Alstom Chemical Looping Technology Status

2nd International Oxyfuel Combustion Conference

John Marion
Corinne Beal, Eric Bouquet, Iqbal Abdulally, Herbert E. Andrus, Jr., Carl Edberg

Yeppoon, Queensland, Australia
12th - 16th September 2011
<table>
<thead>
<tr>
<th>Topic 1</th>
<th>CLC Concepts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Topic 2</td>
<td>MeOx CLC Development Program</td>
</tr>
<tr>
<td>Topic 3</td>
<td>Limestone CLC Development Program</td>
</tr>
<tr>
<td>Topic 4</td>
<td>Long-Term Development &amp; Demo Program</td>
</tr>
</tbody>
</table>
Chemical Looping

Q. What is Chemical Looping Combustion?

A. Oxy-Firing without Air Separation Unit (ASU)

- **Solid Oxygen Carrier Circulates** between Oxidizer and Reducer
- **Oxygen Carrier** carries Oxygen, Heat and Fuel Energy
- **Carrier picks up** O$_2$ in the Oxidizer, leaves N$_2$ behind
- **Carrier Burns** the **Fuel** in the Reducer
- **Heat** produces **Steam for Power**

- **Oxygen Carrier:**
  - Metal Oxide (MeOx): Ilmenite (FeTiO$_3$), Fe, Ni, Mn, Cu... Ores or ore Substrates
  - Limestone-based CaOx, CaS carriers

**Lowest cost option for capturing CO$_2$ from coal**
Chemical Looping
How does it work?

Types of oxygen carriers:
Ca/Metal based

Air reactor
Fuel reactor

DEPLETED AIR
950-1030°C
AMBIENT AIR (O2)

CO₂ + H₂O
850-950°C
FUEL
(E.G. COAL PARTICLES)

950-1030°C
Alstom Chemical Looping Process Attributes

- Avoids large investment costs and parasitic power associated with cryogenic air separation units (ASU’s),
- Captures CO2 at temperatures higher than the power cycle temperatures, thus eliminating the thermodynamic penalty normally associated with CO2 capture,
- Small equipment and low capital cost expected due to fast chemical reactions,
- Uses conventional material of construction and fabrication techniques,
- Largely relies on Alstom’s proven CFB technology,
- Chemical Looping offers the potential for producing electricity and/or hydrogen from coal with CO2 capture.
Alstom’s Chemical Looping Development

Targets:

• Over 90% CO₂ capture from coal
• Less than €15/ton avoided cost of CO₂ capture
• Capital cost 20% < conventional steam plant (w/o CO₂ capture)
• Applicable to retrofit and new coal-fired power plants
• Retrofit < 20% increase in COE
• Beat steam power and IGCC performance and economics, world-wide
• Medium-Btu gas or hydrogen without oxygen plant
• Economical H₂ with production cost < 2.5€/GJ
Alstom’s Chemical Looping Development

**Metal Oxide Based (MeOx)**

ECLAIR Program - EU RFCS funded

Main Features:

- Metal Based Oxygen Carriers such as Fe, Mn, Cu... ores, ilmenite (FeTiO3), or on substrates
- Process based on CFB solids transport
- Carbon stripper for minimizing UBC

**Limestone Based (CaOx)**

US-DOE funded

Main Features:

- Limestone based oxygen carrier – CaS, CaSO4
- Process based on “Fast” Bed
- Sorbent reactivation for increased limestone utilization

*Alstom is pursuing two different chemical looping technologies*
Chemical Looping Process
Focus on Investigations

- Design and Engineering
  Information for Demo Phase
- Scale-up
- Integration
- Advanced Controls concepts
- Process Type and Optimization
- Quality of Product Gases
- Solids Stability and transportation
- Reaction Kinetics
- Heat Transfer
- Flue Gas Cleaning
  • Particle Removal
  • Desulphurization
  • Mercury Removal
  • Flue Gas Drying
- Vent Gases
  Quality & Efficiency of CO2-Separation
- Transport and Sequestration

© ALSTOM 2011. All rights reserved. Information contained in this document is provided without liability for information purposes only and is subject to change without notice. No representation or warranty is given or to be implied as to the completeness of information or fitness for any particular purpose. Reproduction, use or disclosure to third parties, without express written authority, is strictly prohibited.
Alstom - Chemical Looping Process
Development Steps

REFERENCE DESIGN STUDIES

SCALE-UP

2000-2004

1996

Bench Tests
Drop-Tube/TGA

Pilot Plant
10-100 kWth

Prototype
1 & 3MWth

Demonstration
10 - 50 MWe

Commercial Scale
>100 MWe

2011

2014-2016

2017-2023

CFD MODELING, CONTROLS AND TOOL DEVELOPMENT

Reference
Design Studies

Drop-Tube/TGA

Small & Large Cold-Flow-Model

© ALSTOM 2011. All rights reserved. Information contained in this document is provided "AS IS" and is subject to change without notice. No representation or warranty is given or to be implied as to the completeness of information or fitness for any particular purpose. Reproduction, use or disclosure to third parties, without express written authority, is strictly prohibited.
Chemical Looping Reference Studies

<table>
<thead>
<tr>
<th>DATE</th>
<th>PLANT SIZE</th>
<th>STUDY</th>
</tr>
</thead>
<tbody>
<tr>
<td>2006</td>
<td>400 MWe</td>
<td>CO2 Product Gas (Alstom)</td>
</tr>
<tr>
<td>2003</td>
<td>220 MWe</td>
<td>Green House Gas (GHG) with DOE</td>
</tr>
<tr>
<td>2005</td>
<td>455 MWe</td>
<td>ENCAP</td>
</tr>
</tbody>
</table>
Alstom’s Chemical Looping processes provide the lowest potential COE measured against all of the alternatives studied to-date.
<table>
<thead>
<tr>
<th>Topic 1</th>
<th>CLC Concepts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Topic 2</td>
<td>MeOx CLC Development Program</td>
</tr>
<tr>
<td>Topic 3</td>
<td>Limestone CLC Development Program</td>
</tr>
<tr>
<td>Topic 4</td>
<td>Long Term Development &amp; Demo Program</td>
</tr>
<tr>
<td>Topic 5</td>
<td>Conclusion</td>
</tr>
</tbody>
</table>
MeOx Chemical Looping
Simplified Description

Fuel reactor/Reducer: Fuel (C\textsubscript{x}H\textsubscript{y}) + Oxidized Ilmenite (Fe\textsubscript{2}TiO\textsubscript{5}) \rightarrow CO\textsubscript{2} + FeTiO\textsubscript{3} + H\textsubscript{2}O [Endothermic, 850°C]

Air reactor/Oxidizer: Air + Ilmenite (FeTiO\textsubscript{3}) \rightarrow Fe\textsubscript{2}TiO\textsubscript{5} + O\textsubscript{2}-depleted Air [Exothermic, 950°C]

Fuel reactor/Reducer: Fuel (C\textsubscript{x}H\textsubscript{y}) + Oxidized Ilmenite (Fe\textsubscript{2}TiO\textsubscript{5}) \rightarrow CO\textsubscript{2} + FeTiO\textsubscript{3} + H\textsubscript{2}O [Endothermic, 850°C]

Air reactor/Oxidizer: Air + Ilmenite (FeTiO\textsubscript{3}) \rightarrow Fe\textsubscript{2}TiO\textsubscript{5} + O\textsubscript{2}-depleted Air [Exothermic, 950°C]
MeOx Chemical Looping for coal
Status of Development

**GRACE - EU - FP 5**
2002/03

**CLC Gaseous Fuels**
- 10 kW th testing >100 hours
- 70 MWe CLC CFB refinery gas
- CO2 avoidance <25 €/ton

**CLC Gaspower - EU - FP6**
2006/08

**CLC Gaseous Fuels**
- 10 kW th long-term testing (Chalmers)
- 120 kW th testing (Vienna)
- 70 MWe CLC CFB design (Alstom)

**ENCAP - EU - FP6**
2004/07

**CLC Solid Fuels**
- 10 kW th testing
- 455 MWe CLC CFB design

**EU - ECLAIR (RFCS)**
2008/2012

**CLC Solid Fuels**
- 100 kW th testing (Chalmers)
- 1 MW th testing (Darmstadt)
- Industrial design and product ass.

**To Step 3**

**Completed Programs 2002 - 2008**

- Key process steps have been validated independently
- Fundamental tests performed on Pilot Scale (10 - 100 kWth)
- Pilot results to confirm breakthrough potential of technology
Chemical looping - 1 MWth MeOx Prototype - Coal

- Main objectives:
  - Design and operation of a Chemical Looping Combustion (CLC) 1 MWth prototype with coal
  - Assessment of technical, environmental and economical potential of CLC power plants

- 48 months program:
  - Design of main components finalized in July 2009
  - Hot Commissioning started in October 2010
  - First tests with coal scheduled for 3Q 2011

- Budget: 6.5 M€ - Funding: RFCS: 2.27; Alstom: 2.7M€
- Partners: TU Darmstadt, Chalmers, CSIC, SINTEF, Air Liquide, Vattenfall, Alstom
ECLAIR CLC Program
Structure and Deliverables

**WP1: PROJECT MANAGEMENT -**
- **ALSTOM**
  - Administrative support
  - Technical integration

**OXIDE MATERIAL (WP2) - CHALMERS**
Develop and identify best possible oxide carrier (reaction rate, cost).

**PROCESS DEVELOPMENT (WP3) - ALSTOM**
Model and design an optimized fuel reactor for the 1 MWth prototype rig; risk mitigation activity for test phase; address CO2.

**ERECTION AND TESTING (WP4) - TU DARMSTADT**
Collect input from SP2/3 and erect a 1 MWth test rig; smaller scale test rigs (10-100kW) potentially required to iteratively optimize a) oxide materials and b) fuel reactor design details.

**PRODUCT STUDIES (WP5) - VATTENFALL**
Environmental impact study; plant study of a high-efficiency 450 MWe plant.

**MAIN TECHNICAL DELIVERABLE:**
'Prepare, design and operate a prototype test rig (1 MWth) that allows an evaluation of the economical and technical potential of CLC on solid fuels.'
MeOx Supporting Tests for Validating Design

• **100 kWth Pilot Tests**
  - Sub-bituminous coal
  - Ilmenite as oxygen carrier
  - Alternative oxygen carrier(s)

• **Cold Flow Model Tests**

• **Update concept of CLC at 450 MWe**

---

© ALSTOM 2011. All rights reserved. Information contained in this document is provided without liability for information purposes only and is subject to change without notice. No representation or warranty is given or to be implied as to the completeness of information or fitness for any particular purpose. Reproduction, use or disclosure to third parties, without express written authority, is strictly prohibited.
Status of 1MW<sub>th</sub> Prototype in Darmstadt

**Air Reactor:**
- Cold and hot commissioning completed with start up burner

**Fuel Reactor:**
- Cold and hot commissioning completed with start up burner and with coal

**Coal system:**
- Coal storage, milling and transport system commissioning completed
- Coupled reactors

MeOx CLC Program achievements to date
Near Term

- Autothermal Operation: November 2011
- Optimization Test: December 2011 - May 2012
## Agenda

<table>
<thead>
<tr>
<th>Topic 1</th>
<th>CLC Concepts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Topic 2</td>
<td>MeOx CLC Development Program</td>
</tr>
<tr>
<td><strong>Topic 3</strong></td>
<td>Limestone CLC Development Program</td>
</tr>
<tr>
<td>Topic 4</td>
<td>Long-Term Development &amp; Demo Program</td>
</tr>
<tr>
<td>Topic 5</td>
<td>Conclusion</td>
</tr>
</tbody>
</table>
Limestone Based Chemical Looping
CaS - CaSO₄ Loop in CFB Reactors

CaS - CaSO₄ Combustion Loop in CFB Reactors
Calcium-based oxygen carrier process is suited to coal
Alstom’s Limestone Chemical Looping Concept

- Coal is indirectly combusted or gasified by hot oxygen carrying reactant
- The Reactant is not consumed and is alternately reduced (oxygen removed) and oxidized (oxygen replenished) as it cycles between reactors
- The Reactant also carries heat where needed
- In Alstom’s process, calcium compounds from limestone are used as the reactant

**Main Reactions:**

**Air Reactor (Oxidizer)**

\[ \text{CaS} + 2\text{O}_2 \rightarrow \text{CaSO}_4 + \text{Heat} \]

**Fuel Reactor (Reducer)**

\[ 2\text{C} + \text{CaSO}_4 + \text{Heat} \rightarrow \text{CaS} + 2\text{CO}_2 \]

\[ 8\text{H} + \text{CaSO}_4 + \text{Heat} \rightarrow \text{CaS} + 4\text{H}_2\text{O} \]
Chemical Looping Process: Options and Applications

Applications

- CO₂ Capture – PC Retrofit
- CO₂ Capture – CFB Retrofit
- CO₂ Capture-Ready Power Plant
- Advanced Steam Cycles with CO₂ capture

- IGCC with Down-Stream CO₂ Capture
- Industrial Syngas production
- Coal-to-Liquid Fuels

- CO₂ Capture – PC Retrofit
- CO₂ Capture – CFB Retrofit
- CO₂ Capture-Ready PC/CFB Power Plant
- Advanced Steam Cycles with CO₂ capture
- IGCC with CO₂ Capture
- Fuel Cell Cycles with CO₂ Capture
- Industrial Hydrogen with CO₂

Flexible technology with low cost
CaOx Chemical Looping
Status of Development

Completed Programs 2002 - 2008

- Pilot Testing (65 kWth PDU) - successfully completed
- 4.5m Cold Flow Model testing completed - stable solids transport achieved
- 12m Cold Flow Model - Stability achieved, scale-up verified
- Alstom’s Phase IVA - 3 MWth Prototype concept development

© ALSTOM 2011. All rights reserved. Information contained in this document is provided without liability for information purposes only and is subject to change without notice. No representation or warranty is given or to be implied as to the completeness of information or fitness for any particular purpose. Reproduction, use or disclosure to third parties, without express written authority, is strictly prohibited.
Chemical looping – 3 MWth CaOx Prototype - Coal

- **Main objectives:**
  - Design, engineering, construction, commissioning and operation of a 3 MWth CaS prototype,
  - Autothermal operation of CaOx prototype,
  - Proof of concept – deliver data required to scale up to Demo and commercial size

- **50 months program**
  - Shakedown completed
  - First coal fire completed 2Q 2011
  - Autothermal operation Scheduled for 2Q 2011

- **Total budget:** 6.2 M€, cost share by US-DOE and Alstom

- **Partners:** US-DOE/NETL & Alstom
Cold Flow Model Testing Supporting Prototype

Process conditions verified under stable coupled operation with smooth solids transport
Phase IVA - Chemical Looping Prototype

Chemical Looping 3 MWt Prototype Facility
Preliminary Concept

• 1000 lb/hr coal flow
• 1st Integrated Operation
• 1st Autothermal Operation

Phase IV Objective:
Obtain the engineering and operating information required to build and operate a reliable, commercial-size demonstration plant

Prototype:
• Location – Alstom Power, Windsor, CT
• All equipment necessary for viable demo design
• Design, construction, operation by Alstom
Chemical looping reactions were achieved on June 11, 2011.

- **Point “A”** - 360 lb/hr of coal and 1900 lb/hr of air for solids transport were flowing to the reducer.
- **Point “A” to Point “B”** CO₂ concentration is about 35% vol.
- **Point “C”** - The recycle intake was switched from air to recycled product gas. The CO₂ slowly rises as N₂ is washed out of the system.
CaOx Chemical Looping
Path Forward

Near Term

• Autothermal Operation: August - September 2011
• Optimization Test: October 2011 - May 2012

Screens During Initial Hot Coupled Testing
Agenda

Topic 1  CLC Concepts
Topic 2  MeOx CLC Development Program
Topic 3  Limestone CLC Development Program
Topic 4  Long-Term Development & Demo Program
Topic 5  Conclusion
Alstom Chemical Looping
Long Term Development Program

CALENDAR YEARS (CY) & DATES

1. 10-100kWth Pilot

2. 1MWth Prototype
   - European RFCS funding

3. 10-50 MWe Demonstration

Metal Oxides

1. 65kWth Pilot

Limestone

2. 3 MWth Prototype
   - US-DOE Funding

3. 10-50 MWe Demonstration
Demonstration Project Options

- Demo unit size range of 10 to 50 MWe
- Funded demo facility in the EU countries, USA or other
- Demo plant can be either for power, industrial stream, syngas, or hydrogen generation
- Hosted by either a utility, chemical industry, oil/gas/petrochem industry
- New or retrofit application
- Pure CO$_2$ production for either sequestration or EOR
Agenda

Topic 1  CLC Concepts
Topic 2  MeOx CLC Development Program
Topic 3  Limestone CLC Development Program
Topic 4  Long-Term Development & Demo Program
Topic 5  Conclusion
Conclusion

• CLC is a break-through technology in terms of efficiency and economy, and has the potential of being the lowest cost CO2 capture option

• CLC is a flexible technology that can be configured in a new or retrofit application to produce Syngas, hydrogen or power

• ECLAIR & DOE programs are validating MeOx and CaOx Chemical Looping Combustion at 1-3 MWth prototype scale

• Next step before commercial unit will be a subsequent up-scale to 10-50 MW e
Acknowledgments

- **Funding Partners:**
  - EU-RFCS, US-DOE/NETL, Alstom

- **Key Team Members:**
  - Corinne Beal, Eric Bouquet, Herbert E. Andrus, Jr., Paul Thibeault, John Chiu, Carl Edberg, Iqbal Abdulally

- **Key Partners:**
  - TU Darmstadt, Chalmers, CSIC, SINTEF, Air Liquide, Vattenfall, Alstom

*Significant Progress Thanks to These Contributions*
Clean Power Today!™

Technology Mix
Production Efficiency
Carbon Capture & Storage