The 34th International Technical Conference on
Clean Coal & Fuel Systems
May 31 – June 4. 2009
Clearwater, Florida, USA

Alstom's Calcium Oxide Chemical Looping Combustion Coal Power Technology Development

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Introduction

Alstom Power Inc, with major funding from the DOE, has just started Phase IV of a multiphase program to develop an entirely new, ultra-clean, high efficiency power plant process for the global power market. This process, known as Chemical looping, has the potential to be the most efficient and most cost efficient means of capturing CO2 from new and existing coal fired plants, while at the same time providing extremely clean, high efficient operation.

Alstom is a major, worldwide supplier of power plant equipment. Alstom is one of the very few companies, worldwide, that can supply a turnkey power plant which includes the entire boiler/scrubber island and combustion turbine or steam turbine power block of their own design and manufacture. Over 40% of the world's power plant steam generators are of Alstom design. Environmentally, Alstom has pioneered the development of power plant SO_2 scrubbers, CO, NOx and particulate control and most recently mercury capture systems.

Alstom has been developing the Chemical Looping Process for almost fifteen years and has designed and built a small-scale pilot plant at its Windsor Ct. site. The pilot plant has been used in the first three phases of the current development program with the DOE. The first three phases investigated the chemical and mechanical processes that are involved in chemical looping as well as the solids transport control. The recently started Phase IV program will build and test an integrated prototype chemical looping plant with an auto-thermal capability that is roughly the size of a 3Mw thermal plant.

This paper reviews the status of Alstom's Chemical Looping Development program using calcium oxides for the oxygen carrier. It will review the results of the first three project phases and present the status of the current prototype Phase IV.

Alstom's Chemical Looping Technology

Chemical looping is a relatively new technology which converts fuel to energy with inherent capture of carbon dioxide. The concept is based on the transfer of oxygen from the air to the fuel for combustion or gasification by means of a solid carrier without the need for cryogenic or membrane separation to produce oxygen.

The process (see **Figure 1**) consists of an air reactor, where the solid oxygen carrier is oxidized by the O_2 content in the air, and a fuel reactor, where the solid oxygen carrier is reduced by the fuel that is converted to mainly CO_2 and H_2O. After condensing the water vapor, a stream of almost pure CO_2 is obtained. The separation of CO_2 is inherent in the process, resulting from the principle that combustion air and fuel are never mixed.

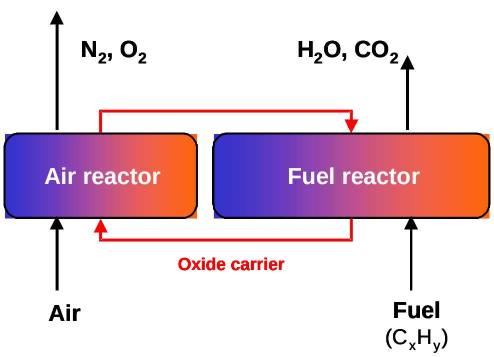


Figure 1 - Chemical Looping Principle

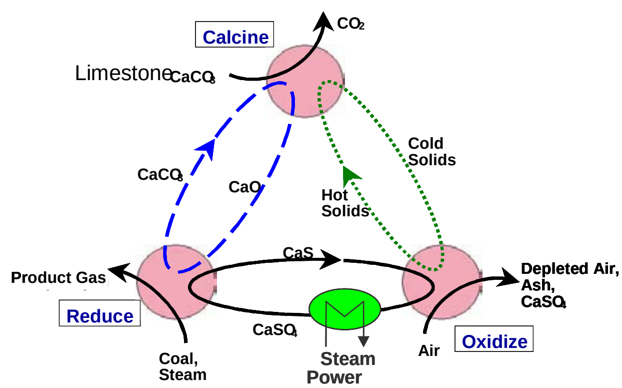


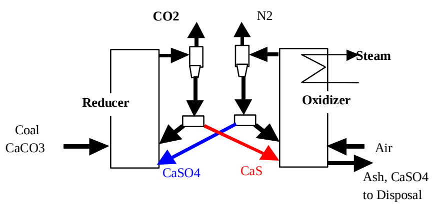
Figure –2 Alstom's Calcium base Chemical Looping Process

Alstom is developing the Chemical Looping Process, utilizing calcium oxides and metal oxides as oxygen carriers to transport oxygen from air to the fuel. The two paths are followed by research teams worldwide, and each path offers specific features in terms of oxygen carrier availability, durability, operating temperature and fuel range.

Alstom's limestone based chemical looping process uses calcium sulfide as the oxygen carrier (**Figure 2**). The process uses air, coal, limestone and steam to produce product gas and capture CO_2. Depending on the system configuration, the Product Gas can be hydrogen, syngas (CO and H_2) and/or CO_2. Heat and product gas produced by the process can be directly used to produce electricity via Rankine cycle, Brayton/Rankin cycle and/or fuel cell cycles in retrofit, repowered or new capacity power plants.

Alstom's limestone based process can be configured in three basic ways as shown in **Figure 3**.

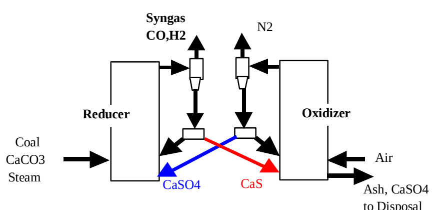
Option 1 (**Figure 3**), Chemical Looping Combustion Steam Power Plant with CO2 capture, is configured utilizing only the bottom loop of **Figure 2**. The process burns coal by using air indirectly as follows: Limestone added to the process captures the sulfur in the coal forming CaS (calcium sulfide) in the Reducer reactor. The CaS is burned in a heat liberating reaction with air in the Oxidizer reactor, producing hot $CaSO_4$ (calcium sulfate). The hot $CaSO_4$ is cycled to the Reducer supplying the oxygen and heat to burn the coal and reduce the $CaSO_4$ to CaS for continuous recycle. An excess air-to-coal ratio of about 1.2 (air-rich) is used. The carbon and hydrogen in the coal leave the Reducer as CO_2 and H_2O (the Product Gas). Water can be removed from this gas stream, and the CO_2 directed to EOR or sequestration. Heat produced by the process is used to make high pressure superheated steam for power generation. $CaSO_4$, coal ash and some unused CaO are bled from the system to prevent sulfur and ash from building up. Fresh limestone ($CaCO_3$) is added to replace the calcium thus removed.



Option 1 – Combustion with CO2 Capture

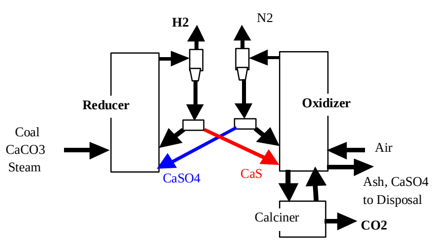
Applications:

- •CO2 Capture - PC Retrofit
- •CO2 Capture - CFB Retrofit
- •CO2 Capture-Ready Power Plant
- •Advanced Steam Cycles



Option 2 – Syngas Production

- •IGCC with down-stream CO2 capture
- •Industrial syngas
- •Coal-to-liquid fuels



Option 3 – Hydrogen with CO2 Capture

- •CO2 Capture - PC Retrofit
- •CO2 Capture - CFB Retrofit
- •CO2 Capture-Ready PC/CFB Power Plant
- •Advanced Steam Cycles
- •IGCC with CO2 Capture
- •Fuel Cell Cycles
- •Industrial hydrogen, CO2

Figure 3 – Alstom's Chemical Looping Process: Options and Applications

Option 2 of **Figure 3,** Chemical looping Gasification with downstream CO2 capture, uses the same process configuration as Option 1. However, Option 2 uses an air-to-coal ratio of about 0.3 (fuel-rich), thereby making a Product Gas consisting of CO and H_2 (syngas). This product gas can be shifted to hydrogen and CO_2 followed by CO_2 separation. The resulting hydrogen can be used for feedstock to a wide range of product applications, or can be burned in a gas turbine, comparable to a conventional IGCC plant. The separated CO_2 would be directed to EOR or sequestration.

Option 3 (**Figure 3**), Chemical looping Gasification with inherent CO2 capture, operates at the same low air-to-coal (fuel-rich) ratio as Option 2, but includes inherent CO_2 capture. To accomplish CO_2 capture, a Calciner is added to the system. The operation of the Calciner is shown in **Figure 2**. Referring to **Figure 2**, steam (H_2O) is added to the Reducer, which oxidizes the CO in the syngas to CO_2 while reducing the H_2O to H_2. The CO_2 is captured by the excess CaO (calcium oxide) which is in the circulating solids, forming $CaCO_3$ (calcium carbonate). The CO_2 is released from the $CaCO_3$ in the Calciner with heat for the reaction supplied by hot solids from the Oxidizer, forming CaO for recycle and reuse in the Reducer.

Alstom’s Chemical Looping process has the following advantages:

- Avoids the large investment costs and parasitic power associated with either cryogenic air separation units (ASU’s) or oxygen transport membranes,
- Captures CO_2 at temperatures higher than the power cycle temperatures, thus eliminating the thermodynamic penalty normally associated with CO_2 capture,
- Small equipment and low capital cost due to fast chemical reactions,
- Uses conventional material of construction and fabrication techniques

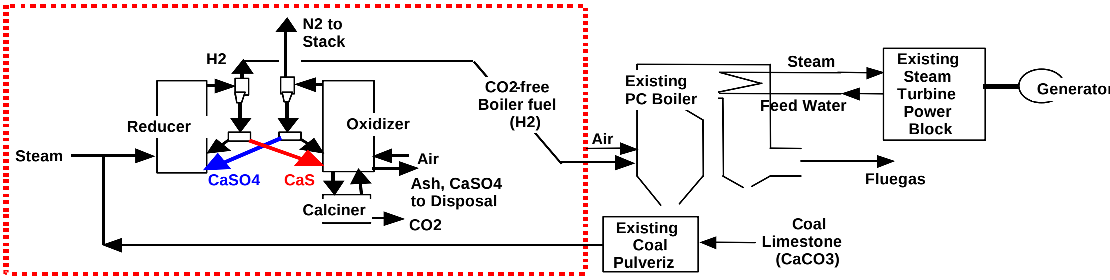
Chemical Looping offers the potential for an extremely cost competitive option for producing electricity and/or syngas from coal with CO_2 capture.

Retrofit Applications

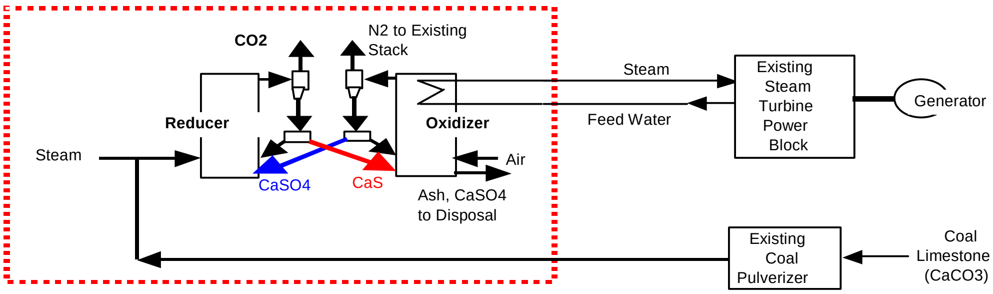
Figure 4 shows two potential retrofit concepts for PC boilers that could be implemented with the development of chemical looping technology.

In concept 1 of **Figure 4**, the chemical looping system produces hydrogen and a separate stream of nearly pure CO2. This is basically option 3 in Figure 2. The hydrogen is used as a fuel for the existing boiler and the CO2 is sequestered or used somewhere else. Limestone is pulverized in the existing pulverizers with the coal. Very little modification of the existing boiler is required to obtain full generator output.

An alternative is shown by concept 2 in **Figure 4**. The chemical looping plant is designed as in option 1 in Figure 2 to produce high-pressure, superheated steam for use in the existing steam generator and a separate stream of CO2. The existing pulverizer is used to grind the limestone as in concept 1. The boiler is not used and full generator output is obtained. Alstom has studied the cost and performance of this configuration based on the results in **Reference 1**. Results show that the cost is competitive with other CO2 technologies. A variation of this concept uses the existing boiler as the oxidizer vessel of the chemical looping system.



Concept 1 – Chemical Looping CO2 -Free Fuel; Minimum Boiler Modification

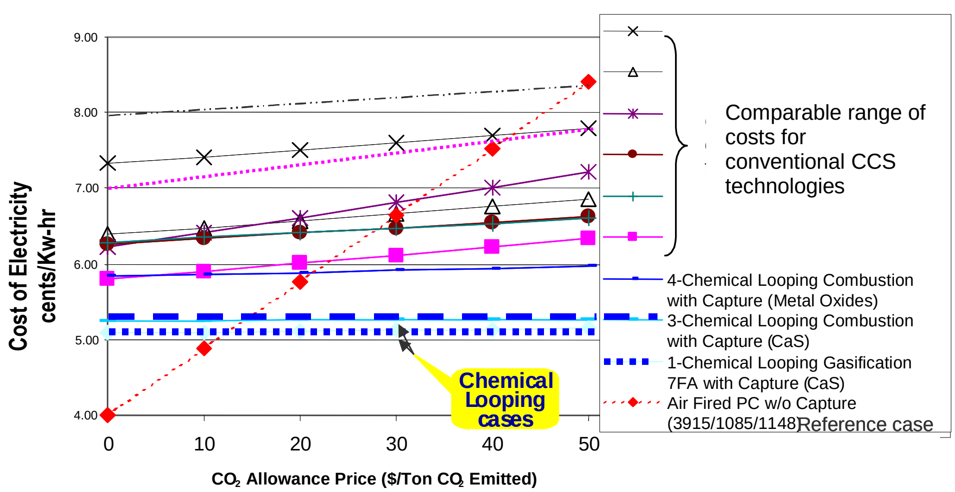


Concept 2 – Chemical Looping Oxidizer Replaces Boiler

Figure-4 PC Retrofit Concepts using Alstom's Chemical Looping Process

New Capacity Economics

The economics of various CO_2 technologies being studied at Alstom for new coal-fired power plants are shown in **Figure 5.** This figure also lists the economic assumptions used. Costs are relative and in 2006 dollars. Comparisons are made with other conventional carbon capture and sequestration (CCS) technologies, including IGCC, post capture, and oxygen firing. Details are beyond the scope of this paper but the analysis is an update of **Reference 1,** adjusted to 2006 dollars



Basis:

- Plant size — 400 MWe
- Steam conditions — 3915 psia/1085 degF/1148 degF/2.5in Hga
- Cost basis — 2006, $US
- Coal cost — 1.5 $/MMBtu
- Levelized capital charge — 13.8%
- Capacity factor — 85%

Figure 5 – Cost of Electricity for CO_2 Capture Technology Options

Figure 5 shows Alstom's Chemical Looping processes provide the lowest potential COE measured against all of the alternatives studied to-date. The Chemical Looping COE is nearly constant with CO_2 allowance price because nearly all (over 95%) of the CO_2 can be captured with this technology. The cost of CO_2 capture for Alstom's limestone-based Chemical Looping coal-fired power plants for these studies is about 11 to 13 $/ton of avoided CO_2..

Coal-Fired Retrofit Economics

The US DOE has set a goal for retrofit of existing pulverized coal-fired (PC) power plants to remove over 90% of the total carbon in the coal as CO_2 for use or sequestration at an additional cost of electricity (COE) which is less than 20% greater than the current cost. Chemical looping can be retrofit to existing CFB boilers as well as to existing PC boilers. This 20% cost increase includes 4% allowed for CO_2 transportation, storage and monitoring costs, leaving 16% for CO_2 capture and compression/liquefaction. This goal places critical restrictions on both equipment cost and on system efficiency.

Retrofit Concept 1 (**Figure 4**) uses CO_2-free hydrogen as a boiler fuel. Given the fact that merchant-grade hydrogen is expensive, it is not obvious that hydrogen can be an economical boiler fuel. However, in the case of Retrofit Concept 1, the hydrogen produced by chemical looping is not merchant hydrogen; its cost is not too much greater than the cost of the coal used to produce it. **Table 1**, based on an internal study, shows cost of hydrogen in Retrofit Concept 1. The Original Plant column shows the PC power plant performance and economics before retrofit. The Hydrogen Production column shows the performance and economics for Alstom's Chemical Looping system retrofitted to the PC power plant. The Hydrogen Retrofitted column shows the original plant's performance and economics after retrofit to CO_2-free hydrogen from the chemical looping system. The Combined Retrofitted Plant column shows the overall performance of the entire plant after retrofit.

The capital cost of Alstom's Chemical Looping system adds about 25% of the original PC power plant cost ($107MM vs $440M). The cost of hydrogen produced by the chemical looping system is $2.61/MMBtu compared to the coal cost of $1.55/MMBtu. The higher cost of hydrogen comes from the yearly capital charge ($14.6MM/yr) and O&M cost ($3.9 MM/yr) required to build and operate the chemical looping system (Capital charge + O&M = $18.5MM/yr). These costs are about ½ of the yearly coal cost ($38.0MM/yr). Therefore, the implied cost of the hydrogen ($2.61/MMBtu) is about 1½ times larger than the coal cost ($1.55/MMBtu). **Table 1** also shows that the cost of electricity (COE) after retrofit (including CO_2 transportation, sequestration and monitoring costs) increases from 4.07 cents/kW-hr before retrofit to 4.72 cents per kW-hr after retrofit. This cost includes CO_2 capture and pressurization to 2000 psia and represents a 15.8% increase in COE. Adding 4% increase in COE for transportation sequestration and monitoring (according to the US DOE performance goal) brings the total COE cost increase over the original non-retrofitted plant to 19.8%. These hydrogen economics are based on DOE cost and performance factors from **References 4 and 5.**

Table 1 – Retrofit Concept 1 Economics

		Base Plant	Chemical Looping Hydrogen Production	Hydrogen Retrofited Power Plant	Combined Total Retrofitted Plant
Capacity Factor	(%)	0.80	0.80	0.80	0.80
Capital Charge Rate	(% of Capital)	13.7	13.7	13.7	13.7
O&M	(% of Capital)	3.8	3.7	2.0	2.3
Coal Cost	($/MMBtu)	1.55	1.55		1.55
Net Power Station Generation	(kW-hr)/yr	2803200000		2660774826	2660774826
Coal Flow,LHV	(MMBtu/hr)	3335	3402		3402
Coal Flow (Pittsburgh Seam)	(lb/hr)	230011	234612		234612
CO2 at 90% capture	(lb/hr)		580664		580664
H2 Flow,HHV	(MMBtu/hr)		3092	3092	
H2 Flow,LHV	(MMBtu/hr)		2614	2614	
H2 Flow	(lb/yr)		355274329.9		
Cost of Hydrogen	cents/lb		15.9		
Cost of Hydrogen	cents/gge	(before Tax, Refining, Lic	34.7		
		Original Plant	**Chemical Looping Hydrogen Production**	**Hydrogen Retrofited Power Plant**	**Combined Retrofitted Plant**
CO2 Capture	**(%)**	**0**	**95%**		**95%**
Plant Cost	**($/kW)**	**1100**	**281**	**1159**	**1440**
Plant Cost	**($MM)**	**440**	**107**	**440**	**547**
Coal Flow,HHV	**(MMBtu/hr)**	**3432**	**3500**		**3500**
Gross Plant Size	**(MW)**	**424**		**424**	**424**
Power Plant Aux Power	**(MW)**	**24**		**24**	**24**
Power Plant Net Plant Size	**(MW)**	**400**		**400**	**400**
Hydrogen Plant Aux Power with CO2 Compression	**(MW)**		**See Note 1**	**20**	**20**
Power Station Net Plant Size	**(MW)**	**400**		**380**	**380**
Net Plant Heat Rate	**(Btu/kW-hr)**	**8580**		**9220**	**9220**
H2 Flow	**(lb/hr)**		**50696**	**50696**	
Net Power Station Generation	**(MM kW-hr/yr)**	**2803**		**2661**	**2661**
Capital	**$MM/yr**	**60.2**	**14.6**	**60.2**	**74.8**
O&M	**$MM/yr**	**16.7**	**3.9**	**8.8**	**12.7**
Coal	**$MM/yr**	**37.3**	**38.0**		**38.0**
Hydrogen	**$MM/yr**			**56.5**	
	$MM/yr	**114.2**	**56.5**	**125.6**	**125.6**
Cost of Coal	**$/MMBtu**	**1.55**	**1.55**		**1.55**
Computed Cost of Hydrogen	**$/MMBtu**		**2.61**	**2.61**	
COE	**cents/kW-hr**	**4.07**		**4.72**	**4.72**
COE relative to Base Case	**fraction**			**1.158**	**1.158**
				Cost of CO2 Capture and Compression (%)	**15.8%**
				Cost of Transport, Store and Monitor (%)	**4.0%**
				Cost Increase for PC Retrofit CO2 Sequestration (%)	**19.8%**

Notes: 1. Auxiliary power for Chemical Looping hydrogen production and CO2 compression are included with the powerplant.
2. Economic assumptions identical to those in Figure 5.

Development Status

Alstom is currently working on Phase IV (a 3MWt prototype phase) of a multi-phase program to develop calcium-based chemical looping. Prior to this, a preliminary investigation (called Phase 0) and three phases (I, II and III) were completed.

Substantial work began in 2003 (Phase 0) with the construction of a small-scale pilot facility (Process Development Unit, PDU) at Alstom's Power Plant Laboratories in Windsor, Connecticut. Construction was completed in calendar year 2003. The PDU is shown in **Figure 6**

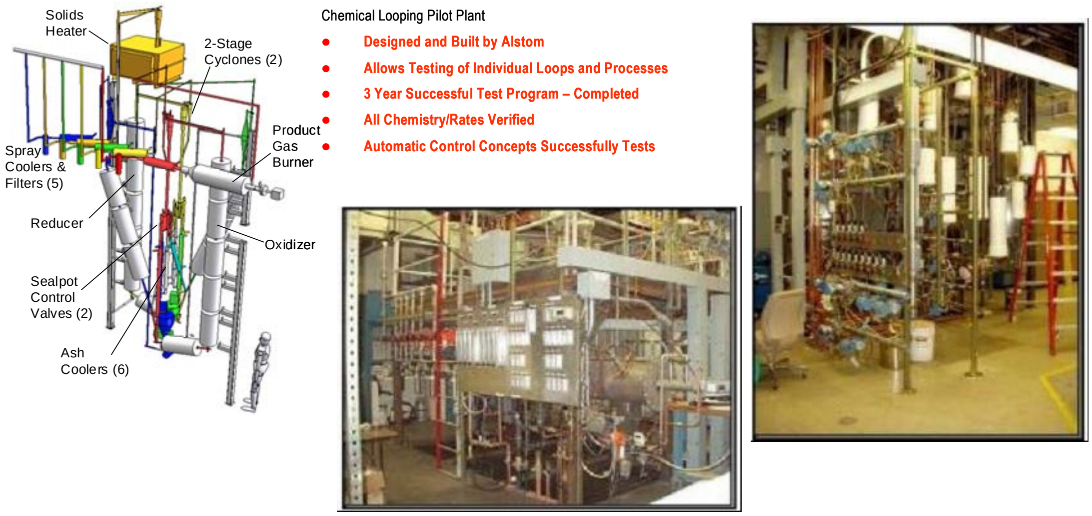


Figure 6 Alstom's Chemical Looping Pilot Facility

In Phase I the PDU was used to develop the indirect combustion loop, including the oxidizer and reducer with CO_2 separation, **Reference 2**. Syngas production from coal was demonstrated with calcium sulfide (CaS) and calcium sulfate ($CaSO_4$). Cold flow modeling of the solids flow characteristics was preformed.

In Phase II, the PDU was used to develop the carbonate loop, this lime (CaO) and calcium carbonate ($CaCO_3$) loop was integrated it with the gasification loop from Phase I and ultimately demonstrated the feasibility of hydrogen production from the combined loops, **Reference 3**. Additional cold flow modeling was performed.

In Phase III, the PDU was used to obtain engineering information to design a prototype of the commercial Chemical Looping concept. The work included modifications to and testing with the PDU, solids transportation studies, control and instrumentation studies and additional cold flow modeling. 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 solids 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.

Cold flow modeling also supported control method investigation. Both the original 15 foot tall model and a newly-built forty-foot tall plastic model was constructed for use in Phase III. This model was used to test scale-up criteria, solids flow control and solids pressure drop. The cold flow models are shown in **Figure 7**.

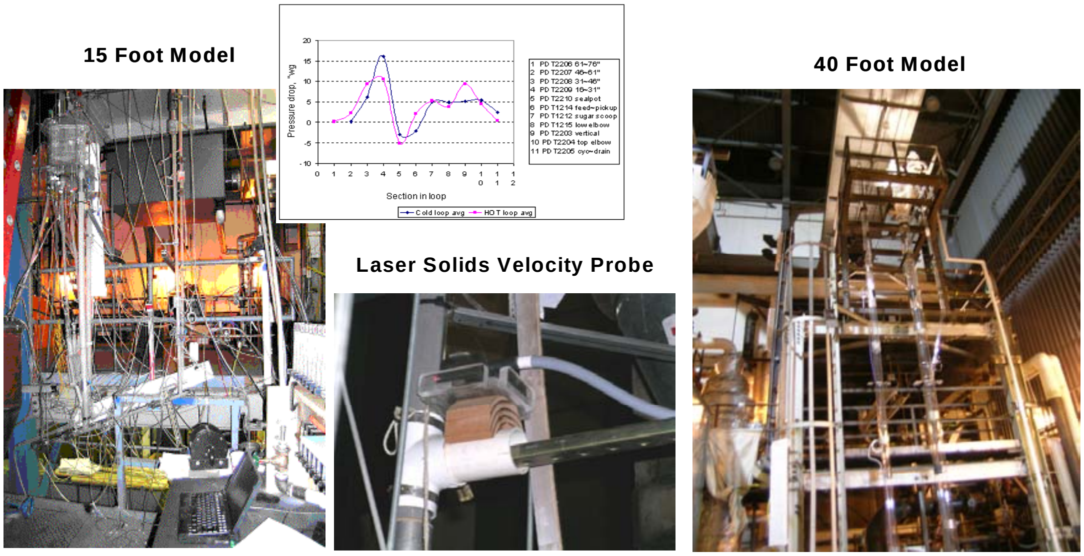


Figure 7 Alstom's Chemical Looping Cold Flow Models

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. An improved solid control valve was developed for uniform solids transport.

Engineering studies were also completed to develop a design for the Phase IV Prototype

The proposed 3 MWt prototype plant was sized to run auto-thermally, 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.

The Chemical Looping Program has made significant progress in the first three program phases, with the following accomplishments:

- Validation of the chemical reactions of Alstom's chemical looping process was accomplished. The following processes were demonstrated and significant data was generated for each:
  - CaS – $CaSO_4$ looping
  - CaO - $CaCO_3$ looping
  - Water gas shift: $CO + H_2O \Leftrightarrow H_2 + CO_2$
  - Hydrogen production
  - Sorbent reactivation
  - CO_2 removal
  - Char gasification/combustion via $CaSO_4$
  - Coal devolatilization

- The PDU was used to show the simultaneous operation of four solids transport loops at ambient and elevated temperature (1800 degrees F).

- The solid control valve operation requirements were established and the steady-state operation was verified. Multi-loop control requirements were established.

- Startup procedures were established for smooth startup. Emergency quick shut-down and quick restart procedures were tested.

- 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 cold flow model testing for fluidization rates was directly applicable to the hot case.

- The cold flow modeling with the 15-ft model, dual-loop 15-ft model and the 40-ft model characterized pressure drop, solids flow and transient relationships.

- Scale-up from a ¾" diameter riser to a 4" diameter riser was tested successfully in cold flow.

- A prototype 3MWt pilot design was created and specifications were developed.

- Economic studies were completed for retrofit applications of Chemical Looping combustion and the COE's were shown to be competitive.

Phase IV Prototype

In Phase IV Alstom will design, build and test a prototype facility in it's Boiler Laboratories in Windsor Ct. that includes all of the equipment required to operate a Chemical Looping plant in a fully integrated mode and with auto-thermal operation, and 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.

Phase IV will include initial testing of non-reactive solids transport (cold flow and perhaps some limited non-reactive hot flow tests) in the Prototype. Further testing will be conducted in a follow-on phase. The first part of Phase IV (Phase IVA) will take about 2 1/2 years to complete, including about 21 months for engineering, procurement, and installation, with the remaining time for testing and development.

Alstom is currently in the process of completing the prototype design and final cost estimate. Final design for the prototype equipment is not complete, however approximate sizes for the reactor vessels and lines have been estimated and a preliminary configuration has been proposed.

Figure 8 shows the preliminary layouts for the prototype. It illustrates the overall size of the plant. The figure on the right shows the reacting and transport volumes of the process components and the figure on the left show the same equipment with the required refractory and insulation. **Figure 9** shows side and front elevations of the preliminary prototype layout.

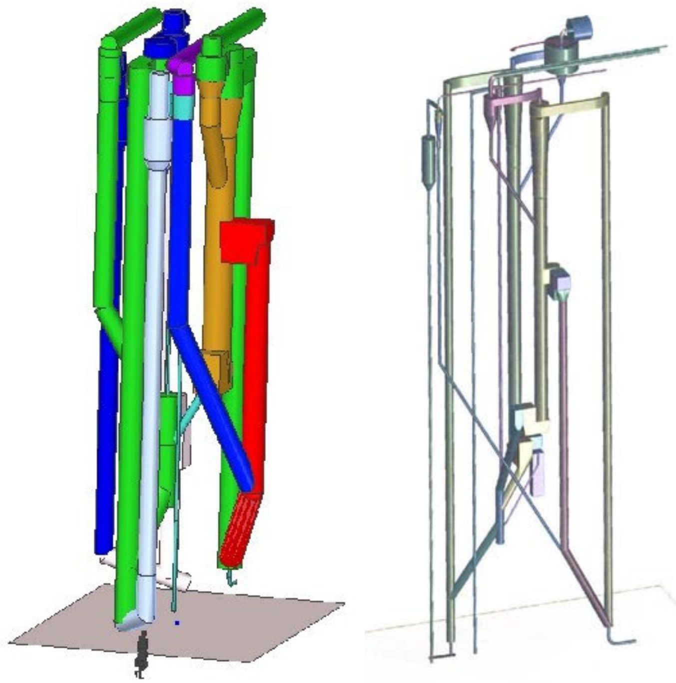


Figure 8 Preliminary Prototype Layout

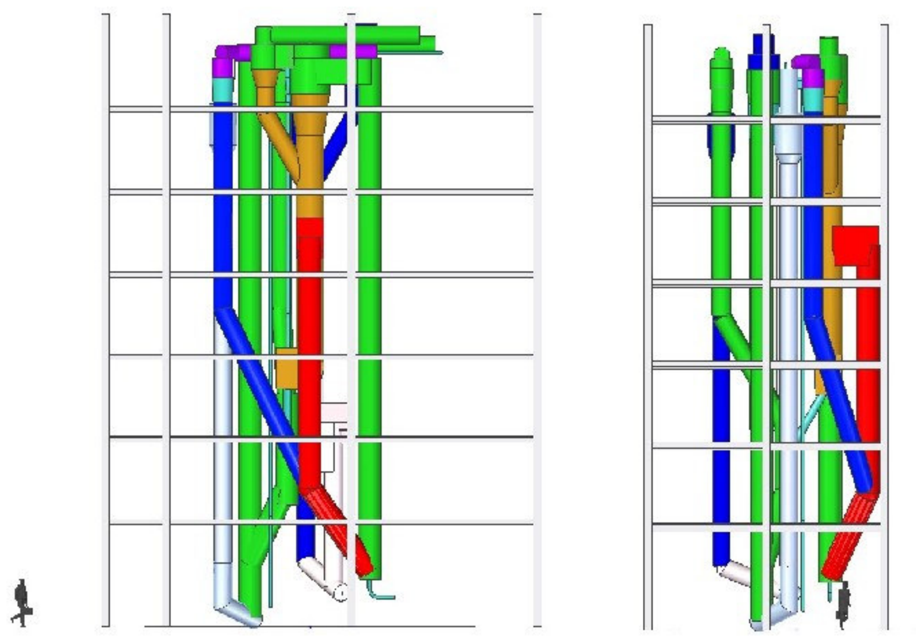


Figure 9 Preliminary Prototype Elevations.

The next major effort is to complete the Prototype EPC, perform initial testing and analyze performance data. The future work would be Phase V (Commercial-size Demonstration Plant).

Acknowledgement
Alstom would like to thank the many people at the US DOE for their sponsorship and help with this work. Alstom would also like to acknowledge the critical contributions of their consultants, Dr. Fred Zenz (PEMM Corp) and Drs. Jim Lim and John Grace, University of Columbia, Vancouver, British Columbia, Canada.

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