1 (Transport Reactors)

Figure 9-3 shows a bird's eye view of the LCL-C™ plant and a comparison of the plant with a pc boiler and CFB boiler for an idea of relative scale.

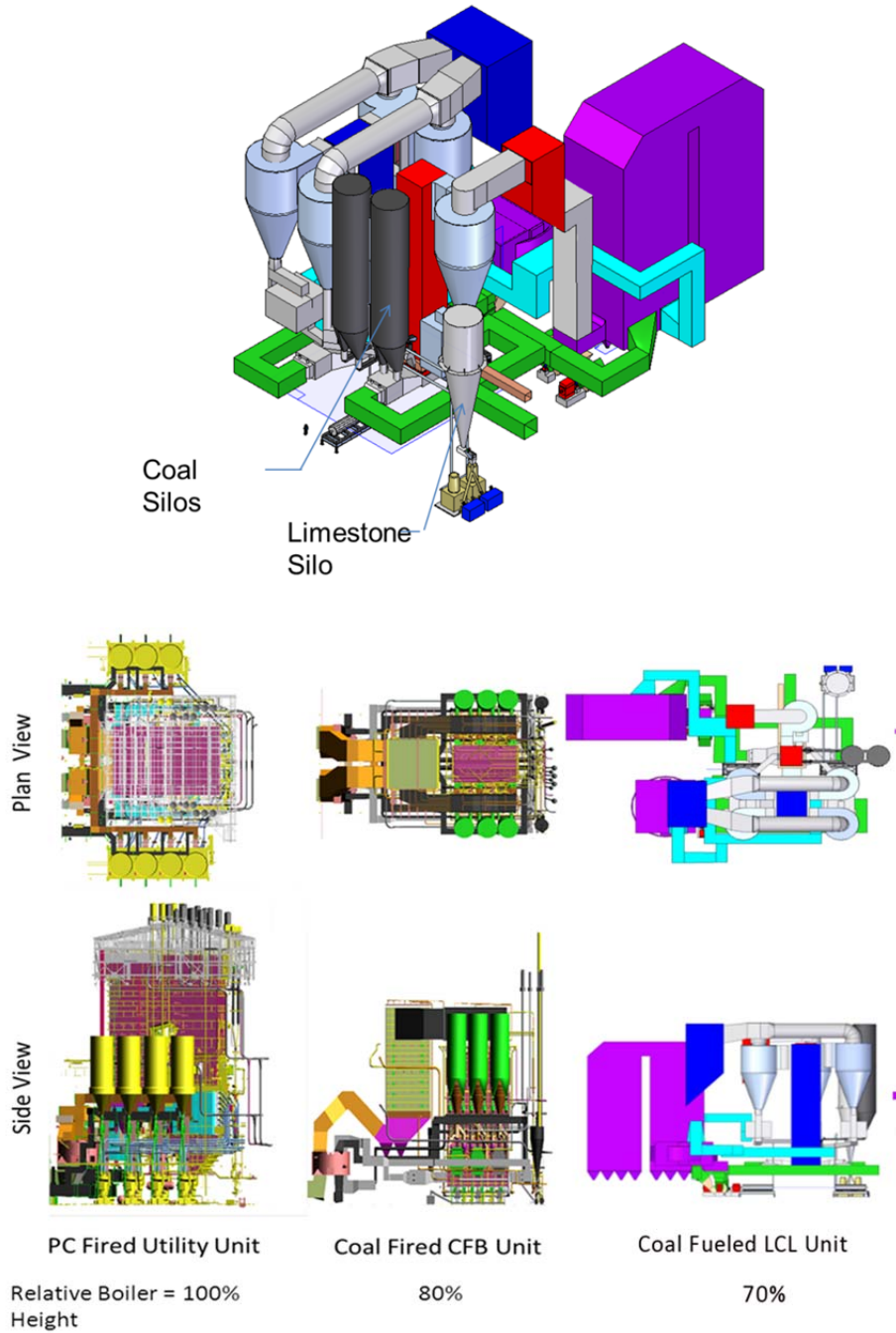


Figure 9-3 – Alstom’s 550 MWnet LCL-C™-based Power Plant

Table 9-2 provides a summary of the major design and performance specifications for the three plants.

Table 9-2 - Major Design and Performance Specifications

	Base Case		Case 1
	DOE Case 11 SCPC without capt	DOE Case 5C Oxy SCPC	LCL-C™ with transport reactors
Capacity	550MW _{net}	550MW _{net}	550MW _{net}
Capacity Factor, %	85	85	85
Coal	Illinois No. 6	Illinois No. 6	Illinois No. 6
Reactor Pressure, MPa (atm)	0.10 (1)	0.10 (1)	reducer 0.10 (1) oxidizer 0.10 (1)
Steam Cycle, MPa/°C/°C (psig/°F/°F)	24.1/593/593 (3500/1100/1100)	24.1/593/593 (3500/1100/1100)	24.1/593/593 (3500/1100/1100)
Condenser pressure, mm Hg (in Hg)	50.8 (2)	50.8 (2)	50.8 (2)
Cooling water to condenser, °C (°F)	16 (60)	16 (60)	16 (60)
Cooling water from condenser, °C (°F)	27 (80)	27 (80)	27 (80)
SO ₂ Control	Wet Limestone Forced oxidation	Wet Limestone Forced oxidation	Limestone added in Reducer NID™ in Oxidizer stream MDEA in GPU
NO _x Control	LNB w/OFA and SCR	LNB w/OFA and SCR	controlled by LCL-C™ process
Particulate Control (A)	Fabric Filter	Fabric Filter	Fabric Filter in Reducer and Oxidizer streams
Mercury Control	Co-benefit capture	Co-benefit capture	Halongated solution injection in Reducer Flue Gas Condenser & Activated Carbon Bed in GPU - Reducer
Mercury removal efficiency, %	90	90	>90%
CO ₂ Control	N/A	Oxy-firing & GPU	LCL-C™ & GPU
Overall CO ₂ Capture	N/A	92.65	>95%
CO ₂ Sequestration	N/A	EOR CO ₂ Specification Sequestration in saline formation	EOR CO ₂ Specification Sequestration in saline formation

The net electrical output, steam cycle, fuel, and environmental requirements are the same in all cases. For Cases 5C and the LCL-C™ case, CO₂ matches the DOE quality specification for enhanced oil recovery. The LCL-C™ plant at greater than 95% CO₂ capture exceeds the DOE's 90% capture goal.

The plant electrical performance is shown in **Table 9-3**. The % Energy Penalty is defined by the following equation:

$$\% \text{ Energy Penalty} = \frac{[\text{net plant efficiency(w/ CO}_2 \text{ capture)} - \text{net plant efficiency(SCPC w/o CCS)}]}{\text{net plant efficiency(SCPC w/o CCS)}}$$

This comparison shows that the LCL-C™ CO₂ penalty is less than 9% compared to the equivalent oxy-fired penalty at 25%.

Table 9-3 - Performance Comparison

		SCPC Case 11	Oxy-PC Case 5C	LCL-C™ Case 1
Reducer Pressure	atm			1
Gross Power Output	MW	580.4	785.9	649.7
Net Power Output	MW	550.0	548.7	550.0
Coal Flow	lb/hr	409,528	549,471	449,595
Main Steam Flow	lb/hr	3,669,421	4,863,464	4,114,272
Fuel Heat Input (HHV)	MMBtu/hr	4,778	6,410	5,245
Net Plant Efficiency (HHV)	%	39.28	29.20	35.78

Auxiliary Load Summary

GPU CO2 Compressor	kW		73,390	59,579
FD Fan (Oxidizer)	kW	1,660	1,500	
ID Fan (Oxidizer)	kW	7,050	7,850	19,557
Reducer ID Fan	kW			
Primary Air Fans	kW	1,300	1,170	
Circulating Water Pump	kW	4,730	6,200	5,966
Cooling Tower Fan	kW	2,440	3,620	3,530
Condensate Pump	kW	800	1,050	1,029
Ground Water Pumps	kW	480		538
Steam Turbine Total Auxiliary	kW	400	400	448
Coal Handling and Conveying	kW	440	500	483
Coal Crush and Feed	kW			104
Pulverizers	kW	2,780	3,740	
Limestone Crush and Feed	kW			1,000
Sorbent Handling & Reagent Preparation	kW	890	1,210	
Ash Handling	kW	530	720	582
NID™ w/o Fan	kW			100
Baghouse (Oxidizer)	kW	70	90	80
Wet FGD	kW	2,970	4,050	
Transformer Losses	kW	1,820	3,000	2,037
Miscellaneous Balance of Plant	kW	2,000	2,000	2,196
SCR	kW	50		
MDEA H2S Removal	kW			701
Claus Plant	kW			1,766
ASU Compressor/Auxiliaries	kW		126,680	
Pressurized dry feeder	kW			
Total Auxiliaries	kW	30,410	237,170	99,697
Total Auxiliaries w/o GPU	kW	30,410	163,780	40,117
Auxiliary Power (% of net)		5.5%	43.1%	18.1%
% Energy Penalty		0.0%	25.7%	8.9%

The supercritical pulverized coal power plants without CO₂ capture was based on Case 11 of a recent DOE study (**Reference 8**). The supercritical oxy-fired pulverized coal fired power plant with 90% CO₂ capture was based on Case 5C of another DOE study (**Reference 9**). All economics are adjusted to the same basis and are expressed in June 2011 dollars. Alstom's LCL-C™ economic study is published as **Reference 7**.

Overnight capital costs for the three plants are shown in **Table 9-4**. The LCL-C™-based plant with CO₂ capture is about 15% more expensive than the PC plant without CO₂ capture, while the Oxy-fired plant with CO₂ capture is over 60% more expensive than the pc plant without capture on a capital cost basis.

Table 9-4 - Overnight Capital Costs (June 2011 \$'s)

Case	Total Overnight Cost (Including Contingencies)		Total Overnight Cost Excluding Process Contingencies)	
	1000\$	\$/kW	1000\$	\$/kW
DOE Case SCPC w/o capture	1,348,407	2452	1,348,407	2452
DOE Case 5C Oxy SCPC	2,187,217	3977	2,125,620	3865
Case 1 LCL-C™ Transport	1,537,343	2795	1,533,278	2788

Figure 9-4 compares the 1st year cost of electricity (COE) for the three alternatives. The yellow portion of the graphs represents the CO₂ transportation and storage (T&S). Comparing the COEs without the T&S shows that LCL-C™ with 95% CO₂ capture adds less than 20% ($97/81=19.7\%$) to the base case cost of electricity without CO₂ capture, easily achieving the DOE goal of less than 35% more than the base case with no CO₂ capture. In comparison, oxy-fired pc with 93% CO₂ Capture adds over 50% ($124/81=53\%$) to the base case COE.

With respect to the avoided cost of CO₂ capture, LCL-C™ avoided cost during the recent study is about \$25 per ton of CO₂ while that of the oxy-fired pc case is about \$80 per ton of CO₂.

In summary, both the recent and previous economic studies of LCL-C™ show it to have great potential for the lowest COE of all CO₂ capture technologies studied to date. The studies also indicate that LCL-C™ can achieve the DOE goals of producing >90% CO₂ capture at a COE which is less than 35% greater than the no-CO₂ capture case.

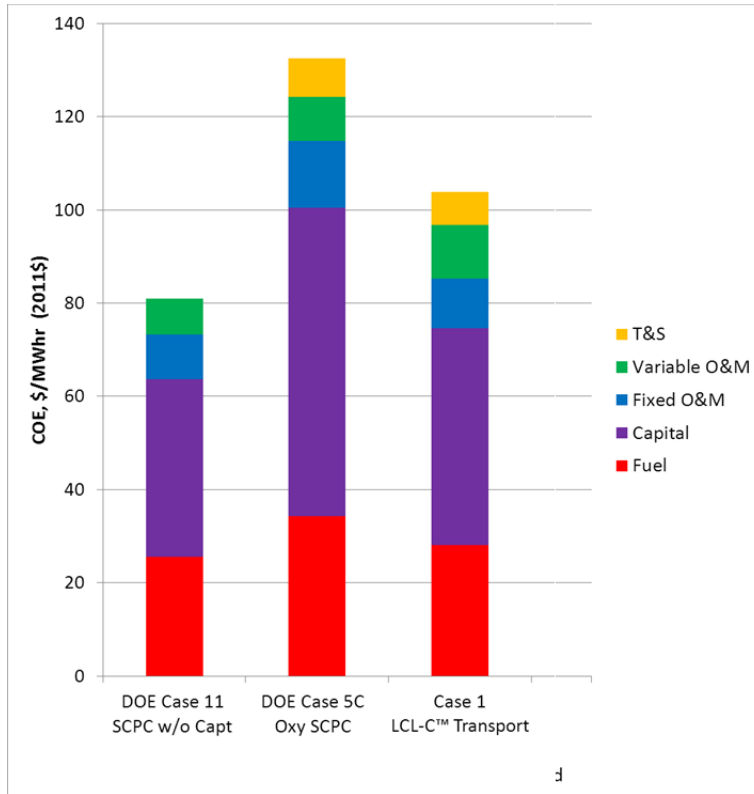


Figure 9-4 – Cost of Electricity Breakdown

10. Future Development Needs

3 MWt Prototype - Further testing (based on results to date)

40 hr Autothermal run

It has been Alstom's intention to continue testing at the prototype to achieve a full 40 hour autothermal test. This was done after the conclusion of Phase IVA.

Sulfur control (SAHE; limestone testing)

One of the results of the testing was that sulfur is sensitive to operating conditions. The SAHE is used to control temperature in the Reducer. The SAHE was not fully operational in the testing done to date. The operation of the SAHE will be developed to improve control of the process. Also limestone testing will be conducted to determine the effect on sulfur management.

Main Dip-Leg gas generation control – solids control

As described in Section 6, the dip-leg solids flow characteristics need to be tested to determine how much effect the generation of gas in the dip-leg has on the recycle solids rate.

RBO gate

To simplify the control of solid circulation and extend the operational range of the prototype unit it was decided to add an RBO gate at the bottom of the cactus extension for minimizing or eliminating the permeation of cactus gas to the Oxidizer. The reacting gas will go up the Reducer riser and part of the solids will go down to the Oxidizer through the RBO in a counter-current flow. This should also enhance the separation of unburned carbon. The RBO gate concept was tested independently. This was shown to be very effective in separating char or coal particles from the circulating solids. The integrated RBO gate from the cold flow model will be tested later in the CFM.

Full load

The maximum coal flow to the Prototype during the testing to date has been in the 50 to 75% range. Prototype testing will continue with the goal to achieve 100% coal Flow, roughly 750 lb/hr, depending on the coal type.

Condensing Heat Exchanger

In order to recycle the Reducer gas for fluidizing and transport gas the gas needs to be cooled to a level which is cool enough for the recycle compressor. This requires cooling the gas below the calculated dew point. The prototype includes a gas condenser. This heat exchanger has operated well with gas outlet temperatures above the gas dew point. A high dust carryover during startup and transient operations has

made it difficult to operate below the dew point due to plugging. Future testing and modifications will be done to address this issue.

Automatic solids control

Once the Prototype testing has established operating experience with solids control, an automatic control system will be developed to manage the solids inventory to simplify operations.

Commercial startup and operating

The prototype testing will lead to optimization testing which will allow Alstom to develop design and operating procedures for a demonstration or a commercial application. Optimization testing will include full load and part load, load change, long term runs and tests for potential demonstration plant coals.

Maximum pressure tests

The Chemical looping system is designed to operate with the Reducer at a higher pressure than the Oxidizer. Even though the Prototype is not intended to operate with very high pressures, the pressure drop between the reactors affects solids flow rates. Testing will be done to determine the optimum pressure to use in the Prototype to control solids flow in the RBO and the RPC.

Cold flow modeling support

Cold flow modeling will continue to be an important tool in analyzing the design and operation of the Prototype. Design concepts are first tried on the cold flow model and operational problems are modeled to help determine operational procedures. The cold flow model is also used for operator training.

Other tests indicated by Phase I of the economic study

Additional testing will be done as a result of the work being done for the economic study in Phase I of the project funded under DOE/NETL Cooperative Agreement No. DE – FE0009484.

11. References

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- 9 Pulverized Coal Oxycombustion Power Plants, DOE/NETL-2007/1291, Aug 2008

Appendix A Test Chronology

A-1 Cold Flow Model Test Chronology

Date	Test objective
3-Nov-10	CL40 startup
9-Nov-10	leak check, Pressure tap check
15-Nov-10	grid pressure drop
18-Nov-10	Fluidizing Velocity test for E. Kentucky FBHE ash
30-Nov-10	Solids feeding test in Reducer
7-Dec-10	Oxidizer grid pressure check, pressure tap range check
9-Dec-10	High circulation rate
14-Dec-10	Loss of Reducer riser top turn
7-Jan-11	Unit back on line
10-Jan-11	solids flow measurement
11-Jan-11	plenum pressure check
13-Jan-11	2 loops circulation
17-Jan-11	4 hr steady circulation test
18-Jan-11	Dip-leg level test
27-Jan-11	Dip-leg level test
28-Jan-11	RBO seal pot orifice changed to 1x0.75" from 2x1.25" and lower 1.25" RBO seal pot orifice changed to 1x0.3125" from 2x1.25" and lower 1.25"
8-Feb-11	chill ash test for solid flow
10-Feb-11	chill ash test for solid flow
11-Feb-11	chill ash test for solid flow
16-Feb-11	ash bulk density
22-Feb-11	chill ash test for solid flow
23-Feb-11	RBO seal pot orifice too small
24-Feb-11	RBO seal pot orifice changed to 1x0.65" from 1x0.315"
25-Feb-11	Dip-leg pressure drop and circulation flow
28-Feb-11	Remove Laser probe
8-Mar-12	chill ash test for solid flow
9-Mar-12	chill ash test for solid flow
10-Mar-12	chill ash test for solid flow
11-Mar-12	chill ash test for solid flow
12-Mar-12	chill ash test for solid flow
22-Mar-12	Solid feed under pressure test, RBO seal, dense bed recovery in cactus
2-Apr-12	solids empty conditions at cactus
3-Apr-12	solids empty conditions at cactus
4-Apr-12	bench 1-7/8 inch test for coal/solid separation

5-Apr-12	characterization of RBO flow
9-Apr-12	RBO control test
10-Apr-12	RBO control test
16-Apr-12	characteristic of RBO runaway
12-May-12	complete the modification of CL-CFM loop extend distance between cactus and RBO inlet
16-May-12	shakedown new RBO, feed test, RBO seal
17-May-12	high circulation test CFM broken at the horizontal duct/cyclone

A-2 Prototype Construction Chronology

Date	Item
07-Jul-10	Main SPCV at LVR Orifice plate cracked, needs to be recast. Insulating refractory installed MTF tiles have been made and are ready to ship
20-Jul-10	Main SPCV is at Kleeberg to weld in tubes, top and side MTF Cone received at Alstom
26-Jul-10	M SPCV delivered MTF Cone installed
05-Aug-10	Reducer parts at LVR before refractory installation Cactus arms were found to be cut too short with horizontal bottoms Cactus to be sent back to Kleeberg for repair Reducer Fluidizing Section (Section #2) ready to be packed with refractory Reducer spool pieces at LVR Cyclones curing
17-Aug-10	Cactus back to LVR after repair Cactus refractory curing north and south arms curing Fluidizing section has insulating refractory layer Other Reducer sections waiting for refractory L SPCV arrived from Kleeberg
25-Aug-10	RBO at LVR in 2 vertical halves, stiffening added LSPCV curing USPCV preparing for insulating refractory layer
26-Aug-10	MTF tiles installed Cactus, arms, fluidizing section and Reducer spool piece #1 received Water Chiller received MTF cyclone support design started
31-Aug-10	Cactus assembled (5 pieces) New cold flow model pieces delivered but not assembled
03-Sep-10	Cactus lifted into place

	MTF outlet tiles installed
7-Sep-10	Upper SPCV Refractory installed at LVR RBO refractory installed ready to be assembled Spool pieces refractory being installed
8-Sep-10	Main SPCV put into place
9-Sep-10	MTF Tiles done, top finished CFM has been assembled
16-Sep-10	RBO lifted into place USPCV lifted into place
30-Sep-10	Dip leg construction
2-Nov-10	LSPCV support cradle under construction at Kleeberg Condenser./Chiller under construction Chamber pots under construction
5-Nov-10	LSPCV cradle installed MTF outlet duct found to be damaged MTF cyclone support installed USPCV cradle installed RPC lifted into steel, not yet installed Reducer Cyclones in place 2nd Cyclone outlet duct installed
10-Nov-10	Chamber pot assembly at Kleeberg Starting water cooled duct assembly at Kleeberg Support for condenser/chiller assembled at Kleeberg
1-Dec-10	Final assembly for Chamber pots at Kleeberg
13-Dec-10	Condenser/chiller arrived and put in place Chamber pots installed Oxidizer Chamber pots outlet ducts installed Burners installed Demister and ductwork installed Water-cooled outlet duct from 2nry cyclone installed Octopus installed

A-3 Chemical Looping Prototype Testing Chronology

Date	Item	Comments
10/26/2010	Shakedown Started	Gas system setup
11/8/2010		Reducer Gas system setup Oxidizer Gas System setup
11/9/2010		Micro Gas Chromatograph shakedown
11/10/2010		ISBF gas system shakedown
12/7/2010		Reducer Main Nozzle DP test
12/13/2010		Process Control and Isolation valve Test
12/14/2010	Air test pt. I	Run ISBF only, test control loops, FGR fan

12/17/2010	Air test pt. II	Determine Oxidizer settings, Air heater control loop
12/20/2010	Air test pt. II, continued	Test Spencer Fan and blow off valve.
12/20/2010	Air Test pt. III	Determine Reducer air Flow settings. Run ISBF w/o burner. Test Fan control.
12/21/2010	Air Test pt. IV	Check Reducer & Oxidizer nozzles
12/22/2010	Shake down complete	Check max recycle gas and air compressor. Run 10000#/hr. in Reducer and 12000#/hr. in Oxidizer. Run Oxidizer and Reducer Burners
1/5/2011	Prototype Testing Started	Mass Flow controllers Test
1/14/2011	Mass Flow tests	Mass Flow controllers Test, continued
1/17/2011	Mass Flow tests	Rotameter and Mass-flow controller test
1/20/2011	Oxidizer Fan Test	Determine DP, Flow rate and fan speed versus flow
1/21/2011	Rotameter and Mass-flow controller test, continued	
2/10/2011	Air Flow Test	Oxidizer Riser Air flow test
2/11/2011	Air Flow Test	Reducer Riser Air flow test
2/18/2011	Solids transport test	
3/4/2011	Solids Feed Test	Rotary valve setup
3/7/2011	Flow meter check out	
3/16/2011	Burner Test	Refractory Heat up, Solids transport
3/17/2011	Burner Test, continued	Also tested condensate pump
3/18/2011	Burner Test, continued	
3/25/2011	Gas Flow Test	Load Solids. Heat up Refractory
3/26/2011	Steam H/X Valve Test	Check Steam Control valve characteristics
3/28/2011	Steam heater test and solids fill-up	
3/29/2011	Solids fill-up continued	Put solids into SPCV, Dip--leg, RPC, FBHWE, MBHE, RBO
3/30/2011	Solids fill-up continued	Fluidizing test in Main SPCV, RBO, Dip leg, RPC
4/1/2011	Solids circulation test	Load solids and circulate solids, not stable
4/3/2011	Solids circulation test	Compressors checked
4/4/2011	Solids circulation test	Flow circulated but not constant

4/5/2011	Solids circulation test complete	Both Reducer and Oxidizer circulation stable with electric warm-up heaters on. Hands free operation for about 1.5 hours
4/6/2011	Inspect unit	
4/7/2011	Solids loading	
4/8/2011	Start circulation and warm-up test	
4/12/2011	Circulation and Warm-up test, continued	
4/13/2011	Circulation and Warm-up test, continued	
4/16/2011	Circulation tests	Reducer Dip leg test. Test grease air, fluidizing and Transport air flows for circulation. Oxidizer only circulation, Reducer circulation
4/18/2011	Circulation tests, continued	Heaters on, SAHE flow tests, burners turned on. First time both burners were on with full circulation.
4/19/2011	Circulation tests, continued	Burners running at max, condenser/chiller DP rising, demister DP rising, solids recirculation is good. Couldn't light reactor natural gas. 24 hours operation with stable circulation while warming up
4/20/2011	Circulation tests, continued	Seal pot parametric tests
4/21/2011	Circulation tests, continued	Pluggages in cyclone
4/22/2011	Circulation tests, continued	ISBF control sys problems. Trouble with electric heater on Ox. Shut down for modifications and cleanup.
5/3/2011	cleanup	Found damage to Main SPCV
5/10/2011	Air Tests	Testing new 'special 'air system, fill unit
5/11/2011	Circulation tests, continued	Circulation started, warm-up started
5/12/2011	Circulation tests, continued	Coal feeder started. Limestone feeder startup. Natural gas to Reducer is lighting up.
5/13/2011	Circulation and warm-up tests completed	Shut down to clean out.
5/14/2011	cleanup	

5/27/2011	Fluidizing lance air test.	
6/5/2011	Start operational testing	Solids fill-up
6/6/2011	Circulation and warm-up	Started up but had main fuel trip (MFT)
6/7/2011	Circulation and warm-up	Started up and ignited NG warm-up burners, solids circulating well
6/8/2011	Circulation and warm-up, continued	Experiencing some solids control problems, coal flow started Operating temp to 1794 F. Coal feed plugged. Shut down
6/9/2011	Circulation and warm-up, continued	Oxidizer bottom plugged
6/10/2011	Circulation and warm-up, continued	Oxidizer cleaned up, restarted. Circulation difficult, adjusting fluidizing air flows.
6/11/2011	Operational Test completed	Prototype heated up to operating temperature, coal flow started, several main fuel trips (MFT's) when switching to recycle gas. Multiple hot restarts successful. Chemical looping reactions for a short time.
8/9/2011	Pretest checkout	New CO ₂ injection system tested
8/17/2011	SAHE DP test	
8/30/2011	Camera Inspection	
9/1/2011	Reducer Gas Analyzer test	
9/7/2011	Oxidizer Inspection	
9/22/2011	pressure drop test	All process equipment tested for pressure drop without solids
9/24/2011	Supplemental testing started	Solids fill-up
9/26/2011	Cold flow tests	Completed cold flow tests, started heating up
9/27/2011	Circulation and warm-up, continued	Heated up, natural gas lit off, coal flow started. Plugged RPC, cleared and restarted. New plug. Shut down.
9/28/2011	Circulation and warm-up, continued	Started up, had several plugs , cleared plugs and started up again
9/29/2011	Circulation and warm-up, continued	Heated up, natural gas lit off. RBO not working. Shut down.
10/3/2011	Circulation and warm-up, continued	Repaired RBO. Set up for running. Started circulating

10/4/2011	Circulation and warm-up, continued	Heated unit up to operating temperature, fuel to full coal. Problems with RPC, ox cyclone solids flows
10/5/2011	Circulation and warm-up, continued	Shut down to fill RBO and restart. Refractory damage in Ox cyclone. Shut down.
10/6/2011	Clean and inspect	
10/7/2011	start facility repair	
10/10/2011	solids fill-up	
10/11/2011	Circulation and warm-up	Prototype heated up, coal flow started.
10/12/2011	Testing continued	Solid flows not stable, shut down for plumbing changes, and restart. Coal feed chute glowing.
10/13/2011	Testing continued	Coal feeder issues. Used full CO ₂ to Reducer. Coal flow to 300#/hr. Coal chute glowing
10/14/2011	Testing continued	Feed system erratic. Coal and solids feed interrupted but restored.
10/15/2011	Supplemental testing stopped	Coal feed stopped, RV problems. Started natural gas test, then shut down.
10/16/2011	Start facility inspection and repair	Modifications to major systems needed: Coal Feed, RPC, and Cyclone.
5/15/2012	Modifications done. Reducer Test Preparation	Solids feed system component test. Air system tests.
5/21/2012	Reducer test started	Solids fill-up. Oxidizer cold flow air test. Reducer cold flow air test.
5/22/2012	Reducer Test Continued	Circulating solids. N ₂ used for Reducer transport. Coal feed started. New feed system working well.
5/23/2012	Reducer Test Continued	Feeding Charcoal for test. Restarted with Adaro coal for test. Shutting down for h/x leak.
5/24/2012	Facility repairs	Cyclone vortex finder, Oxidizer outlet duct H/X need repairs. Clean and re-inspect unit.
6/4/2012	Restart Reducer Tests	Solids fill-up. Start circulating and Warm-up
6/5/2012	Reducer testing completed	Started coal feed. Adaro P.C. Coal feed to 350 #/hr. Shut down
6/6/2012	Inspect unit	Need some minor repairs.
7/2/2012	Test prep.	Air/gas tests.
7/9/2012	Prep. For Oxidizer testing.	Solids fill-up

7/10/2012	Oxidizer Testing	Circulation started. RBO operation erratic
7/11/2012	Oxidizer Testing	Hot SAHE flow test. Shut Down test when ball valve on Oxidizer fill port failed. Reset and restart. Shut down because RBO wasn't working
7/12/2012	Repairs	RBO refractory repair. Slag in Oxidizer needs to be removed
7/19/2012	Repairs	Slag burnout successful
7/23/2012	Oxidizer test continued	Circulation started. SAHE test.
7/24/2012	Oxidizer test continued	Coal feed started Test started. Coal feed at 250#/hr. New Test with coal at 450#/hr. Tripped by data system. Restart
7/25/2012	Oxidizer test continued	Coal to 550 #/hr. Natural gas off, auto-thermal operation. Coal to 800 #/hr.
7/26/2012	Oxidizer test completed	Auto-thermal operation continued for 12 hours total. Near 100% carbon conversion. Changed to Pitt. #8 coal. Restart. Tried steam in Reducer. SAHE testing. Shut down.
8/10/2012	Prepare for supplemental test.	Solids fill-up
8/13/2012	Supplemental test start-up	Circulation started.
8/14/2012	Testing continued	Warm-up. Hi Oxidizer delta p. SAHE test. Start coal feed. Start testing
8/15/2012	Testing continued	Attempted on-line fill of RPC, recirculated solids
8/16/2012	Testing continued	Circulation stopped to fix fill valves. Circulation re-started. Shut down
8/17/2012	Facility cleanup and inspection	Found loose refractory piece in Seal pot
8/21/2012	Testing Suspended, Inspection	Found damage to Oxidizer tiles. Testing suspended for now.

Appendix B Prototype Operation

Shakedown of the Prototype unit commenced in October, 2010 with the commissioning of the gas analysis systems for the Oxidizer, Reducer and Reducer outlet gas flare. Shakedown proceeded in a systematic fashion, checking each component to ensure proper and complete installation as well as testing core functionality against specified design criteria. Purchased equipment such as fans, pumps, heaters, etc. were checked for operation and control. Instrumentation (Thermocouples, Pressure Cells, Mass Flow Controllers/Meters, Control Valves, etc.) were verified as to correct placement, calibration, range and communication to the DCS. Controls implemented in the DCS were vetted for performance and safety logic implementation. Fabricated components (solids control lances, riser flow nozzles and other equipment) were characterized.

Upon completion of component level shakedown, the facility was prepared to be run through a series of Air Tests. These tests were intended to demonstrate integrity of the facility flow paths, characterize the facility flow and pressure drops, as well as to define limits of operation for support equipment. These tests were also to incorporate and verify operation of additional equipment such as:

Start-up Fans - Define flow and stall characteristics
Electric Heaters - Verify operation and controllability, determine max heat input
Orifice Flow Measurements - Verify feedback, cross-check calculated flows
Recycle Gas System - Check compressor operation, control, limits, and stability
Chiller System - Check operation and control
Condensate System - Check pressure isolation, pH neutralization
Steaming Heat Exchangers – Check water flow measurements, control valves
Oxidizer / Reducer Reactors - Determine flow vs. pressure drop, limits of operation

During these tests, the natural gas warm-up burners were fired for the first time, defining their maximum heat input and operational envelope. **Figure B-1** shows the operator starting the air fans during this testing, while **Figure B-2** shows the control engineer monitoring the control system.



Figure B-1 - Start-up for the Air Tests



Figure B-2 - Monitoring the Control System

Following the Air Tests, several tests were initiated to validate solids preparation and handling equipment. These tests verified operation of the outside material feed system (feed hopper, roll-crushers, incline screw, bucket elevator, etc.) that would be used for both coal and ash supply to the unit. These operations included successful tests to demonstrate successful size-grading and transport of the CFB solids to the storage hopper.

In March 2011, tests were run to warm up the main loop refractory for the first time with sustained electric heater and burner operation. The solids pneumatic fill-up system was also tested and successfully used to load CFB solids into the Prototype for anticipated cold flow solids transport testing. These tests established solids fill-up procedures (fill rates, component capacities, level determinations, equipment settings, etc.) that would be used for all future testing. Once equipment was successfully loaded

with solids, tests commenced to characterize Seal Pot Control Valve (SPCV) lance flow and fluidizing performance. Once all SPCVs were full, the Oxidizer and Reducer loops could be isolated and tested independently for the first time.

Cold flow solids transport testing began in April 2011 with the goal of achieving stable dual-loop operation prior to hot testing. Initial attempts resulted in high solids loss as operators had to become familiar with the characteristics of the system. Using SPCV and air flow settings suggested by the cold flow model, operators were able to progress to a stable operating mode. Stable dual-loop solids circulation in the Prototype was achieved on April 5, 2011 which represented a major milestone in the commissioning process. Settings for this operation were recorded and data was logged for analysis. The solids transport was stable enough to allow 'hands off' operation up until the prototype was intentionally shut down for the evening after about an hour of operation.

The next series of tests was performed in mid April 2011, and was targeted at achieving stable dual-loop solids circulation in a warm-up mode, with both electric heaters and gas burners in operation to demonstrate a complete warm-up cycle of the Prototype. Solids circulation was started and run for a 24-hour period during which the process was heated slowly, starting with electric heaters and progressing through the load range of the gas burners. Although the prototype was operating well throughout the startup, the maximum achievable temperature was limited to about 600-700 degrees F while circulating solids. An additional attempt was made to increase the riser temperature by running the burners without solids circulation. A successful light-off of main natural gas injection in the Reducer riser was made once the riser temperature exceeded 1300 degrees F, although this could not be sustained with circulating solids. These tests experienced intermittent solids hang-ups at various times due to overfilling, operational imbalance and improper fluidizing and grease air application. A variety of techniques was employed to resolve these hang-ups, one of which over-pressurized and damaged the Main SPCV. Overall, these tests achieved a significant amount of operator training and generated operational data which was logged for subsequent analysis.

After making repairs to the MSPCV, modifications to the gas valves and combustion air supply to the burners, and adding a grease air system designed to prevent pressure tap pluggages, the unit was restarted in May 2011. The unit was again run for over 24 hours with improved natural gas flow to the burners. For the first time, main natural gas injection in the Reducer was successful while circulating solids. The solid fuel feed system was commissioned and coal was fed to the process for the first time. Coal feed rate was restricted to 100 pounds per hour with supplemental natural gas and the unit briefly reached 1450 degrees F. Syngas was made in the Reducer for the first time.

In early June 2011, the prototype was restarted after minor equipment modifications and an upgrade of the natural gas delivery system for the burners. With these improvements, the riser temperatures were able to be raised high enough to sustain main natural gas ignition in both the Oxidizer and Reducer risers while

maintaining solids circulation. The Oxidizer was heated up to full operating temperature. Coal was fired along with natural gas in the Reducer.

In mid June 2011, the prototype was restarted. Previous modifications and acquired operator experience allowed rapid warm-up to operating temperatures. Coal was fired for about an hour at rates up to 360 pounds per hour. **Chemical looping reactions were achieved on June 11, 2011.** Reducer riser air was eliminated as the recycle gas compressors were switched to recycle mode to provide transport gas for solids transport in the Reducer.

Preparations were made for a new series of test runs in August 2011. A new batch of solids was obtained from the Warrior Run CFB. The solids used in the previous tests were replaced because the extended startup testing caused size degradation and contamination.

Control logic in the DCS was modified based on previous operational experience. In previous tests, the control system was responsible for a number of nuisance trips due to overlapping safety interlocks and overly conservative settings for trip points.

A cryogenic CO₂ gas system was installed on the Prototype and the piping system was modified to allow selection of air or CO₂ for the Reducer riser air, Grease Fluidizing and Transport air (GFT), SAHE fluidizing air, and the coal feed chute cooling air. The CO₂ system was intended to temporarily replace the recycle gas system to allow testing to concentrate on the core process chemistry and mitigate some existing equipment issues. A system pressure drop test was done without solids in the prototype. The system was then filled up with the new solids and cold flow tests were conducted.

During the previous tests, it had been difficult to establish solids flow through the SAHE. New fluidizing lances were installed to mitigate this problem and the SAHE was tested with cold solids. In these new tests, the first significant SAHE solids flows were achieved and the pressure drop characteristic of the SAHE was developed for control purposes.

The prototype was then tested in hot operation mode during the week of September 26, 2011. During these tests a series of pluggages in the RPC caused the unit to be started and stopped a number of times. During the last warm-up attempt, it was determined that there was low solids crossover flow through the Reducer Bottom Outlet (RBO). The Prototype was shut down to inspect for issues. It was found that two large pieces of the RBO roof refractory had broken and fallen down, thereby blocking the solids flow. The rest of the system was inspected and found to be in good order. The RBO was repaired and the prototype was set to operate again on October 3rd. **Figure B-3** shows the Lower section of the Oxidizer and Reducer and the smaller of the pieces removed from the RBO.



Figure B-3 – RBO (left) and the smaller of two refractory pieces removed from the RBO (right)

The unit was restarted on October 3, achieving a full warm-up and transition to coal. However, the unit had to be shut down due to overheating surfaces on the Oxidizer cyclone and Oxidizer outlet duct. It was later determined that solids had gotten behind the hard face refractory and eroded out several areas of insulation, resulting in the overheating.

The Oxidizer outlet duct and Oxidizer cyclone were repaired and the unit was restarted on October 11. During this testing the coal feed was erratic; resulting in several starts and stops to attempt to regain coal feed. The system progressively deteriorated until the lower 4" fuel feed rotary valve ceased to operate and the prototype was shut down.

The final milestone for this phase of the overall program was to achieve sustained auto-thermal operation for 40 hours. Due to a series of mechanical difficulties, auto-thermal operation was not realized within the original project schedule or budget. Two issues were identified which were primarily responsible for preventing auto-thermal operation of the Prototype. Interrupted and/or erratic coal flow was occurring due to excessive rotary valve gas leakage (**Figure B-4**). Additionally, periodic interruption of solids recycle was occurring in the RPC due to a combination of surging cross-over flows and a restrictive recycle leg geometry (**Figure 7-4**). Solutions to these issues were devised and implemented.

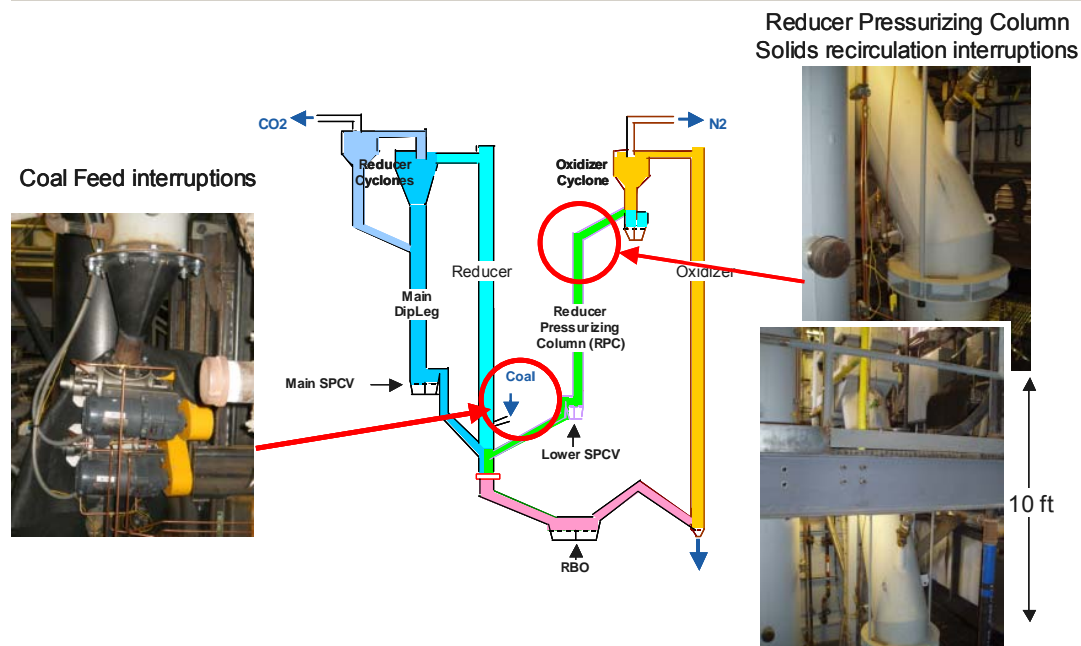


Figure B-4 – Prototype Mechanical Problem Areas

To correct the previous issues with intermittent coal feed and feed pipe pluggages, it was determined that the feed system would be redesigned. A new fuel nozzle design was implemented to include a silicon carbide fuel chute into the Reducer riser, a water-cooled section, and a purge/sweep gas connection. The feed line to the nozzle was increased in size with larger 8-inch rotary valves replacing the original 4-inch valves. The new 8-in valves were raised to both prevent direct radiation from the riser from overheating the valves, and to increase the distance between the two valves, thereby increasing the height of the solids pressurizing column. To accommodate the new arrangement, the Luxme drag conveyor was also modified to supply solids to elevation 52 rather than elevation 34.

The Reducer Pressurizing Column (RPC) had been experiencing intermittent solids flow problems during previous testing. As shown in **Figure B-4**, the RPC was originally designed with a bend to extend from the Oxidizer cyclone to the lower seal pot. It was determined that the RPC would be redesigned to be straight without any bend. This involved moving the Oxidizer cyclone to be positioned directly over the lower seal pot, and modifying the outlet duct from the Oxidizer to the Oxidizer cyclone. The new components are shown in **Figure B-5**.

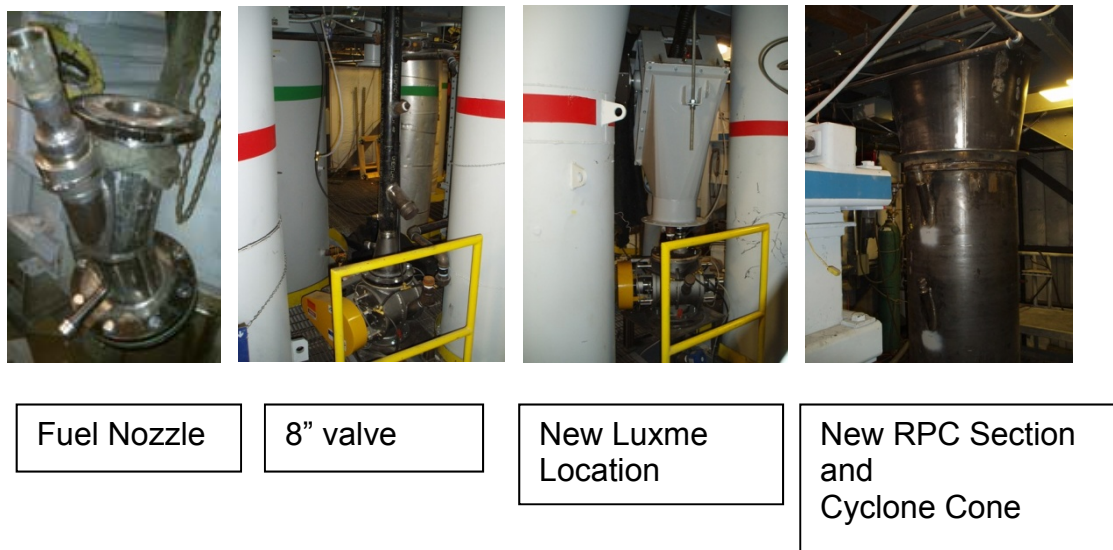


Figure B-5 – Modified Fuel feed, RPC and Cyclone Components

In April 2012 the new coal feed system was tested. A series of tests were performed using pulverized Illinois #6 coal to determine coal feed versus elevated rotary valve discharge pressure. The tests showed that the new coal feed system could feed coal from atmospheric pressures into a back pressure similar to the maximum Reducer operating pressure.

Modifications to the RPC and Oxidizer cyclone were completed in May, 2012.

Upon completion of the modifications, tests were planned for the Prototype as part of a comprehensive plan to attain auto-thermal operation. Tests were designed to characterize the Reducer operation, the Oxidizer operation and then to integrate the results and operate the prototype in the auto-thermal mode.

In May and June 2012, the 'Reducer Test' was executed, which meant running the Prototype in a "decoupled" mode. Decoupling means that the Reducer heat was supplied by supplemental natural gas firing in the Oxidizer, instead of relying solely on the Oxidizer exothermic chemical reactions to supply heat as would be the case in the auto-thermal mode of operation. In this mode the Oxidizer is being used predominantly as a heat source to maintain temperature in the Reducer. Testing and sampling were targeted at just the Reducer without having to characterize the Oxidizer at the same time. The objectives of the Reducer test were to show the Reducer chemical looping reactions and to evaluate the Reducer performance. The data produced was the coal and CaSO₄ conversions, solids recycle rate and the Reducer solids loading.

The May 2012 Reducer testing was interrupted by a water leak in the water-cooled outlet duct exiting the Oxidizer cyclone. (**Figure B-6**) Water was able to leak into the cyclone and from there into the RPC dip-leg, resulting in ash agglomeration and plugging of the RPC column, as can be seen in the right hand image of **Figure B-6**.



Figure B-6 - Location of Water leak in Oxidizer Cyclone Outlet Duct

This duct was repaired, the RPC cleaned out, and the unit restarted on June 4. However, another water-cooled ductwork failure, this time on the exit of the secondary Reducer cyclone, (**Figure B-7**) caused a similar forced shut-down and end to the Reducer testing. As can be seen in the right-hand picture of **Figure B-7**, the water leak in the outlet duct caused ash build-up and eventual gas flow obstruction.



Figure B-7 - Location of Water Leak in Reducer Secondary Cyclone Outlet duct

Even though there were several mechanical issues, the Reducer tests were very successful. The results showed that, 1) all chemical looping reactions were realized, 2) there was a high carbon burn-up efficiency of greater than 98% and 3) there was low carbon carryover to the Oxidizer. Oxygen demand was 15 to 20%. SO₂ release can be controlled by varying the excess air to fuel ratio.

In July 2012 the Prototype was prepared for the 'Oxidizer Test' and characterization. The purpose of this test was to verify the Oxidizer reactions. The intent was to use fuels of varying reactivity in the Reducer and determine carbon carryover and CaS conversion in the Oxidizer. Various sources of calcium were used as a CaSO₄ source.

The unit was started in July 2012 to execute the 'Oxidizer Test'. Solids cross-over through the RBO was erratic from the beginning and the unit was shut-down for inspection. It was determined that another section of refractory roof had failed in the RBO and had fallen and lodged in the flow path obstructing solids flow (**Figure B-8**).

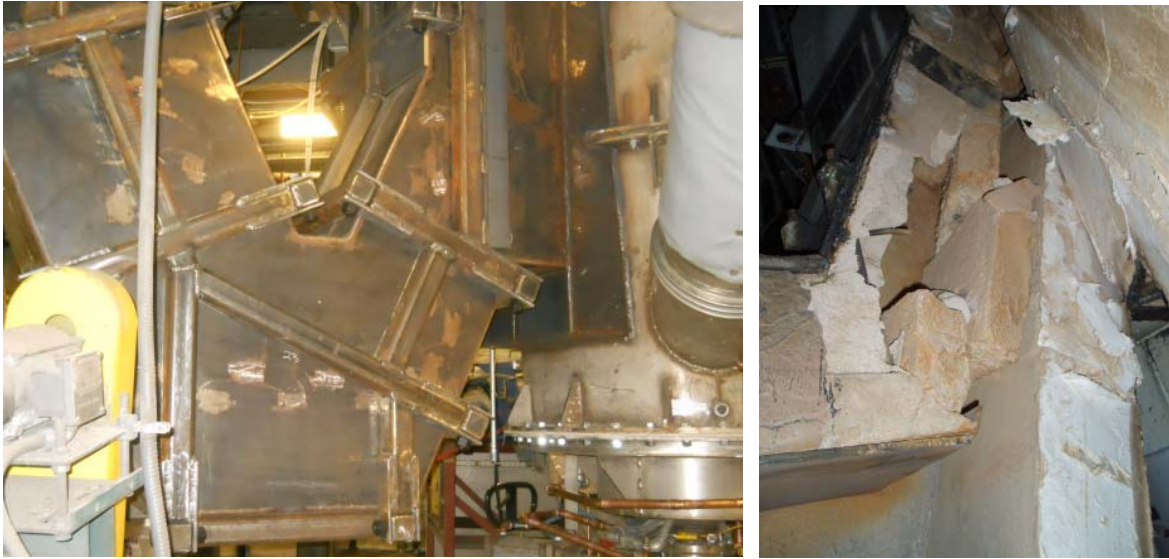


Figure B-8 – Location of Refractory Failure in the RBO

The RBO was repaired and additional inspections during the downtime revealed a significant amount of slag accumulation on the walls of the Oxidizer riser as well as around the Oxidizer air inlet, **Figure B-9**. The slag build-up was due to high alkali ash generated during previous charcoal testing under a parametric test conditions where the Oxidizer was maintained at excessively high temperatures.



Figure B-9 – Slag Build-up in the Oxidizer

The Oxidizer burner was fired without solids circulation and with the bottom removed to allow the slag to be melted out of the Oxidizer, **Figure B-10**.

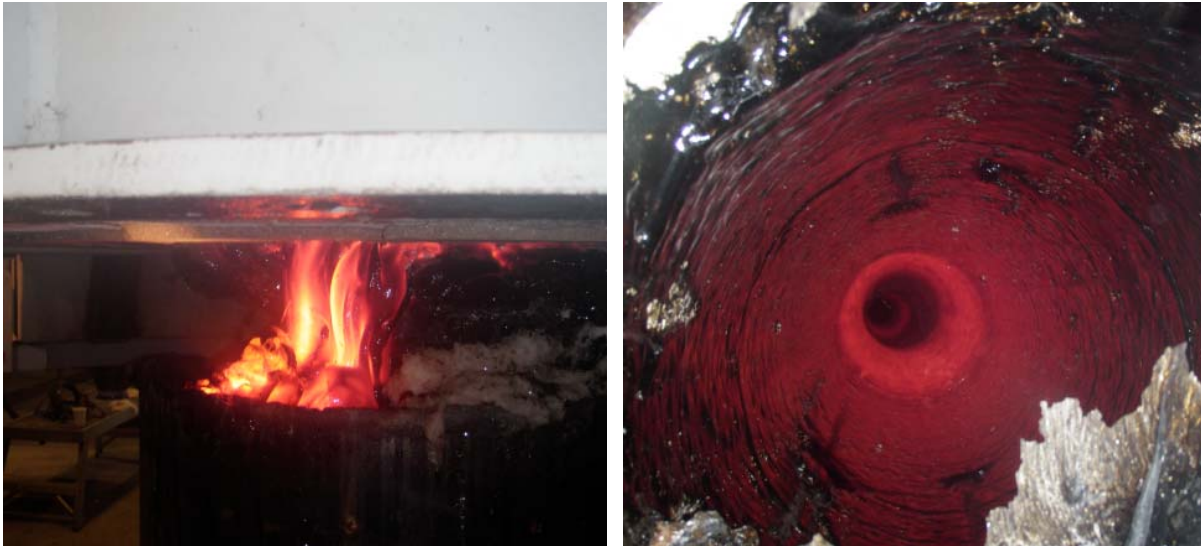


Figure B-10 – Slag Being removed from the Oxidizer

The unit was restarted for Oxidizer testing on July 23, 2012. During this test run, all test matrix conditions were executed, and **Auto-thermal Operation was achieved on July 26, 2012**. Auto-thermal operation was sustained for a combined total of 12 hours before the unit was intentionally shut-down.

The Prototype was prepared for additional testing, and was started on August 13, 2012. The unit was brought up to Auto-thermal conditions, but then experienced a loss of solids circulation through the Lower RPC SPCV. The unit was shut-down for inspection, and a refractory brick was found lodged in the outlet of the seal-pot, **Figure B-11**.



Figure B-11 – Refractory brick in Seal-pot

Further investigation revealed that the Oxidizer riser refractory lining had failed with multiple large cracks in the liner tiles, allowing refractory pieces to enter the process, **Figure B-12**. This failure ended this round of testing.



Figure B-12 – Cracks in the Refractory Tiles in the Oxidizer