APPENDIX B: CARBON DIOXIDE CAPTURE TECHNOLOGY SHEETS

CHEMICAL LOOPING

MAGNETICALLY FLUIDIZED BED REACTOR DEVELOPMENT FOR THE LOOPING PROCESS: COAL TO HYDROGEN PRODUCTION R&D

Primary Project Goals

The University of Florida (UF) is developing novel fluidized bed and magnetically stabilized bed reactor systems that use a chemical looping process with metal oxide sorbents to separate hydrogen (H_2) and carbon dioxide (CO_2) from coal-derived synthesis gas (syngas).

Technical Goals

- Conduct laboratory-scale testing to investigate chemical, heat, and mass transfer in the fluidized and magnetically stabilized bed reactors, and develop modeling/simulation tools.
  - Determine optimal reaction pathways and operation conditions for iron (Fe)-, and alloyed Fe-metal oxide powders in both reducing and oxidizing environments.
  - Evaluate the chemical kinetics for reaction pathways.
  - Characterize chemical, thermal, and fluid transport properties of fluidized bed and magnetically stabilized bed reactors.
  - Investigate reactivity and durability of Fe, Fe/zirconia (Zr), and Fe/magnesium oxide (MgO).
  - Conduct a techno-economic analysis.
- Design, construct, and operate a bench-scale system to further evaluate the viability of the process upon successful completion of the laboratory-scale testing.

Technical Content

The metal oxide looping process is a two-step process, and in its simplest form steam is injected into a reactor containing a reduced metal oxide [e.g., iron oxide (FeO)]. The steam oxidizes the FeO to produce magnetite (Fe_3O_4) and high purity H_2 is liberated. The H_2 is captured by condensing the water vapor from the steam and H_2 mixture. In the second step, the Fe_3O_4 must be reduced so that water splitting can proceed in a cyclic manner. The looping process uses carbon monoxide (CO) produced from the gasification of coal to reduce the Fe_3O_4. The advantages of the chemical looping process are that the H_2 produced via water splitting is highly pure, and the reduction step can be accomplished at sufficiently low temperature (400–850 K) to enable a commercially viable reactor.

Research efforts focus on: detailed thermal management throughout the process to enable efficient recuperation of heat; advanced reactor design that enables rapid kinetics; Fe or other metal powders which are stable and highly reactive over thousands of cycles; and operation in thermodynamically favorable regimes to maximize H_2 production and minimize the formation of Fe carbide compounds. The successful design of an efficient and cost-effective chemical reactor will ensure rapid kinetics, a homogenized thermal field, a high production rate, uniform solids distribution, completed reaction pathways, and low pressure drop with minimal energy consumption.

Technology Maturity:
Laboratory-scale

Project Focus:
Chemical Looping for Fluidized Bed Reactor

Participant:
University of Florida

Project Number:
FE0001321

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Partners:
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Performance Period:
10/1/09 – 9/28/12

The fluidization of magnetic powders has received considerable attention in the literature. The majority of the fluidization approaches utilize magnetically assisted fluidization. In this process, a uniform steady magnetic field is applied to a conventional fluidized bed to stabilize it. The advantage of operating in this regime is that sintering, which occurs during the oxidation step, freezes the bed, and the reactor maintains its high porosity, surface area, favorable chemical kinetics, and low pressure drop. The application of the magnetic field serves to stabilize the fluidized bed to promote bed uniformity, which is favorable for chemical kinetics and eliminates bubbling. Magnetically stabilized fluidized beds provide enhanced uniformity of void fraction, enhanced heat transfer, and enhanced reactivity. In addition, a conventional fluidized bed reactor is being studied for comparison with the magnetically stabilized bed. A blend of Fe and silica (Si) powder is used to suppress particle sintering and sustain fluidization.

Figure 1 shows the process flow diagram for the chemical looping process. Coal is the input to the system, and the outputs consist of highly pure H_2 and highly concentrated CO_2 that is suitable for sequestration. The energy content of gasifier products and heat released during the oxidation step drives the complete chemical looping process. Steam at the desired temperature is obtained by using the high temperature syngas. Treated syngas is reheated to the required reduction temperature using the raw syngas. Two identical reactors are used in the process in order to maintain a continuous stream of products. While one reactor operates in the oxidation mode producing H_2, the other reactor operates in the reduction mode regenerating the Fe bed.

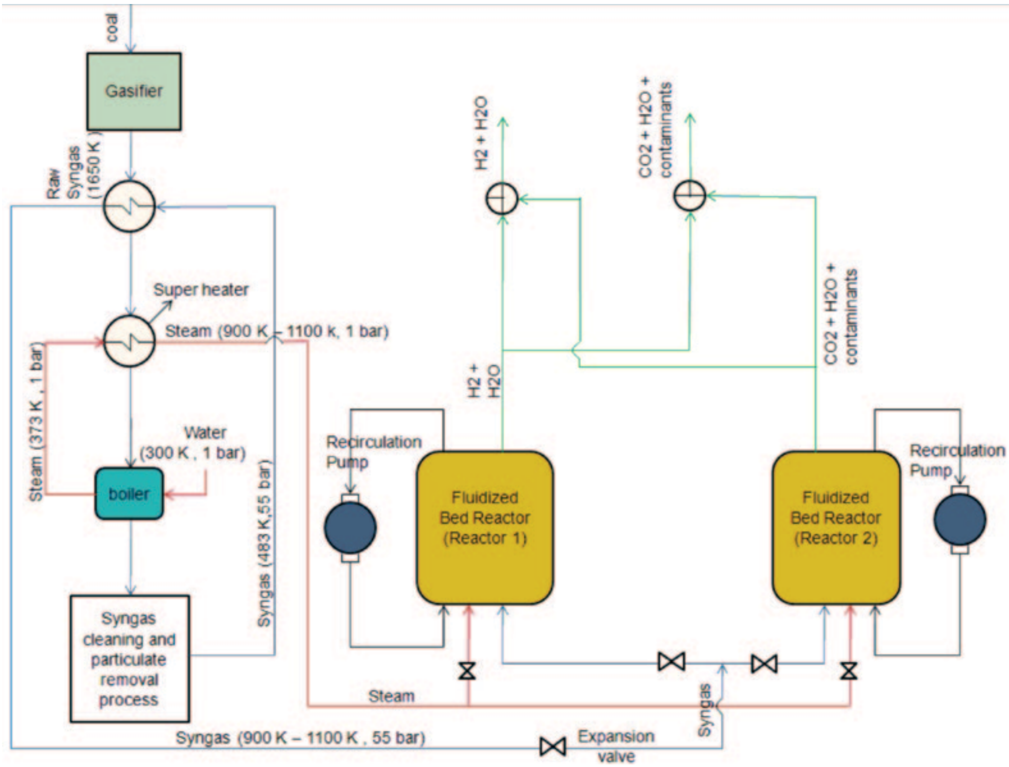

Figure 1: Process Flow Diagram of the Chemical Looping Process Using Cleansed Syngas for the Oxidation Step

A laboratory-scale magnetically stabilized reactor has been fabricated, and its performance is under investigation. The cylindrical reactor shown in Figure 2 is fabricated with a quartz wall and can accommodate the upper operating temperature limit of the reactor, 800 °C. A porous ceramic frit is positioned at the entrance of the reactor in order to evenly distribute the flow. Two magnetic poles produce a transverse magnetic field and create magnetic chains of Fe particles within the bed. The magnetic chains repel each other, because of their polarity, and form a naturally porous structure. The reactants enter the reactor from the bottom and exit through the top. The reactor is insulated with high temperature ceramic fiber insulation.

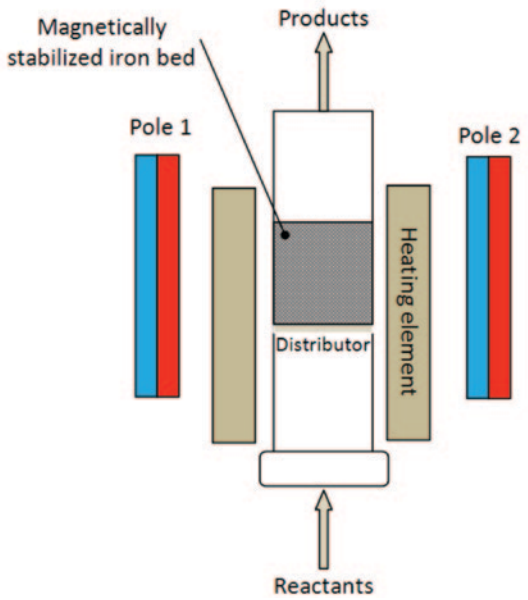

Figure 2: Magnetically Stabilized Bed Reactor

This reactor concept has inherent advantages and disadvantages. The high porosity and low pressure drop through the bed are advantageous. In addition, this reactor concept advantageously exploits the particle sintering during the oxidation step. Because the bed is frozen due to sintering, transverse thermal transport through the bed is reduced. The vertical flow configuration lends itself to mathematical modeling of the fluid, thermal, and species transport. Such modeling will prove useful to reliably predict the large-scale throughput in a scaled-up design. A major objective of this work is to utilize the experimental measurements to develop a mathematical framework to accurately model the magnetically stabilized bed reactor performance over a range of different operating conditions.

Technology Advantages

- Chemical looping enables extraction of high purity H_2 and sequestration-ready CO_2 from syngas near gasification operating conditions to obtain improved thermal efficiency over more traditional gas separation methods that operate at low temperatures and pressures.

- Metal oxide sorbents with magnetic properties have the potential to reduce pressure drop, provide more uniform solids distribution, and aid in solids transport within the magnetically stabilized bed reactors.

  - Large surface area available to enhance reaction rate per unit volume.

  - Enhanced mixing provides more uniform temperature field.

  - Reactive powder surface properties are easily modified (e.g., enhance reactivity and modify radiant properties).

  - A uniform stabilized bed with no large voids can be sustained, thus more uniform flow through the bed is established.

  - The bed stabilization characteristics are well controlled through the magnetic input field configuration and strength.

  - Low velocity vapor flow can be sustained in order to increase the residence time.

  - Stoichiometric flow can be sustained.

R&D Challenges

- Iron powders have a tendency to sinter at high temperature.
- Maintaining stability of powder reactivity over many cycles.
- Multi-scale, multi-physics modeling effort is required.

Results To Date/Accomplishments

- Completed a comprehensive parametric chemical equilibrium study for the chemical looping cycle based on Fe and Fe oxides. A thermodynamic investigation of the H_2 production step indicates that H_2 is favored at low temperatures with steam to H_2 conversion exceeding 90% at reaction temperatures below 700 K. The H_2 yield is independent of pressure.
- Reaction conditions were determined for obtaining energy and cost-effective operation of the chemical looping process.
- Constructed and tested a laboratory-scale experimental system to evaluate H_2 production performance in the magnetically stabilized bed reactor. Investigated the optimum conditions for providing the best reaction results using stationary matrix of Fe–Si.
- Devised three distinct plant layouts for reaction temperature ranges of 500–900 K; 900–1,100 K; and 1,100–1,200 K, respectively. Results from a thermal management study for the proposed chemical looping process indicate that no external energy is needed for looping cycle based H_2 production, but system configurations vary with temperature. Simulation of multiple cycles indicates that temperatures in the 900–1,000 K range will maximize H_2 yield.
- Demonstrated a high yield of H_2 production within the magnetically stabilized bed reactor over several looping cycles.

Next Steps

- Cycle reactors through repetitive oxidation and reduction cycles and characterize the stability of the bed reactivity over repeated cycles.
- Use the fundamental kinetic studies to construct a reaction rate law that is consistent with observations, and test the validity of the rate law applied to the reactor H_2 and CO_2 production.
- Continue with powder characterization studies before and after reactions.
- Test alloyed iron powders for chemical reactivity.
- Combine mass, momentum, energy, and species transport simulation modules, and test fidelity of the computational code against several test cases.
- Develop a reactor scale-up design strategy from laboratory to bench scale.

Final test results will not be available until after the September 2012 project completion date.

Available Reports/Technical Papers/Presentations

A. Mehdizadeh, R., Mei, J. F., Klausner and N., Rahmatian. “Interaction forces between soft magnetic particles in uniform and non-uniform magnetic fields.” Acta Mechanica Sinica, 26: 921–929, 2010.

COAL DIRECT CHEMICAL LOOPING RETROFIT TO PULVERIZED COAL POWER PLANTS FOR IN-SITU CO_2 CAPTURE

Primary Project Goals

Ohio State University (OSU) is developing an iron oxide (Fe_2O_3)-based chemical looping process for retrofit on existing coal-fired power plants.

Technical Goals

- Select optimum iron-based oxygen carrier. Evaluate the reactivity, recyclability, and physical strength of different Fe_2O_3-based oxygen carrier particle compositions.
- Demonstrate bench-scale (2.5 kWth) coal direct chemical looping (CDCL) system including fuel reactor demonstration and coal char and volatile conversion. Determine optimum fuel reactor operating conditions to gasify coal char using oxygen carrier particle.
- Demonstrate sub-pilot scale (25 kWth) CDCL system including integration of fuel reactor and combustor with continuous solid circulation at reaction temperature. Operate integrated sub-pilot system for a minimum of 50 continuous hours with the optimal oxygen carrier. Determine the fate of nitrogen oxide (NO_x) and sulfur via integrated system testing.
- Conduct ASPEN simulation based on the CDCL test results.
- Conduct techno-economic study.

Technical Content

Researchers at OSU are developing a one-step CDCL process to produce electric power and high-purity carbon dioxide (CO_2) in retrofit power plant applications. While preliminary tests with the bench-scale reactor have shown 90–95% coal char conversion and >99% volatile conversion, the primary focus of this project is to identify the optimal oxygen carrier chemical composition and conduct integrated, continuous CDCL testing at the sub-pilot (25 kWth) scale.

As shown in Figure 1, the CDCL system consists of a fuel reactor and a combustor. The moving-bed fuel reactor utilizes a countercurrent gas-solid contacting pattern to maximize the conversion of the Fe_2O_3-based oxygen carrier, as it transfers oxygen to facilitate coal combustion. The combustor, an entrained-flow reactor, uses air to pneumatically transport the oxygen carrier back to the fuel reactor, while re-oxidizing the oxygen carrier and generating a significant amount of heat. A portion of the heat generated in the combustor is used for steam generation via the high-temperature exhaust gas, while the remainder is carried to the fuel reactor by the hot regenerated particles to supply the heat required for coal combustion.

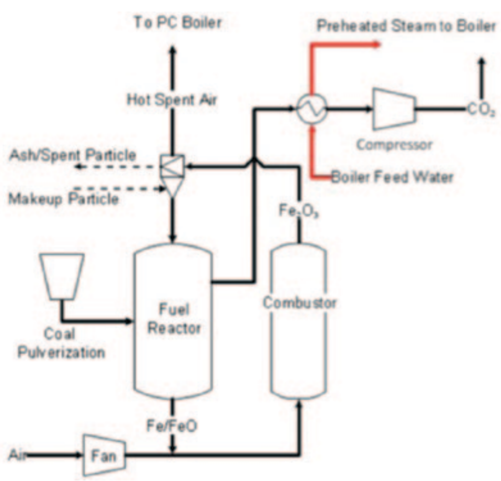

Figure 1: CDCL Process Flow Diagram

Technology Maturity:
Laboratory-scale

Project Focus:
Coal Direct Chemical Looping for Retrofits

Participant:
Ohio State University

Project Number:
NT0005289

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Babcock & Wilcox Power Generation Group, Inc.
Clear Skies Consulting
CONSOL Energy, Inc.
Shell/CRI/Criterion, Inc.

Performance Period:
1/1/09 – 12/31/11

The oxygen carrier consists primarily of Fe_2O_3 based on earlier tests that showed an acceptable oxygen capacity and no loss of activity during more than 100 redox cycles in a thermogravimetric analyzer (TGA) test. To optimize the reactivity, recyclability, and physical strength of the Fe_2O_3-based oxygen carrier for the CDCL process, OSU researchers evaluated the performance of different support materials and promoters using a TGA and a fixed-bed reactor. These initial screening experiments were used to select the 10 most reactive and recyclable particle compositions, which were subjected to additional reactivity and physical strength tests. These 10 particles were tested to measure their reactivity with coal char in an inert environment and their tolerance to carbon deposition using TGA. The particles were then pelletized for further evaluations, such as pellet strength and reactivity, using a fixed-bed. After eliminating pellets with unacceptable strength and reactivity, the five most promising Fe_2O_3-based composite oxygen carrier particles were identified.

Bench-scale (2.5 kWth) testing of the five most promising oxygen carrier particle compositions in a moving-bed reactor will be used to determine the optimal oxygen carrier particle composition for the CDCL process. A series of bench-scale tests have been conducted for more than 50 hours.

Using the sub-pilot scale (25 kWth) testing unit shown in Figure 2, the integrated CDCL process will be evaluated during a minimum of 50 hours of continuous operation with the optimal oxygen carrier particle composition. During testing, OSU researchers will monitor the composition of outlet gases [including CO_2, sulfur dioxide (SO_2), and (NO_x)], attrition of the oxygen carrier, and the ash separation effectiveness of the cyclone system.

To quantify the performance and potential benefits of the CDCL process, detailed modeling and a techno-economic analysis of the system will be conducted by CONSOL Energy.

Figure 2: Sub-Pilot Scale (25 kWth) CDCL Unit

Technology Advantages

- An air separation unit is not required for oxygen production.
- CO_2 separation simultaneously takes place with the coal conversion.
- The CDCL process is a versatile technology that can produce power, synthesis gas (syngas), or hydrogen (H_2), while offering fuel flexibility.

R&D Challenges

- Scale-up issues.
- Solids handling and transport.
- Oxygen carrier capacity, reactivity, and attrition.
- Slow reaction rates between the oxygen carrier and coal char.
- Ash management.

Results To Date/Accomplishments

- Completed analyses for selection of optimum oxygen carrier and support particle. Identified five Fe_2O_3-based oxygen carrier particles. Testing of the oxygen carrier particles included evaluation of recyclability, carbon deposition tolerance, reaction with coal char, and pellet strength and reactivity.
- Demonstrated coal conversion by oxygen carrier using a TGA for solids analysis and a fixed-bed experiment for gas analysis.
- Conducted bench-scale testing (2.5 kWth) of coal char conversion. Studied the effects of H_2O (steam) and CO_2 as gasification enhancers on metallurgical coke char with the goal to determine the optimum oxygen carrier. Achieved 97% char conversion with H_2O (steam) as the gasification enhancer and 88% char conversion with CO_2 as the gasification enhancer.
  - The conditions that produce the highest conversion are the use of steam as an enhancer gas, higher temperatures, higher char residence times, and higher oxygen carrier to char ratios. However, all of these factors need to be optimized, since a high residence time will result in a larger, more capital-intensive setup, and a higher temperature will result in possible sintering of particles. Furthermore, the use of steam is a parasitic energy requirement, so conversion using steam needs to be controlled.
- Conducted solid handling study for sub-pilot scale demonstration using the cold model reactor.
- Initiated construction of sub-pilot scale (25 kWth) system.

Next Steps

- Complete construction of the sub-pilot scale system and integrated CDCL testing for at least 50 continuous hours.
- Conduct ASPEN simulation studies.
- Complete a techno-economic analysis.

Final test results will not be available until the December 2011 project completion date.

Available Reports/Technical Papers/Presentations

General project information is available on DOE/NETL website at: http://www.netl.doe.gov/technologies/coalpower/ewr/co2/oxy-combustion/in-situ.html

"Chemical Looping Systems for Fossil Energy Conversions," John Wiley and Sons, Inc., Hoboken, NJ, USA, October 2010. http://www.wiley.com/WileyCDA/WileyTitle/productCd-0470872527.html

"Coal Direct Chemical Looping (CDCL) Retrofit to Pulverized Coal Power Plants for In-Situ CO_2 Capture," Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, PA, September 2010. http://www.netl.doe.gov/publications/proceedings/10/co2capture/index.html

"Coal Direct Chemical Looping Retrofit for Pulverized Coal-fired Power Plants with In-Situ CO_2 Capture," Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, PA, March 2009. http://www.netl.doe.gov/publications/proceedings/09/CO2/index.html

DEVELOPMENT OF COMPUTATIONAL APPROACHES FOR SIMULATION AND ADVANCED CONTROLS FOR HYBRID COMBUSTION-GASIFICATION CHEMICAL LOOPING

Technology Maturity:
Laboratory-scale

Project Focus:
Chemical Looping Simulation and Control

Participant:
Alstom Power

Project Number:
NT43095

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Partners:
Taft Engineering, Inc.
University of Illinois Urbana-Champaign (UIUC)

Performance Period:
7/12/07 – 3/31/11

Primary Project Goals

Alstom is developing advanced computational models and optimizing control systems for chemical looping processes.

Technical Goals

- Identify sensor and control needs for chemical looping processes.
- Develop process simulation models with dynamic capability to evaluate control methods.
- Incorporate advanced process controls into the chemical looping plant design process.
- Investigate advanced process controls for complex solids flow and gas pressure control.
- Develop a control system design concept for the chemical looping prototype facility.

Technical Content

Alstom is developing advanced computational models and optimizing control systems for chemical looping processes, such as the hybrid combustion-gasification process shown in Figure 1. Chemical looping is a two-step process which first separates oxygen (O_2) from nitrogen (N_2) in an air stream in an air reactor. The O_2 is transferred to a solid oxygen carrier. The oxygen is carried by the solid oxide and is then used to gasify or combust solid fuel in a separate fuel reactor. As shown in Figure 1, a metal or calcium material (oxygen carrier) is burned in air forming a hot oxide (MeO_x or CaO_x) in the air reactor (Oxidizer). The oxygen in the hot metal oxide is used to gasify coal in the fuel reactor (Reducer), thereby reducing the oxide for continuous reuse in the chemical looping cycle.

Chemical looping is applicable to both new and retrofit plants and has the flexibility to be designed in a number of configurations. The reactor can be operated in a partial combustion mode, to generate a carbon monoxide (CO)-rich syngas, which in another variant, can be shifted to produce hydrogen (H_2). Alternately, it can operate in full combustion mode, resulting in exhaust of carbon dioxide (CO_2) and water. The three main configurations are: Option 1, chemical looping combustion with CO_2 capture; Option 2, chemical looping gasification with downstream CO_2 capture; and Option 3, chemical looping gasification to produce H_2 with inherent CO_2 capture.

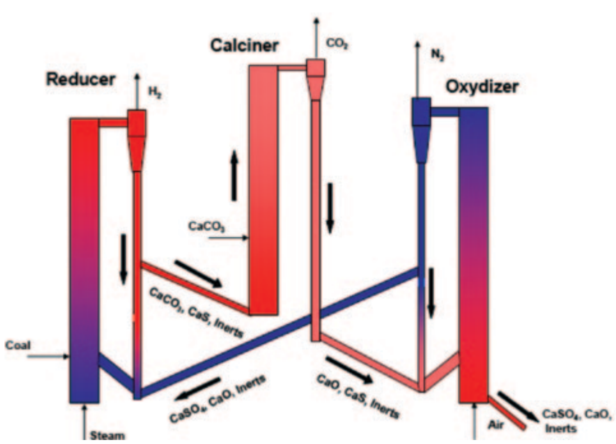

Figure 1: Alstom's Hybrid Combustion-Gasification Process

Chemical looping is a process with multiple material and energy streams inter-connected between the multiple reactors. In order to obtain and maintain optimal conditions for operation with reduced waste stream volume and minimum required energy, advanced optimizing control systems are required. As such, process control development is needed to operate the system in a safe, integrated, and optimized fashion and is viewed as critical for enhancing the performance of the chemical looping system. This project is developing model-based controls that can be used to operate the system. Approaches to model development and control algorithms are being developed by researchers at Alstom and the University of Illinois Urbana-Champaign (UIUC).

Alstom is developing computational models to gain a better understanding of the chemical looping process behavior and to develop control strategies, including: a two-loop cold flow model, a dual-loop hot flow model (without reactions), and a real-time dual-loop simulator. The dual-loop simulation platforms are configured to test conceptual control designs. For example, it was used to investigate both linear and non-linear control concepts and evaluate control strategies with different sensors and actuators. In addition to developing process models and advanced controls applications, Alstom is developing advanced sensors, such as the ultrasonic-time of flight and the image-based laser-light spot and triangulation prototype level sensors.

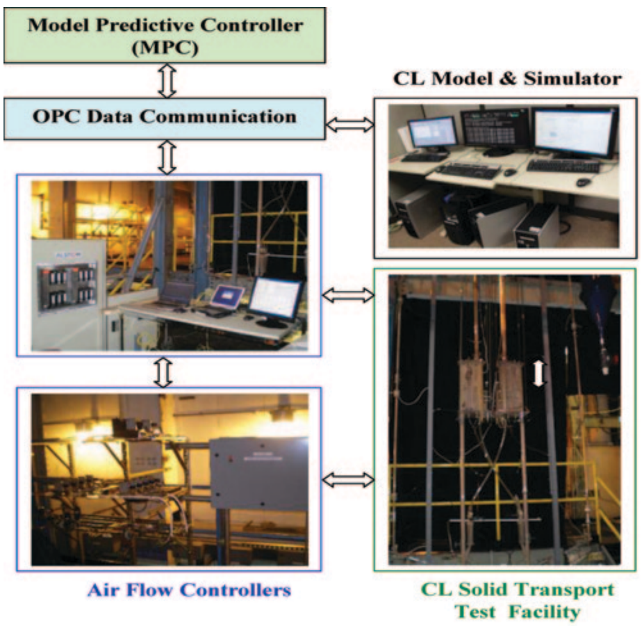

Figure 2: Experimental Facility Control Testing

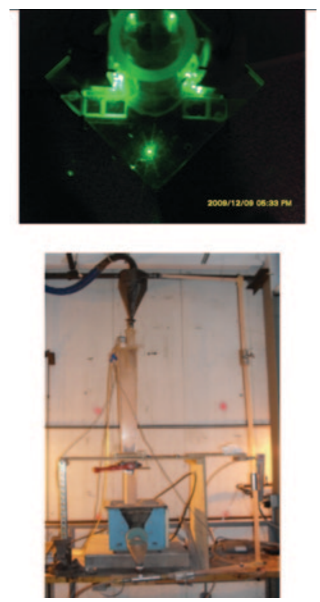

Figure 3: Sensor Testing

Technology Advantages

Power plants using conventional circulating fluidized bed or transport reactor technology do not require very sophisticated control since there is only a single, uncontrolled recycle loop. However, it is anticipated that power plants using a chemical looping process that has more complex multi-loop controlled solids circulating and transfer loops will require more sophisticated and demanding process control systems. The overall advantage is to develop advanced multivariable optimizing controls integrated early into the process development cycle to ensure a plant level design that is more controllable and reliable.

Advanced control systems for chemical looping will provide for more stable and continuous operation of the process, thus enabling high efficiency, high reliability, low environmental impact, and reduced costs. Project investigations have shown that traditional controls are more subject to interactions and disturbances and hence less robust to maintaining stable loop control when compared to model-based control of the same system, suggesting that this approach may be essential for reliably operating multiple cross-flowing loops together in a continuous manner.

R&D Challenges

Challenges include the development of real-time, fast, and dynamically accurate response models for use in simulation and dynamic control of the chemical looping multi-loops, followed by the inclusion of new measured control variables and reliable instrumentation as input into the model-based control. Additional challenges will be to scale-up the computational models and simulation tools and integrate the advanced controls with the scale up of the chemical looping process from the current laboratory scale to a commercial demonstration size unit. This will include consideration of the appropriate process dynamics, chemical reactions, and externalities so the control can account for a large number of variables and the changes in process dynamics at the larger size units that will impact stable loop control.

Results To Date/Accomplishments

- Developed process and control performance benchmarks.
- Completed process characterization by developing an understanding of the dynamic operation and control issues at the cold flow and chemical looping test facilities.
- Completed process modeling and simulation.
- Validated chemical looping process models.
- A two-loop cold flow model has been validated with extensive test data.
- A real-time dual-loop cold flow simulator has been developed to test control designs.
- A hot-loop model (without reactions) has been developed and parameterized using data from the chemical looping process development unit (PDU) test facility.
- The dual-loop simulation platform is completed and was used to evaluate different control strategies with various sensors and actuators.
- Conceptual proportional-integral-derivative (PID) control and model predictive control (MPC) designs have been completed and tested with the simulator.
- A real-time linear MPC controller was revised and tested for the 15-foot dual-loop facility.
- Initiated scale-up modeling and simulation of a larger cold flow solids transport test facility.
- Completed further scale-up to develop models and multi-loop simulations for the 3-MW_{th} chemical looping prototype test facility being constructed by Alstom under DOE/NETL project No. DE-NT0005286.
- Evaluated a nonlinear model predictive control (NMPC) based on the development of an initial reduced order model (ROM) for dual-loop controls.
- Completed testing of advanced sensors. Both the solids level sensor and the two-phase mass flow sensor candidates were tested and confirmed that a direct measurement of both level and mass flow rate are feasible and significantly aid in the process control. Soft sensing based on the measurement of differential pressures has also been investigated.

Next Steps

Final results will not be available until after the March 2011 project completion date.

Available Reports/Technical Papers/Presentations

The 33rd International Technical Conference on Coal Utilization and Fuel Systems, Clearwater, FL, USA, June 1–5, 2008, "Simulation and Advanced Controls for Alstom's Chemical Looping Process," Xinsheng Lou, Carl Neuschaefer, and Hao Lei.

51st ISA Power Industry Division Symposium and 18th Annual Joint ISA POWID/EPRI, Controls and Instrumentation Conference, Scottsdale, AZ, USA, June 8–13, 2008, "Simulation and Advanced Controls for Hybrid Combustion-Gasification Chemical Looping Process," Xinsheng Lou, Carl Neuschaefer, and Hao Lei.

International Pittsburgh Coal Conference, Pittsburgh, PA, USA, September 21–24, 2009 "Dynamic Simulation and Advanced Controls for Alstom's Chemical Looping Process," Xinsheng Lou, Carl Neuschaefer, Hao Lei and Abhinaya Joshi.

Modelling, Controller Design, and Computational Tools for the Closed-Loop Control of the Cold Flow Fluidized Bed Rise, submitted to the journal of Nonlinear Phenomena in Complex Systems by UIUC Dong Ye, Shu Zhang, Vivek Natarajan, Bryan Petrus, and Joseph Bentsman.

An invited presentation on this project was given by Mr. Carl Neuschaefer at the workshop on advanced controls organized by DOE/NETL aligned with 2008 ISA Power Conference in Scottsdale, AZ, USA.

2010 International Pittsburgh Coal Conference, Istanbul, Turkey, October 11–14, 2010, "Development of Real-time Dynamic Simulation of Chemical Looping Process for Advanced Controls," Hao Lei, Xinsheng Lou, Abhinaya Joshi and Carl Neuschaefer.

HIGH PURITY HYDROGEN PRODUCTION WITH IN-SITU CARBON DIOXIDE AND SULFUR CAPTURE IN A SINGLE-STAGE REACTOR

Primary Project Goals

Ohio State University (OSU) is developing a Calcium Looping Process (CLP) to enhance hydrogen (H_2) production by integrating the water gas shift (WGS) reaction with high-temperature carbon dioxide (CO_2), sulfur, and halide removal from synthesis gas (syngas) in a single-stage reactor for integrated gasification combined cycle (IGCC) applications.

Technical Goals

- Reduce steam requirement and operate at near-stoichiometric steam consumption.
- Evaluate the regenerability of the calcium oxide (CaO) sorbent by repeated in-situ carbonation and regeneration for 10–100 cycles.
- Demonstrate simultaneous removal of CO_2, sulfur, and halides using a CaO sorbent in the bench-scale, fixed-bed unit.
- Produce either a 90–95% H_2 stream without WGS catalyst, or a 99+% high-purity H_2 stream with WGS catalyst at high temperatures and pressures.
- Demonstrate H_2 production with the sub-pilot-scale testing unit.
- Perform a techno-economic feasibility study for different integrated process scenarios using Aspen modeling.

Technical Content

The WGS reaction, which converts most of the syngas carbon monoxide (CO) to H_2 and CO_2 by reacting the CO with steam over a bed of catalyst, can be utilized to enhance H_2 production. The excess steam serves to drive the WGS equilibrium toward the products. The reaction is exothermic and, due to equilibrium constraints, typically consists of two stages: (1) high-temperature shift that benefits from high reaction rates at elevated temperatures; and (2) low-temperature shift that yields more favorable reaction equilibrium.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_{rxn} = -41.2 \text{ kJ/mol}$$

OSU researchers are developing the CLP that combines the WGS reaction and high-temperature, sorbent-based acid gas removal in a single-stage reactor, as shown in Figure 1. By implementing the CLP near the high-temperature reaction zone, syngas cooling and re-heating is no longer required, and the process may eliminate the need for the WGS catalyst. A CaO sorbent is used as the circulating material for in-situ removal of CO_2, sulfur, and halides. By incorporating sorbent-based CO_2 removal, not only is a near sequestration-ready stream of CO_2 produced, but plant efficiency and H_2 production are increased by driving the WGS reaction further to completion.

Technology Maturity:

Laboratory-scale

Project Focus:

Calcium Looping Process for Hydrogen Production

Participant:

Ohio State University

Project Number:

NT43059

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Partners:

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Consol Energy, Inc.

Performance Period:

7/5/07 – 4/30/11

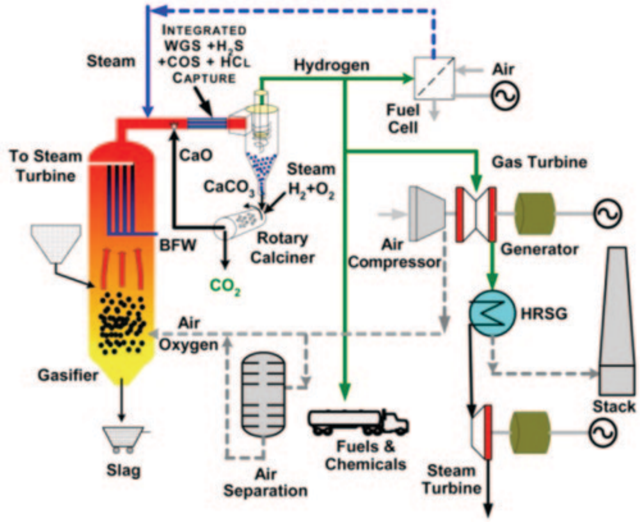

Figure 1: Calcium Looping Process for Enhanced Hydrogen Production with In-Site CO_2 and Sulfur Capture in a Single-Stage Reactor

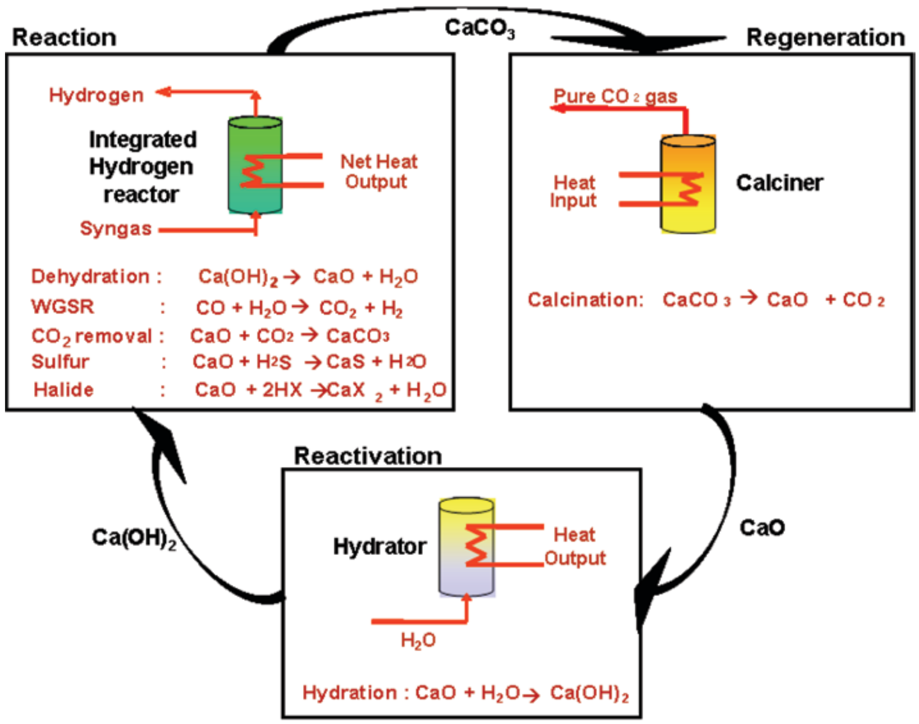

Figure 2: Illustration of the Reaction Schemes in the Calcium Looping Process

As shown in Figure 2, the CLP is comprised of three reactors: (1) the carbonator, where high-purity H_2 is produced and contaminant removal takes place; (2) the calciner, where the CaO sorbent is regenerated and a sequestration-ready CO_2 stream is produced; and (3) the hydrator, which reactivates the CaO sorbent. The carbonator (either a fixed, fluidized-bed, or an entrained flow reactor) operates at high pressures ranging from 20 to 30 atm and temperatures of 550–650 °C. The thermodynamic constraint of the WGS reaction is overcome in the carbonation reactor by the incessant removal of the CO_2 product from the reaction mixture, which enhances H_2 production. This is achieved by concurrent WGS reaction and carbonation reaction of CaO to form calcium carbonate ($CaCO_3$), thereby removing the CO_2 product from the reaction mixture and obviating the need for a WGS catalyst and excess steam addition. The CLP does not require syngas pretreatment, because the CaO sorbent also controls hydrogen sulfide (H_2S), hydrogen chloride (HCl), and carbonyl sulfide (COS) to parts-per-billion (ppb) levels. Key parameters for the CaO sorbent are provided in Table 1.

Table 1: Solid Sorbent Parameters

	Parameter	Current R&D Value	Target R&D Value
Sorbent Properties	Type of sorbent	CaO powder	CaO powder
	Heat of adsorption (kJ/mole CO_2)	-178.3	-178.3
	CO_2 loading/working capacity, wt%	45–55%	55%
	Surface area, m^2/g	14–32	14–32
	Particle density, cm^3/g	1.150 g/cm^3	1.150 g/cm^3
	Packing density, cm^3/g	1.289 g/cm^3	1.289 g/cm^3
	Particle size (mm)	0.01–0.05	0.01–0.05
	Heat capacity (kJ/K/kg)	0.96(CaO)–1.23($CaCO_3$)	0.96(CaO)–1.23($CaCO_3$)
	Thermal stability, °C	Much higher than the temperature of operation	Much higher than the temperature of operation
	Hydrothermal stability, °C	N/A	N/A
Process Configuration	Attrition rate (fluidized bed), %/year	N/A since micron sized particles are used	N/A since micron sized particles are used
	Cycle time (fixed bed), minutes	N/A	N/A
	Pressure drop (fixed bed), psia	N/A	N/A
Operating Conditions	Adsorption temperature, °C	600	600
	Adsorption pressure, atm	1–30 atms	1–30 atms
	CO_2 capture efficiency, %	>99%	>99%
	Regeneration method	Calcination in N_2, or pure CO_2	Calcination in CO_2
	Regeneration temperature, °C	700–950	700–950
	Regeneration pressure, atm	1	1
Heat Integration	Required regeneration steam temperature, °C	External steam not required for regeneration	External steam not required for regeneration
Miscellaneous	Sorbent make-up rate, kg/kg CO_2	N/A	—
Product Quality	CO_2 purity, %	N/A	>99%
	N_2 concentration, %	N/A	<1%
	Other contaminants, %	N/A	—
Process Performance	Electricity requirement, kJ/kg CO_2	N/A	N/A
	Heat requirement, kJ/kg CO_2	N/A	N/A
	Total energy (electricity equivalent), kJ/kg CO_2	N/A	N/A

The spent sorbent, consisting mainly of $CaCO_3$, is regenerated back to CaO in the calciner, which operates at atmospheric pressure in a rotary, or a fluidized-bed system. Calcination occurs at temperatures above 900 °C in the presence of 1 atm CO_2, but CO_2 dilution via steam addition or syngas combustion in a direct-fired calciner permits calcination at lower temperatures. The regenerated CaO sorbent is then conveyed to the hydrator.

The hot solids from the calciner are then cooled to 500–600 °C and hydrated via contact with low-temperature steam in the hydrator. The calcination process causes sorbent sintering, which reduces the sorbent's reactivity; the hydration process reverses this effect by increasing the pore volume and surface area available for reaction with the gas mixture. The calcium hydroxide [$Ca(OH)_2$] decomposes in the carbonator to produce CaO and steam. The steam obtained from the dehydration reaction is used for the WGS reaction. Hence, no excess steam is required in the CLP as the WGS steam is supplied to the hydrator.

Technology Advantages

- The simultaneous removal of CO_2 drives the WGS reaction to completion, which due to operation at feed conditions (high temperature and pressure), will increase plant efficiency.

- The process also eliminates the need for a WGS catalyst.
- No separate steps necessary for removal of sulfur and halide impurities.
- High-quality exothermic heat available from all three reactors can be used to generate electricity.

R&D Challenges

- Waste disposal.
- Solids handling and transport.
- Design of a high-temperature steam hydrator.

Results To Date/Accomplishments

- Determined optimum temperature (600 °C) for H_2 production and impurity removal.
- Identified temperature range for CO_2 capture while reducing excess steam requirements.
- Identified process conditions for H_2S and halide capture.
- Combined WGS, carbonation, and sulfidation reactions conducted in the absence of a catalyst.
- Designed and fabricated a cold model for the carbonator.
- Developed the sorbent reactivation process by hydration and achieved sustained reactivity for multiple cycles.
- Conducted cold flow and hot flow tests using air to ensure proper functioning of the sub-pilot-scale unit.
- Successfully conducted high-temperature CO_2 capture tests using CaO in the sub-pilot-scale unit.

Next Steps

- Conduct sub-pilot-scale testing of combined WGS and CO_2 capture to evaluate process feasibility.
- Complete Aspen simulation studies.
- Complete techno-economic analysis.
- Design a 1–5 MWe pilot-scale CLP unit.

Final test results will not be available until after the April 2011 project completion date.

Available Reports/Technical Papers/Presentations

Ramkumar, S. and Fan, L.-S; Calcium Looping Process for Clean Fossil Fuel Conversion. *Proc. 26th Intl Pittsburgh Coal Conf.*, Pittsburgh, PA, September 2009.

Ramkumar, S.; Connell, D. and Fan, L.-S.; Calcium Looping Process for Clean Fossil Fuel Conversion. 1st *Meeting of the High Temperature Solid Looping Cycles Network*, Oviedo, Spain, September 2009.

Ramkumar, S. and Fan, L.-S; Calcium Looping Process for Clean Fossil Fuel Conversion. 8th *World Congress of Chemical Engineering*, Montreal, Canada, August 2009.

ALSTOM'S CHEMICAL LOOPING COMBUSTION PROTOTYPE FOR CO_2 CAPTURE FROM EXISTING PULVERIZED COAL-FIRED POWER PLANTS

Primary Project Goals

Alstom Power is to design, build, and test a 3-MW_{th} limestone-based chemical looping combustion (CLC) prototype facility.

Technical Goals

- Design a CLC prototype that consumes approximately 454 kg/hr (1,000 lb/hr) of coal and uses calcium sulfate ($CaSO_4$) as an oxygen carrier.
- Test cold flow solids transport.
- Characterize the environmental performance of the CLC prototype facility.
- Develop design information for a larger-scale CLC commercial demonstration plant.

Technical Content

Alstom is to scale up the limestone-based CLC process from a 65-kWth pilot, which was successfully demonstrated in an earlier project, to a 3-MW_{th} prototype facility that is to be operational in 2010 and 2011. CLC utilizes a metal oxide or other compound, in this case limestone ($CaSO_4$), as an oxygen carrier to transfer oxygen from the combustion air to the fuel. Since direct contact between fuel and combustion air is avoided (Figure 1), the products of combustion [carbon dioxide (CO_2) and water] are kept separate from the rest of the flue gases (primarily nitrogen). CLC splits combustion into separate oxidation and reduction reactions. The carrier releases oxygen in a reducing atmosphere to react with the fuel. The carrier is then recycled back to the oxidation chamber to be regenerated by contact with air. Calcination of hot solids produced in the oxidation reactor produce a concentrated stream of CO_2 in lieu of the dilute CO_2 stream typically found in flue gas from coal-fired power plants.

Prior to DOE/NETL involvement, Alstom constructed a small-scale pilot facility [process development unit (PDU)] at its Power Plant Laboratories in Windsor, CT, that was completed in 2003. The PDU was subsequently used in the DOE/NETL project. In Phase I, Alstom developed the indirect combustion loop with CO_2 separation, and also synthesis gas (syngas) production from coal with the calcium sulfide (CaS)/$CaSO_4$ loop utilizing the PDU facility.

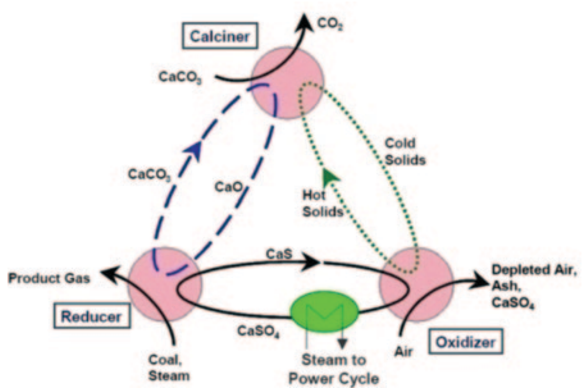

Figure 1: Limestone-Based CLC Process

Technology Maturity:

Prototype scale, 3-MW_{th}, 1,000 lb of coal/hr

Project Focus:

Chemical Looping Combustion Prototype

Participant:

Alstom Power

Project Number:

NT0005286 (continuation of NT41866)

NETL Project Manager

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Dr. John Grace and Dr. Jim Lim, University of British Columbia
Dr. Janos Beer, MIT

Performance Period:

9/30/03 – 9/30/11

In Phase II, Alstom developed the carbonate loop [lime (CaO)/calcium carbonate ($CaCO_3$)], integrated it with the gasification loop from Phase I, and demonstrated the feasibility of hydrogen production from the combined loops.

In Phase III, Alstom operated the small pilot plant to obtain engineering information to design a prototype of the commercial chemical looping concept. The activities included modifications to the Phase II chemical looping PDU, solids transportation studies, control and instrumentation studies, and additional cold flow modeling.

In the current Phase IV activities, Alstom is to design, construct, and operate a 3-MW_{th} CLC prototype that includes process loops to transfer solids and oxygen between the reducing and oxidation reactors. The facility has the ability to combust coal, gasify coal, or produce hydrogen; however, hydrogen is not expected to be produced during this particular project. Alstom plans to conduct seven weeks of cold flow and hot flow testing, with CO_2 vented to the atmosphere. Information gleaned from prototype testing will be used to develop a technical plan and cost estimate for a subsequent larger-scale commercial demonstration project at a full-scale power plant. Figure 2 is a photograph of the 40 foot-tall cold flow model and Figure 3 is a general arrangement drawing of the 3-MW_{th} prototype facility. The prototype includes a reducing reactor, an oxidation reactor, and process loops to transfer solids and oxygen between the two reactors using limestone as the oxygen carrier.

Figure 2: 40-Foot Cold Flow Model

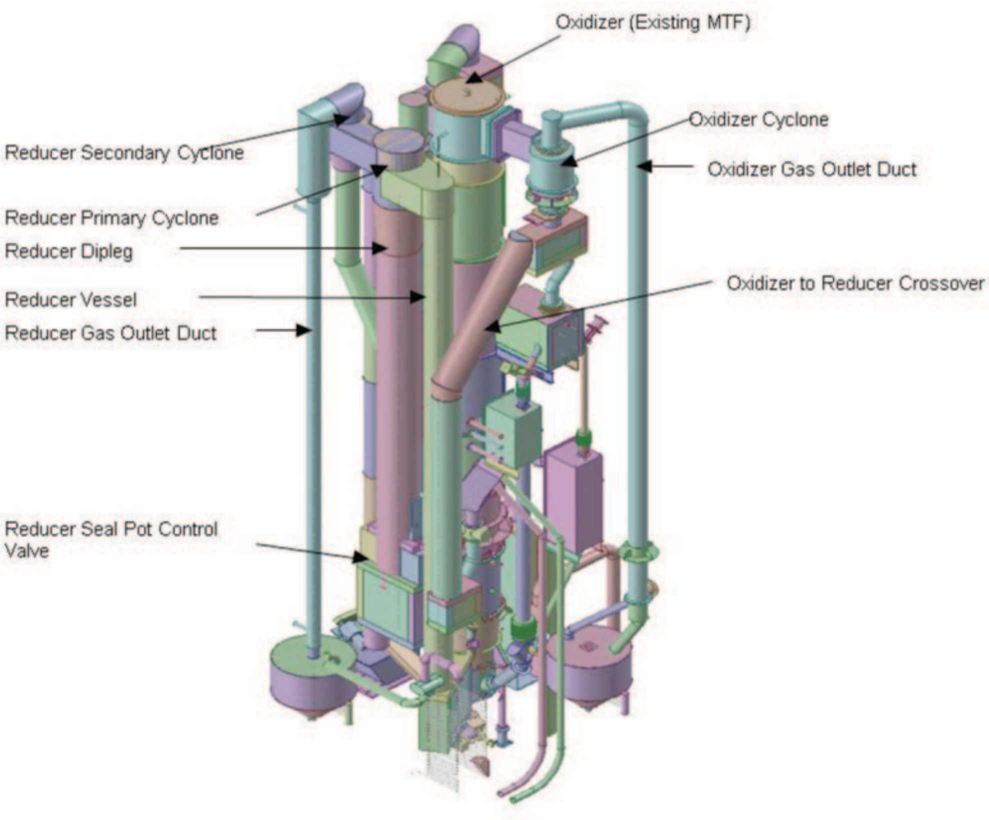

Figure 3: General Arrangement of 3-MW_{th} Prototype Test Facility

Technology Advantages

- An air separation unit (ASU) is not required for oxygen production.
- CO_2 separation takes place during combustion.
- The technology can produce power, syngas, or hydrogen, while offering fuel flexibility.

R&D Challenges

- Scale up issues.
- Solids handling and transport.
- Oxygen carrier capacity and reactivity.

Results To Date/Accomplishments

Phases I, II, and III were completed In the earlier project (NT41866) and Phase IV is being conducted under the current project (NT0005286).

Phase I:

- It is practical to build a chemical looping system using the CaS to $CaSO_4$ reaction without losing sulfur as either sulfur dioxide (SO_2) or hydrogen sulfide (H_2S).
- High gasification rates can be obtained in a chemical looping system even with low reactivity coals.
- It is possible to operate three interactive solids transport loops (oxidizer, reducer, and sorbent activation) at elevated temperatures (1,800 °F).
- It is possible to start up and heat up the solids transport loops interactively.
- The chemical looping PDU design concept was 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.

Phase II:

- The PDU demonstrated operation of five parallel loops cold and four parallel at operating temperatures.
- CaO and $CaCO_3$ 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 revealed what the hot PDU behavior will be like.
- Important control strategies were tested and validated.
- The sorbent activation vent system can accurately measure flow from the sorbent reactivation reactor.

Phase III:

- It is feasible to build an approximately 3-MW_{th} 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.
- High efficiency cyclone performance 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 to a 1,000 lb/hr coal flow prototype should be feasible.
- The performance of the cold flow models has shown a good correlation to the performance of the hot PDU.
- The chemical looping concept is ready for the prototype phase.

Phase IV:

- Design and construction of the 3-MW_{th} prototype facility is in progress.

Next Steps

- Complete construction and begin prototype operation/testing/modification/development.
- Update commercial economics analysis.

Final test results will not be available until after the September 2011 project completion date.

Available Reports/Technical Papers/Presentations

General project information is available on DOE/NETL website at: http://www.netl.doe.gov/technologies/coalpower/ewr/co2/oxy-combustion/prototype.html

"Alstom's Calcium Oxide Chemical Looping Combustion Prototype Development," Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, PA, September 2010. http://www.netl.doe.gov/publications/proceedings/10/co2capture/index.html

"Chemical Looping Combustion Coal Power Technology Development Prototype," Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, PA, March 2009. http://www.netl.doe.gov/publications/proceedings/09/CO2/index.html

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.

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.

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.