Alstom's Chemical Looping Prototypes, Program Update

Abdulally, Iqbal[a]; Beal, Corinne[b]; Andrus, Herbert[c]; Epple, Bernd[d]; Lyngfelt, Anders[e]; Lani, Bruce[f]

[a]*Alstom Power, Inc., 200 Great Pond Drive, Windsor, CT 06095 USA* iqbal.f.abdulally@power.alstom.com
[b]*Alstom Power Systems SA, 12 Rue Jean Bart, Massy, France 91300* corinne.beal@power.alstom.com
[c]*Alstom Power, Inc., 200 Great Pond Drive, Windsor, CT 06095 USA* herbert.e.andrus@power.alstom.com
[d]*Technische Universität Darmstadt, Petersenstr, 30, D-64287, Darmstadt Germany* bernd.epple@est.tu-darmstadt.de
[e]*Chalmers Tekniska Högskola, S-412 96, Göteborg, Sweden* Anders.Lyngfelt@chalmers.se
[f]*US DOE, NETL, 3610 Collins Ferry Rd., Morgantown, WV 26507 USA* Bruce.Lani@NETL.DOE.GOV

37th International Technical Conference on Clean Coal & Fuel Systems
June 3-7, 2012
Clearwater, FL, USA

ABSTRACT

Alstom Power is developing Chemical Looping Processes utilizing limestone or Metal oxides (MeOx) as oxygen carriers to transport oxygen from air to the fuel. These technologies have the capability to capture CO_2 from new and existing coal-fired power plants while maintaining high plant power generation efficiency compared to competing technologies. The power plant concept is based on a hybrid combustion-gasification process utilizing high temperature chemical and thermal looping technology. The chemical and thermal looping technology can also be configured as a hybrid combustion-gasification process producing a syngas or hydrogen for various applications while also producing a separate stream of CO_2 for use or sequestration.

Following validation of the MeOx concept at 10 kW scale, two pilot facilities were built within the ÉCLAIR program: A 100 kW flexible pilot to perform long term testing and to test alternative oxygen carriers: and a 1 MWth prototype, based on circulating fluidized bed technology (CFB) mode of operation. This prototype is the first MeOx chemical looping unit designed to operate under autothermal conditions. The Limestone Chemical Looping (LCL™) development has also progressed through three phases and is currently in Phase IVA. This Phase IVA program includes designing, building and testing a 3 MWth prototype of the LCL™ process that integrates all of the equipment and systems required to operate the facility. This 3MWth prototype is the first LCL™ unit designed to operate under autothermal conditions. Both prototypes have completed commissioning and are currently in the testing phase of the programs.

Cold flow models (CFMs) of various sizes including the prototype size were built in parallel to the hot test facilities on both programs and successfully operated. These CFMs were used to investigate the solids transport mechanisms and develop operating approach, as well as operator training for the prototypes. Operation of these facilities will be used to characterize performance and develop design information for future plants.

The progress to date of the MeOx and LCL™ chemical looping programs is reported in this paper. This includes an overview of the results obtained in the MeOx based ÉCLAIR program, which has received a financial co-funding support from the European Union – Research Funding for Coal and Steel (RFCS) and the LCL™ Phase IVA program co-funded by the US DOE National Energy Technology Laboratory (NETL).

1. INTRODUCTION

Chemical looping technology is a novel process, which utilizes a solid oxygen carrier to provide oxygen to either a combustion or gasification process. This technology produces either steam for power generation or clean hydrogen fuel while capturing carbon for sequestration. This is a "game changing" technology in terms of overall efficiency and cost, and is the lowest costing technical approach that has been identified to date for coal power with carbon capture and sequestration [8].

Alstom Power is developing Chemical Looping Processes utilizing limestone or Metal oxides (MeOx) as oxygen carriers to transport oxygen from air to the fuel. These technologies have the capability to capture CO_2 from new and existing coal-fired power plants while maintaining relatively higher plant power generation efficiency compared to competing technologies. The power plant concept is based on a hybrid combustion-gasification process utilizing high temperature chemical and thermal looping technology. The chemical and thermal looping technology can also be configured as a hybrid combustion-gasification

*Corresponding Author: Tel.: +860-285-4183, Fax: +860-285-3473
E-mail address: iqbal.f.abdulally@power.alstom.com

process producing a syngas or hydrogen for various applications while also producing a separate stream of CO_2 for use or sequestration.

A significant progress has been made in Alstom so far in developing the Chemical Looping Processes. This paper is an overview of Alstom's Chemical Looping concepts and development activities to date in Europe and in the USA, including prototype testing that is currently in progress on two prototypes, one for each of the two technologies.

2. MeOx CHEMICAL LOOPING DEVELOPMENT

2.1 Reference Studies

Starting in 2002 (GRACE – EU FP5 an EU funded program), Chemical Looping Combustion (CLC) has been developed first with natural gas combustion, which was seen as an enabling initial step to the application of CLC to solid fuels. The CLC technology has then been applied and tested for solid fuels (ENCAP – EU FP6 an EU funded program). A screening of possible oxygen carriers has been done at lab scale. Tests with South African coal and petcoke have been conducted with success at 10 kWt scale in a test setup built for solid fuels in Chalmers University. A conceptual design for a Greenfield 455 MWe advanced chemical looping circulating fluidized bed (CFB) coal-fired power generation plant has been developed for capture of CO_2 by ALSTOM. The costing of this plant and evaluation of cost of electricity has confirmed the favourable economic potential of Chemical Looping compared to other CO_2 capture technologies.

Considering the encouraging technical and economical results, a decision to build a 1 MWt prototype has been made and has received a financial support from EU-RFCS (Research Fund for Coal and Steel).

2.2 Modeling and Tool Development

Figure 1 represents the main equipment of the MeOx-based Chemical Looping prototype. Special equipment, called the "Carbon Stripper" is installed between the two reactors to allow separation of unburnt carbon and the solid oxygen carrier, and to allow recirculation of the carbon to the Fuel Reactor. Some engineering studies were done to design the carbon stripper. Numerical modeling have been performed in collaboration with a French University, IMFT in Toulouse (Fluid Mechanic Institute of Toulouse), using a multiphase Code (Neptune®) to determine the influence of key parameters (fluidization, residence time, geometry) on the separation efficiency.

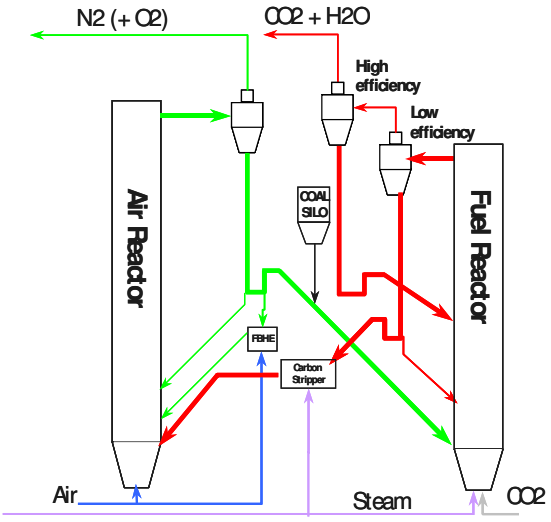

Figure 1: General drawing of MeOx Chemical Looping System

Figure 2 illustrates a view of the numerical model while Figure 3 shows a cold flow model that was built to validate the modeling results. These studies have allowed the geometry of the carbon stripper and its operating conditions to be defined for the 1 MWt prototype.

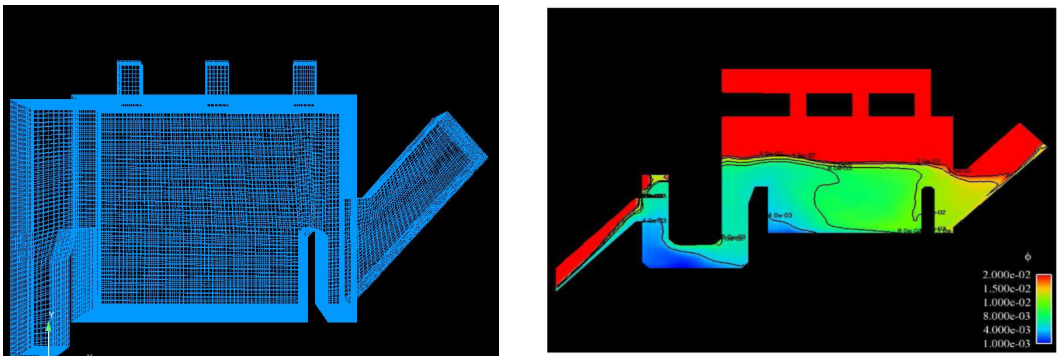

Figure 2: Carbon stripper Numerical Model Study and results.

Figure 3: Cold flow model of carbon stripper

2.3 Testing at Chalmers University

In 2006, the first operation of a 10 kW chemical-looping unit in Chalmers University, Sweden, was accomplished using bituminous coal and pet coke [2, 3]. The oxygen carrier used as bed material was ilmenite, a low-cost naturally occuring ore consisting of iron-titania oxides. The fuel was fed to the fuel reactor bed from above, leading to volatiles escaping largely unconverted. Later, the unit was reconstructed to in-bed feeding, giving significantly improved gas conversion defined as the quantity of oxygen that has been supplied to the gases leaving the fuel reactor divided by the quantity needed to achieve complete combustion. Thus, this means that if the gas conversion is 90% then 10% of the total oxygen needed for the combustion would need to be supplied to the gas leaving the fuel reactor, e.g. by so-called oxygen polishing of the gas from the fuel reactor [5]. A study where part of the ilmenite was substituted by lime showed further improvement in gas conversion [4]. Moreover, operation using a manganese ore showed that gas conversion could be significantly improved compared to ilmenite, typically increasing the gas conversion from around 80% to almost 90% using pet coke as fuel [5].

More important than the high improvement in gas conversion was the unexpected increase in CO_2 capture, i.e., the ratio of carbon in gaseous form that leaves the fuel reactor to the total carbon in gaseous form that leaves both fuel and air reactor, which was increased from around 70% to around 96%. This indicated that the rate of steam gasification was increased by a factor of four or more. Later laboratory experiments have indeed verified that this manganese ore increases the steam gasification rate by a factor of five for pet coke [1]. A drawback of the manganese ore that was used, however, is a high production of fines, suggesting a moderate lifetime. In 2012, a 100 kW solid fuel chemical-looping combustor pilot was taken into operation at Chalmers. The unit is more advanced than the 10 kW unit and has a fuel reactor in the form of an internally circulating fluidized bed. The bed material is returned from the fuel reactor using a separate circulation riser, leading to a four-chamber carbon stripper with the purpose to reduce the loss of carbon to the air reactor, i.e. to improve CO_2 capture. A cold-flow model of the unit has been built [6].

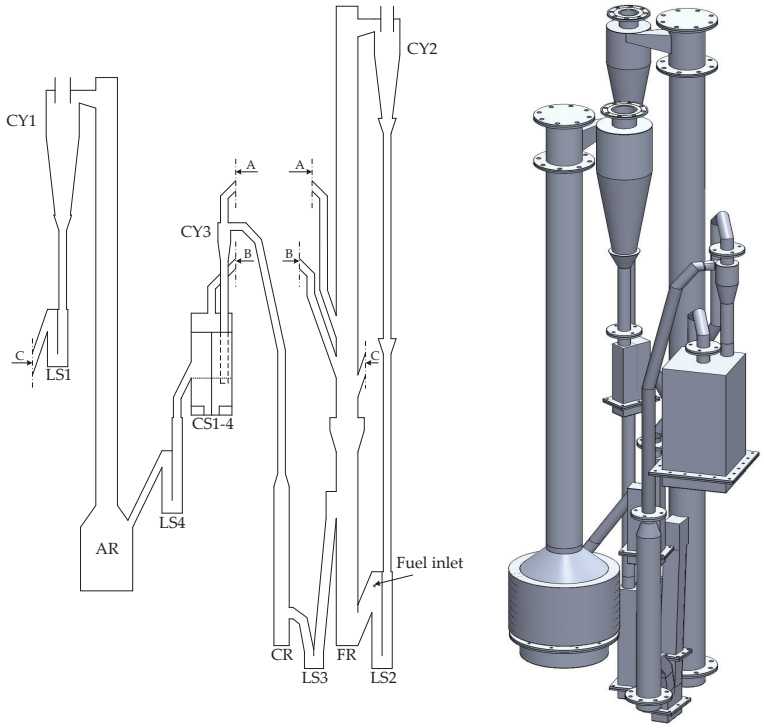

Figure 4: A 2D and 3D sketch of the 100 kW unit. The fuel reactor riser is 5 m tall. FR=fuel reactor, AR=air reactor, CR=circulation riser, LS=loop seal, CY=cyclone, CS=carbon stripper

The cold-flow model indicates that the design gives a high operational stability. Thus, both the global circulation rate between the two reactors, as well as the internal circulation rate in the fuel reactor, can be varied in a large range with little effect on the distribution of bed material between fuel and air reactor. The operational experiences so far show that the unit works without any problems. The gas conversion reached seems to be typically 3-4% higher in this unit as compared to the 10 kW unit [6, 7]. Also, the CO_2 capture was clearly higher, around 95% using a bituminous coal. A sketch of the unit is shown in Figure 4.

2.4 Testing at Darmstadt University

Within the ECLAIR project, a 1 MW_{th} CLC prototype has been designed and erected at Technische Universität Darmstadt in Germany. The general arrangement of the 1 MWth test unit based on two interconnected circulating fluidized bed reactors is illustrated in Figure 5.

The air reactor consists of a riser with 8.66 m height and 0.59 m diameter, a cylone, a downcomer with 0.2 m diameter, a loop seal, and a return leg. The primary air enters the reactor through a windbox and nozzle grid (30 nozzles). As the reaction in the air reactor is strongly exothermic, excess heat is extracted by five movable cooling tubes located at the top of the air reactor. The fuel reactor riser is 11.37 m high and 0.4 m in diameter with a conical shape at the bottom. Steam enters the reactor through a windbox and nozzle grid (5 nozzles). The solid flow from the air reactor to the fuel reactor is controlled by a screw conveyor that is attached to a loop seal below the air reactor cyclone. The solid flow from fuel to air reactor is controlled by a double loop seal configuration.

The separation of unreacted char from oxygen carrier particles leaving the fuel reactor occurs in two steps. A low-efficiency cyclone with a reduced efficiency compared to normal cyclones is attached to the fuel reactor. Since the unreacted char particles are much smaller and lighter than the oxygen carrier particles, the low-efficiency cyclone separates the unreacted char particles from oxygen carrier particles. The oxygen carrier particles leave the cyclone via the conical part and enter the carbon stripper, whereas the unreacted char particles leave the cyclone via the vortex finder, are separated from gases in the high-efficiency cyclone solids, and are transferred back to the fuel reactor. The second step of the particle separation occurs in

the carbon stripper that is operated as bubbling fluidized bed. The unreacted char particles are re-introduced into the fuel reactor whereas the oxygen carrier is returned to the air reactor.

All components that are required to run the air reactor have been tested and put into operation in 2010. The air reactor was heated to nominal operation temperature of 1050°C by means of a bed lance fired with propane. Circulation of ilmenite was achieved in hot operation. Hence, air reactor commissioning was finalized successfully. The first fuel reactor commissioning test was performed in February 2011 with ilmenite as bed material. Stable circulation was achieved for several hours at a temperature of 1000°C. After that, a commissioning test of the double loop seal was conducted. The fuel reactor was operated in circulating mode, and material was transferred to the air reactor. The amount of material transferred to the air reactor could be controlled by adjusting the loop seal fluidization velocity of the lower loop seal. The remaining part of the solids flow was recycled to the fuel reactor.

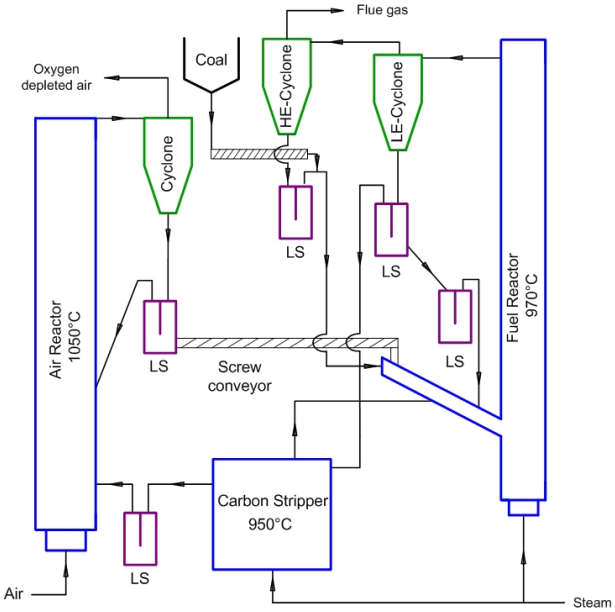

Figure 5: Principal layout of the Darmstadt University 1 MWth chemical looping pilot

In summer 2011, the pilot was operated in the design configuration (see Figure 5) including both CFBs, carbon stripper, and all loop seals. Material was exchanged between both reactors. The screw conveyor was operated with varying rotary speed to control the mass flow from air reactor to fuel reactor. A characteristic for the screw conveyor was determined in hot conditions.

However, a significant particle loss through high-efficiency cyclone was noticed. Subsequent tests showed that the particle loss was caused by a back flow of gases through the loop seal. This problem could be resolved by increasing the weir height of the loop seal below the high-efficiency cyclone. CLC tests in autothermal operation are scheduled for May/June 2012.

2.5 Next Steps: MeOx Chemical Looping Program

First phase of the development of MeOx chemical looping at 1 MWt scale will end in summer 2012. A second phase will be launched in order to test several types of fuels and other oxygen carriers.

Some modifications of the Fuel Reactor design will also been studied to improve the conversion efficiency. Extended operation on the Chamler's 100 kWt unit will also been performed to find optimal operating conditions and provide data to validate models.

3. LIMESTONE-BASED CHEMICAL LOOPING (LCM™) DEVELOPMENT

3.1 Reference Studies

Since late 1900s, Alstom has performed several tests on bench scale apparatus that include a drop tube furnace system and 4" bubbling fluidized bed combustor as part of Alstom's internal research project, prior to the DOE programs that followed this effort. The results from these tests were used to determine the reaction rates of the main reactions, which in turn were used as the design basis for the small-scale 65 kWth pilot that was later built (2003) and used for testing. Since 2003, Alstom has completed Phase I, II & III testing on a small-scale 65 kW_{th} process development (PDU) facility under the US DOE/NETL Cooperative Agreement [9,10,11] and is currently performing testing on a 3 MWth prototype under another US DOE/NETL Cooperative Agreement , which is scheduled to be completed by September 2012. Testing in the 65MW_{th} PDU verified most of the important chemistry and solids transport (using cold flow model testing in parallel) required for the LCL™ process:

- Successful CaS –$CaSO_4$ looping without losing sulfur in the oxidizer when burning CaS to make hot $CaSO_4$
- Successful gasification of several fuels including Pittsburgh Seam 8 coal.

- Carbon/$CaSO_4$ gasification rates are fast enough for low cost gasification.
- Rapid, CaO assisted water-gas shift reaction to shift steam (H_2O) and the CO.

The PDU represents a successful scale-up in capacity of well over a factor of 100 from the previous bench scale work. Additionally, the use of transport reactors operating at high solids loadings for high volumetric efficiencies was verified and the ability to recycle solids between the various reactors was verified. As a result of this work, all of the chemistry required for the LCL™ process has been verified and reaction rate data has been obtained at conditions that will be encountered in the full-scale system.

The main conclusions from the results of Phases I, II and III are:

- The rates exceeded the rates used in the original design of the equipment.
- Many of the process steps such as the $CaCO_3$ calcination to CaO + CO_2, and the CaO and sulfur to $CaSO_4$ are similar or identical to those used in commercial CFB boiler technology.
- The reactor can be of conventional refractory/carbon steel design.
- The raw feedstock materials are among the earths most common: coal, limestone, water and air.
- The oxygen transport vehicle is the same as the sulfur capture product, $CaSO_4$ and therefore has no additional cost over CFB usage. The $CaSO_4$ can transport more oxygen per pound than air and vastly more than metal oxides such as iron and nickel.
- Similar to the CFB, the coal ash is fully oxidized since it is drained from an oxygen rich reactor and special treatment is not required.

The rates that were determined from these tests impled that small reactors can be used for the Oxidizer and the Reducer. Their small size is enabled by the high chemical reaction rates combined with higher temperatures and higher solids loadings. These increase the volumetric carbon conversion rate within the Reducer and the CaS combustion rate within the Oxidizer. Smaller equipment size translates into lower capital cost. Accordingly, the CLC island equipment is significantly lower than the cost of a CFB as discussed in the 2003 Greenhouse Gas Report [8]. This study included a comparison of a 210 MWe-gross LCL™ vs. an already operating Warrior Run air-fired CFB project, both firing a bituminous coal. Figure 6 shows that the chemical looping boiler island equipment is smaller than the CFB for the same power output, requiring significantly reduced building volume and overall weight.

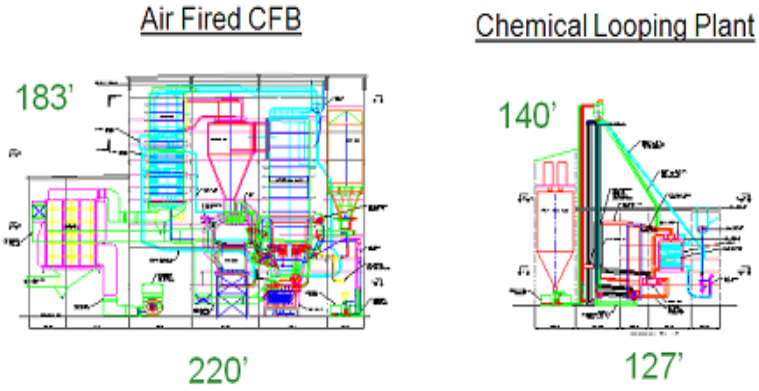

Figure 6: Comparison of an Air-Fired CFB and CLC Boiler Island

3.2 Modeling and Tool Development

Alstom has also performed computational simulation of the CLC prototype to understand and refine its design and operation. In the future, it is envisaged that this simulation tool, through extended validation, will help to modify the model to represent scaled up commercial size units. Typically, the validation of dense phase is extremely difficult for the model. However, Alstom has made selected validation of cold flow model operation, which has indirect sectional measurement of pressure drop, which has compared well.

Chemical looping simulations have been conducted for portions of the 3 MWt prototype geometry using Barracuda® a dense-phase modeling software package licensed from CPFD Software, LLC. Alstom has applied Barracuda® to a range of different CFB geometries as well as smaller scale experimental models. For the Chemical looping system, a portion of the reducer column was modeled assuming isothermal, non-reacting conditions and gas and solids flow boundary conditions from hot operation. The cyclone return legs from both the reducer and oxidizer column were simplified to avoid the complexity of including the cyclones and seal pots. With these assumptions, the reducer column and reducer bottom section were examined to study the solids transport and solids residence times. The geometry of the modeled section is shown in Figure 7 highlighting the particles solids colored by velocity. The slower moving solids are blue and concentrated in the reducer bottom

and return leg. In these regions, the solids are densely packed, while in the reducer and columns the particle velocities are higher, consistent with the transport regime. A detailed view of the "cactus zone" where these solids enter the reducer are shown in Figure 9. The mixing of the two solids streams where they enter the reducer column is a key area located above the fluidizing gas section. The solids split and mixing of these two solid streams can be clearly identified using the capabilities of

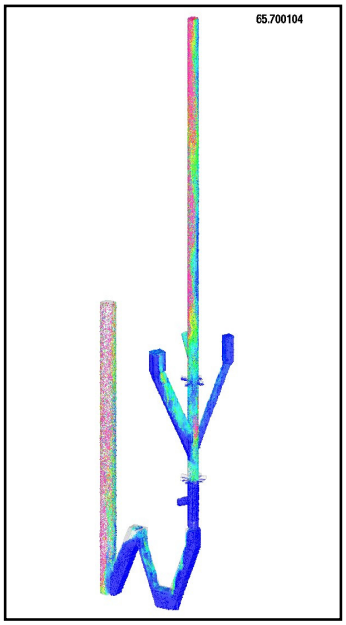

Figure 7: Baracuda Simulation of the Chemical Loop reducer column (color range 0 – 25m/s)

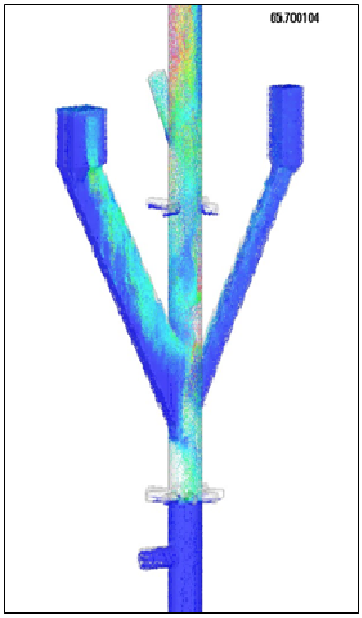

Figure 8: Mixing of solids streams above the fluidizing gas grid 0-25 m/s

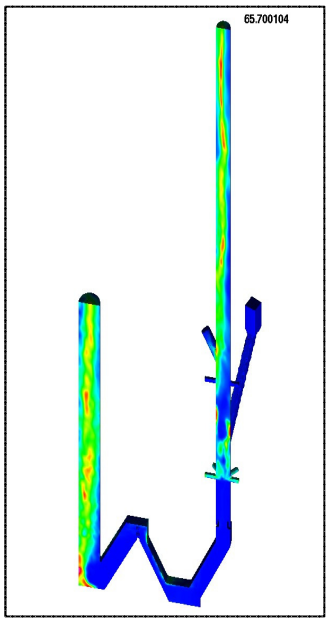

Figure 9: Instantaneous velocity in the reducer and oxidizer column (color scale range 0 -25 m/s)

the Barracuda® software. These transient flow simulations enhance the understanding of the solids/gas interactions that are also studied using cold flow models. A detailed view of the cactus zone where these solids enter the reducer is shown in Figure 8.

Examination of the impact of geometry modifications and the ability to tailor the solids input using a continuous particle size distribution function for each solid stream is a key advantage of Barracuda compared to other multiphase simulation packages. The gas/solids streams can be tracked individually using animations of instantaneous flow conditions, or time averaged quantities. The gas velocity distribution in the reducer column is coupled to the solids, and this interaction is inherently transient. For example, the vertical velocity distribution viewed at 65 seconds into the transient simulation is complex, as shown in the centerline gas velocity plot in Figure 9.

Using simulation tools such as Barracuda® to study the chemical looping process is extremely valuable to Alstom's development process.

3.3 Testing at Alstom Power Plant Laboratories

3.3.1 Cold Flow Modeling

As a part of Phase IVA, a 40-foot tall, 2.5:1 scaled-down cold flow model (CFM) of the Prototype was completed based on the Prototype design (Figure 10).

Airflow control methodology was developed by testing individual loops. Solids were loaded into the CFM in early December 2011 and as soon as the airflow was started, solids began circulating. Stable solids flow was achieved within minutes of startup. The individual solids loops could be operated independently. Transport of solids to various locations in the loop circuits was simulated. Typical transport operation in the CFM was done by first re-circulating solids to the reducer. Solids were then circulated from the reducer to the oxidizer and back to the reducer.

After initial operation of the CFM, minor modifications were completed including larger nozzle openings at the inlet injection ports to avoid choking flow problems based on operational feedback. A series of tests were conducted to get the key relationship between loop balances.

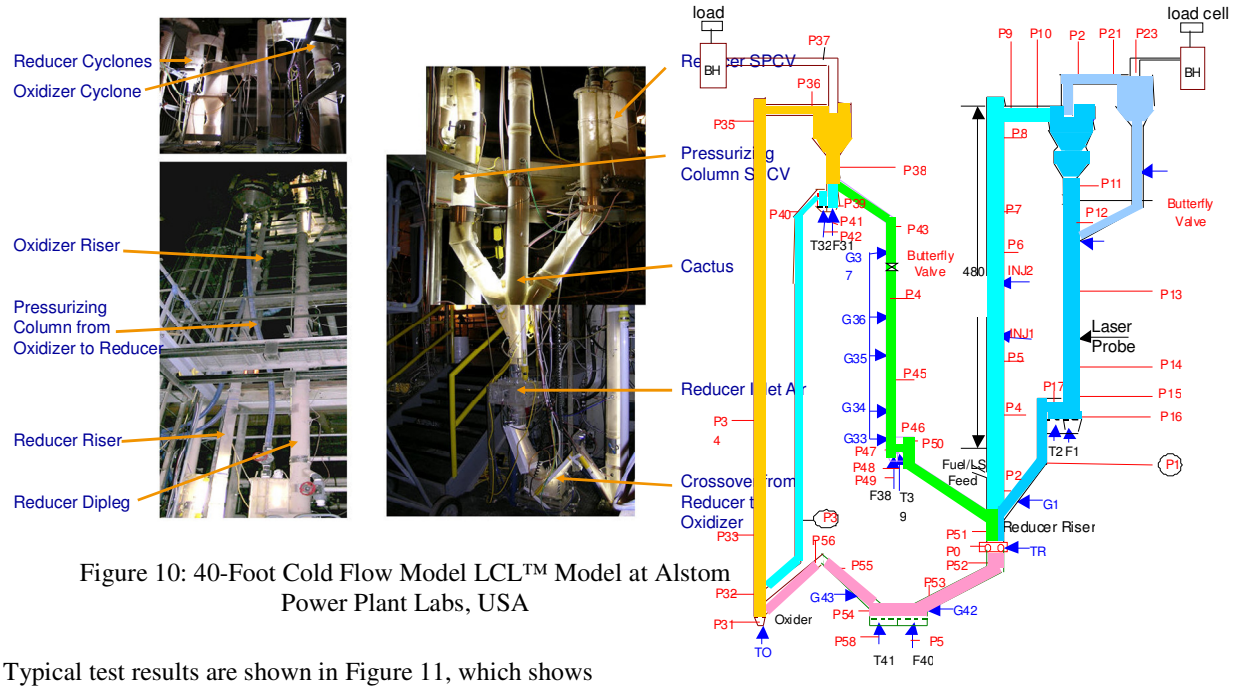

Figure 10: 40-Foot Cold Flow Model LCL™ Model at Alstom Power Plant Labs, USA

Typical test results are shown in Figure 11, which shows the pressure along the loops for a 4-hour steady state demonstration run. The CFM was run for an extended period and achieved very stable flow conditions. The data shown is a snapshot of the pressures along the solids flow paths around the chemical looping reactors. The color code on the graph corresponds to the locations shown in the diagram at the top of Figure 14. The data was recorded every few seconds and each instant can be plotted in the same way. The data analysis software is capable of animating the entire time span. When this is done, the graph as shown in the figure barely moves over the entire 4-hour test. This shows that the solids flow in a system with this configuration is very stable and this configuration can be operated easily.

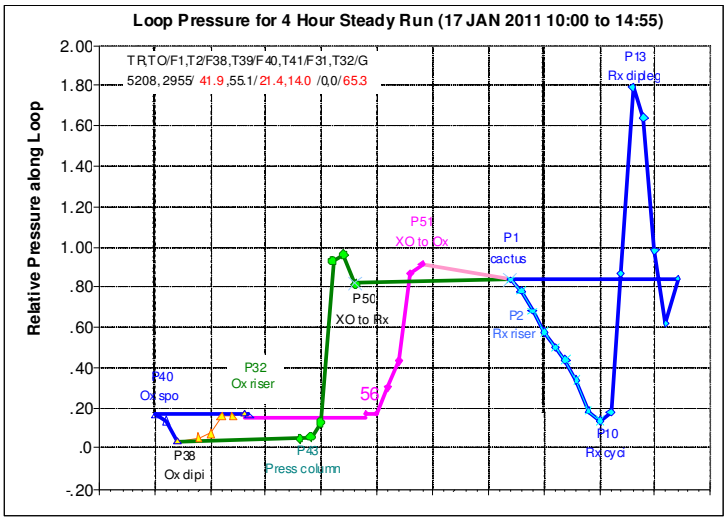

Figure 11: Test Results for the Prototype Cold Flow Model during a 4-Hour Test

The first runs of the CFM generated valuable operating data for the prototype operation. The CFM testing has continued to further characterize operation with the same ash that will be used in the prototype. The CFM was also used to train the Prototype operators. This has proved an invaluable aid to operators because its Plexiglas walls permit the operators to see how the solids transport work, a benefit that is not available with the Prototype.

3.3.2 Calcium based Prototype Operation

Construction of the prototype shown in Figure 12 was completed in late 2010 followed by the shake-down and commission of the facility. Shakedown and subsequent air testing revealed the necessity for some minor equipment, controls and electrical modifications, which were completed in early 2011.

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.

The prototype was initially charged with recycle ash from a commercial CFB. Initial operations with solids included testing and 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.

Coupled operation of the reactors in cold and warm non-reactive conditions was easily achieved from the very early days of commissioning thanks to input and operator training on the CFM. The Prototype project has made significant progress toward achieving fully integrated operation. During the second quarter of 2011, there has been a series of test operations with the prototype facility from cold solids flow to hot combustion. Each operation has built experience levels and insight with the fully integrated chemical looping process. A summary of the main achievements during this period are as follows:

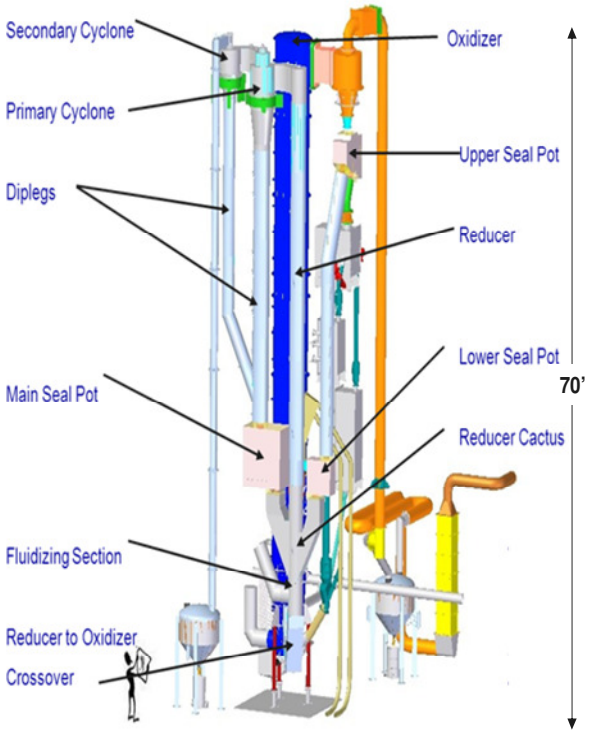

Figure 12: Side View of 3MWth Prototype

1. The cold flow model was started up and shaken down in October 2010. The unit was filled with solids and after starting the airflow, the solids in the two simulated reactor loops immediately began circulating. Operating procedures were developed and a significant amount of data was obtained to help plan the operation of the prototype. Operator training was done.

2. Air tests were conducted in December 2010 on the Prototype. Several changes were made to a number of air system components and controls. These tests set the stage for solids transport tests.

3. In early April 2011, solids flow was initiated in the Prototype. Using air settings suggested by the CFM, 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. The prototype was intentionally shut down for the evening after about an hour of operation.

4. In mid April 2011, the Prototype was started up and run for a 24-hour period. The process was heated up to about 600-700 ºF using a combination of natural gas burners and electric air heaters. Heat up was limited to about 600-700

ºF. The prototype was operating well throughout the startup. A significant amount of operator training and operational data was logged for subsequent analysis.

5. 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 ºF.

6. In early June 2011, the prototype was restarted after minor equipment modifications and upgrading 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.

7. In mid-June 2011, the prototype was started and quickly heated up to operating temperatures. The Sorbent Activation Heat Exchanger was started up. Coal was fired for about an hour to 360 lb/hr. Chemical looping reactions were achieved on June 11, 2011. Air was turned off and the recycle gas compressors were switched to recycle mode to provide transport gas for solids transport in the reducer.

The sequence of events during the 11 June 2011 tests included warm-up by external natural gas burners until the reactors were hot enough to inject natural gas directly into the oxidizer and the reducer. Coal at 150 lb/hr was started through the reducer injection lance along with limestone. Temperature in the coal feed nozzle immediately dropped, indicating endothermic gasification had started locally. Coal was brought up to 360 lb/hr (about 50% design load). Air and natural gas were phased out. The recycle gas compressors had been started using an ambient air inlet. They were then switched to recycle product gas and the ambient air inlet was shut off. At this point, the only oxygen supply was from the reactor solids oxygen carrier. The data shows that at this time the reactor was producing CO_2, which means that the chemical looping reactions were occurring in the combustion mode.

In spite of the short run time, chemical looping performance experience was collected. Figure 18 shows the reducer performance. At point "A", 360 lb/hr of coal (heavy blue) and 1900 lb/hr (heavy yellow) of air for solids transport (provided by the recycle compressor) were flowing to the reducer. This airflow provides about 50% of the theoretical oxygen required to burn this coal. The O_2 concentration (magenta) is due to leakage into the reducer gas sampling system. The leakage varied over the period covered by Figure 18, probably due to Reducer pressure conditions and reducer gas sampling system control response.) Point "B" indicates where coal flow was interrupted. Very little CO is present in the product gas. Correcting for O_2 leakage in the sampling system shows that the CO_2 concentration between Point "A" and Point "C" is about 35% with the balance as N_2 from the Reducer transport air. This ratio would be 21% to 79% if all of the oxygen to form the CO_2 came from the air. The extra oxygen for the CO_2 came from the reaction of hot $CaSO_4$ with the carbon in the coal.

At Point "C" of Figure 13, the recycle intake was switched from air to recycled product gas. At this point, one would expect to see the CO_2 slowly rise to 100% as N_2 was washed out of the system. This is observed in the figure as CO_2 is starting to rise from about 35% to about 40%.

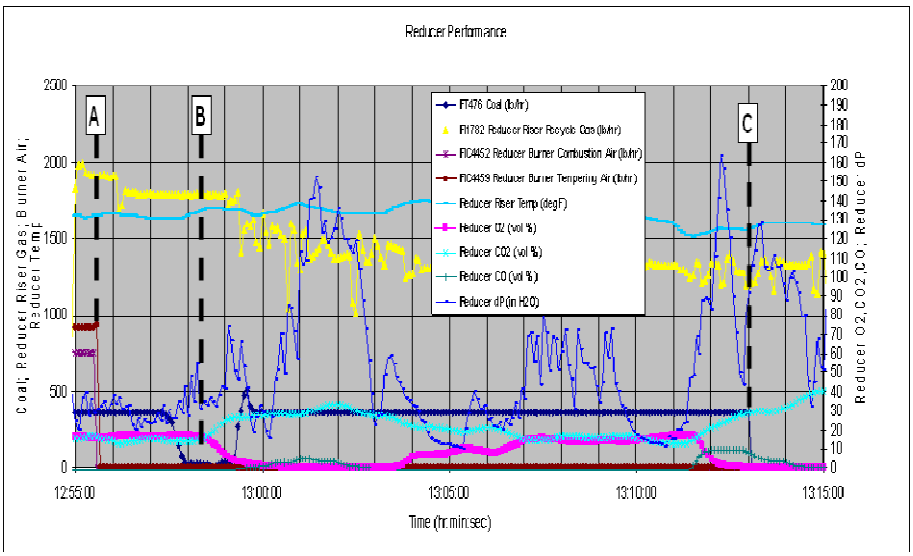

Figure 16: Prototype Chemical Looping Performance During Initial Start-up and Testing

It is also noted that CO concentration goes to zero in Figure 13 when the reducer solids loading (as shown by the reducer pressure drop [dP]) is at its higher levels. This is as expected because a higher solid loading means higher $CaSO_4$ to CO ratio for conversion of CO to CO_2.

Similar results were obtained during an operating period in early October 2011. It was at this stage that it was clear that the fuel feed

system and the solids transfer line form the oxidizer to the reducer needed modifications to alleviate problems of fuel and ash flows into the reducer. Modifications are expected to be completed in May 2012 and final testing completed by August 2012. The Prototype project has made progress toward achieving fully integrated operation. Important accomplishments are: Controlled solids recirculation in the cold flow model and the prototype

1. Online heat up of the process by external electric heaters, external natural gas burners and direct injection of natural gas into the reactors.
2. Coal firing at relatively low reactor temperatures with low tar formation.
3. Coal firing at design temperature with no evidence of tar formation.
4. Coal and sorbent feeding online.
5. SAHE operation (throughput and controls needs work).
6. Hot restart after main fuel trip.

3.5 Next Steps: Limestone based Chemical Looping (LCL™) Program

Going forward the plan is to complete systematic testing to reach auto-thermal operation on the 3 MWth prototype by the summer of 2012. Once auto-thermal operation has been achieved, Alstom will continue characterizing the prototype through parametric studies. The key process parameters currently planned for evaluation in future test campaigns are:

1. Fuel type;
2. Stoichiometric ratio;
3. Coal fineness;
4. Load level and change;
5. Reactor temperatures, both reducer and oxidizer;
6. Reducer operating pressures;
7. Superficial velocity of the reactors;
8. Limestone type; and
9. Limestone fineness.

Several test campaigns will be conducted to conduct the parametric study. These test campaigns will help develop operating experiences and performance data to optimize the CLC process, and eventually to design a large scale CLC demonstration program.

SUMMARY

Since late 1990s, Alstom has committed significant resources to develop CLC techologies with parallel efforts in Europe and the USA. These efforts include techno-economic studies, modeling, bench-scale testing, cold flow modeling and pilot tests, that have culminated into the ongoing testing on a 3MWth limestone based and 1MWth metal oxide prototypes. This has helped Alstom to gain significant know-how and will continue to be a leader in the devleopment and commercialization of CLC technology, which has the potential of being the lowest cost carbon capture, storage and utilization technology.

REFERENCES

[1] Arjmand, M., H. Leion, A. Lyngfelt and T. Mattisson (2012) 'Use of Manganese Ore in Chemical-looping Combustion (CLC) – Effect on Steam Gasification' Accepted for publication in Int. Journal of Greenhouse Gas Control

[2] Berguerand, N. and A. Lyngfelt (2008a) 'Design and operation of a 10 kWth chemical-looping combustor for solid fuels - Testing with South African coal' Fuel, 87,(12), 2713-2726.

[3] Berguerand, N. and A. Lyngfelt (2008b) 'The use of petroleum coke as fuel in a 10 kWth chemical-looping combustor' International Journal of Greenhouse Gas Control, 2,(2), 169-179.

[4] Cuadrat, A., C. Linderholm, A. Abad, A. Lyngfelt and J. Adánez (2011) 'Influence of limestone addition in a 10 kWth Chemical-Looping Combustion unit operated with pet coke' Energy and Fuels 25, (10), 4818–4828.

[5] Linderholm, C., A. Lyngfelt, A. Cuadrat and E. Jerndal (2012) 'Chemical-looping combustion of solid fuels – operation in 10 kW unit with two fuels, above-bed and in-bed fuel feed and two oxygen carriers, manganese ore and ilmenite' accepted for publication in *Fuel*.
[6] Markström, P. and A. Lyngfelt (2012) 'Designing and operating a cold-flow model of a 100 kW chemical-looping combustor' accepted for publication in Powder Technology.
[7] Markström, P., A. Lyngfelt and C. Linderholm 'Chemical-Looping Combustion in a 100 kW unit for Solid Fuels' 21st International Conference on Fluidized Bed Combustion, Naples, June 3-6, 2012.
[8] Nsakala, N. Y. and Liljedahl, G. N., Greenhouse Gas Emissions Control by Oxygen Firing in Circulating Fluidized Bed Boilers, Alstom Power – U.S. DOE Report, PPL Report No, PPL-03-CT-09, 15 May 2003.
[9] Andrus, H. E., Jr., et. al., Hybrid Combustion-Gasification Chemical Looping Coal Power Technology Development – Phase 1 Final Report, U.S. DOE, December 29, 2004
[10] Andrus, H. E., Jr., et. al., Hybrid Combustion-Gasification Chemical Looping Coal Power Technology Development – Phase II Final Report, U.S. DOE, June 9, 2006.
[11] Andrus, H. E., Jr., et. al., Hybrid Combustion-Gasification Chemical Looping Coal Power Technology Development – Phase III Final Report, U.S. DOE, Sept, 30, 2008.