Development in Oxyfuel Combustion Technologies for Coal Fired Power Plants with CCS
(Part 3: Flue Gas Processing and CO$_2$ Processing Unit)

Stanley Santos
IEA Greenhouse Gas R&D Programme
Cheltenham, UK

Instituto de Inginieria UNAM
28$^{th}$ March 2012
Oxyfuel Perspective…

What is the best way to manage the non-CO$_2$ components to meet any CO$_2$ specification requirement and maximize some of the implicit advantages i.e. efficiency and zero emissions?
What are the impurities?

- Coming from coal
  - H$_2$O
  - PM
  - SOx
  - Hg
  - HCl, HF

- Coming from oxygen
  - O2
  - N2
  - Ar

- Coming from coal and oxygen
  - NOx
  - N$_2$O
  - CO

Other Impurities to consider...
- O2, N2, Ar, water from air ingress
- NH3 from SCR/SNCR
- Other trace elements
What are the locations to manage impurities?

- Air Separation Unit (ASU)
- Coal handling and preparation
- Boiler
- Environmental Island
- CO$_2$ Compression and Purification Unit (CO$_2$ CPU)
What are the locations to manage impurities?

<table>
<thead>
<tr>
<th></th>
<th>PM</th>
<th>H₂O</th>
<th>SOx</th>
<th>NOₓ</th>
<th>HCl</th>
<th>Hg</th>
<th>N₂</th>
<th>O₂</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASU</td>
<td></td>
<td></td>
<td>✓</td>
<td></td>
<td></td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal handling &amp; preparation</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Boiler</td>
<td></td>
<td></td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Environmental Island</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>CO₂ CPU</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

2 impurities are key for their impact on LCOE (CAPEX and OPEX): H₂O and SOx
What are the **best** locations to manage impurities?

<table>
<thead>
<tr>
<th></th>
<th>PM</th>
<th>H$_2$O</th>
<th>SOx</th>
<th>NOx</th>
<th>HCl</th>
<th>HF</th>
<th>Hg</th>
<th>N$_2$</th>
<th>Ar</th>
<th>O$_2$</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASU</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal handling &amp; preparation</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Boiler</td>
<td></td>
<td></td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Environmental Island</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>CO$_2$ CPU</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

- Environmental island functions could be significantly reduced
- CO$_2$ CPU becomes the main emission control equipment

The world leader in gases for industry, health and the environment
Flue Gas Processing Unit
Flue Gas Processing Units
(Summary of Results @ Schwarze Pumpe Pilot Plant)

• **Test on Electrostatic Precipitator (ESP)**
  - Completed and Results better than expected as compared to air firing.

• **Test on Flue Gas Desulphurisation (FGD)**
  - Different design – with external oxidation tank.
  - SO2 removal (achieved up to 99.7% removal)
  - SO3 removal (achieved ~65% reduction)
Experiences from the pilot plant
Impact on slurry chemistry

- No major differences have been encountered.
- No negative impact of higher CO₂ partial pressure on reaction system.
  - CO₂ seems to enhance the limestone/chalk dissolution
  - Degassing of dissolved CO₂ in the external reaction tank.
- Slightly lower pH during Oxyfuel operation
- Higher moisture content led to water condensation in pre-cooler during Oxyfuel conditions. Water condensation could be prevented by reduction of cooling duty to avoid local sub-cooling.

Samples taken during operation without hydrocyclone. Actual values (especially Chloride) are expected to be higher.
Experiences from the pilot plant
Impact of the operating conditions on the removal rate – Slurry flow rate

Influence of flowrate on SO2 removal efficiency

Slurry recirculation flow rate [m³/h]

100% 80% 70% 67%
Experiences from the pilot plant
Performance parameters – SO$_3$ removal rate

- Early measurements indicated low removal rate for SO$_3$ (approx. 40%)
- Probably caused of aerosol formation by “shock cooling” due to the local surface temperature (Formation H$_2$SO$_4$ aerosols from SO$_3$ → only marginally removable from flue gas)
- After modifications good removal rate could be achieved.
FGC System

- Flue Gas Condenser operates very similarly to typical flue gas condensers used in various biomass fired CHP plant in Sweden.

- Potential improvement for heat recovery has been identified by various equipment manufacturers
CO₂ Processing Unit
Overview of Development of CPU over the last 5 years...

- Recognition of the NOx and SOx reaction by Air Products (presented during GHGT Conference – June 2006)
  - This has led to the rapid technology development among the industrial gas producers.
- Identification of potential impact of Hg to the operation of the CPU.
- Development of the use of impure CO₂ as refrigerant driven mostly by reducing energy penalty.
- Work on further recovery of CO₂ in the vent of CPU.
Air Products Oxy-Fuel CO\textsubscript{2} Capture and Purification - with Air Products PRISM® Membrane

- **Boiler Steam Cycle**
- **Heat Recovery**
- **Sour Compression & AP Acid Gas Column**
  - Raw Flue Gas
  - Condensate Collection
  - Process Condensate

- **TSA Unit**
- **Mercury Removal**
- **CO\textsubscript{2} Compression**
- **Auto-Refrigerated N\textsubscript{2}, Ar, O\textsubscript{2} Removal Process**
  - Major Utilities
    - Cooling Water
    - Electric Power
  - O\textsubscript{2} and CO\textsubscript{2} Rich [To Boiler]
  - Offgas [To Atmosphere]
  - Expander

- **Product CO\textsubscript{2}**

- **Optional APCI PRISM® Membrane**

- Needs Engineering Data
- Mature Tech, Needs Data
- Commercial
NOx SO₂ Reactions in the CO₂ Compression System

- We realised that SO₂, NOx and Hg can be removed in the CO₂ compression process, in the presence of water and oxygen.
- SO₂ is converted to Sulphuric Acid, NO₂ converted to Nitric Acid:
  - NO + ½ O₂ = NO₂  (1) Slow
  - 2 NO₂ = N₂O₄  (2) Fast
  - 2 NO₂ + H₂O = HNO₂ + HNO₃  (3) Slow
  - 3 HNO₂ = HNO₃ + 2 NO + H₂O  (4) Fast
  - NO₂ + SO₂ = NO + SO₃  (5) Fast
  - SO₃ + H₂O = H₂SO₄  (6) Fast
- Rate increases with Pressure to the 3rd power
  - only feasible at elevated pressure
- No Nitric Acid is formed until all the SO₂ is converted
- Pressure, reactor design and residence times, are important.
CO₂ Compression and Purification System – Removal of SO₂, NOx and Hg

- SO₂ removal: 100%
- NOx removal: 90-99%

1.02 bar
30°C
67% CO₂
8% H₂O
25%
Inerts
SOₓ
NOₓ

30 bar to Driers
Saturated 30°C
76% CO₂
24% Inerts

BFW
15 bar
Condensate
Dilute H₂SO₄
HNO₃
Hg

Water

Dilute HNO₃

19
The effect of Pressure on SO$_2$ and NO Conversion (1 sl/min, 7 and 14 barg)


<table>
<thead>
<tr>
<th></th>
<th>14 bar g</th>
<th></th>
<th>7 bar g</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inlet (Point A)</td>
<td>After Compressor &amp; Receiver (Point C)</td>
<td>Conversion</td>
<td>Inlet (Point A)</td>
</tr>
<tr>
<td>ppm SO$_2$</td>
<td>900</td>
<td>20</td>
<td>98%</td>
<td>950</td>
</tr>
<tr>
<td>ppm NO$_x$</td>
<td>520</td>
<td>50</td>
<td>90%</td>
<td>390</td>
</tr>
</tbody>
</table>
Key Learnings from Imperial College Work

- NO oxidation rate confirmed to increase rapidly with increased pressure
- At low temperature (~ 30-50 °C), SO$_2$ oxidation to SO$_3$ / H$_2$SO$_4$ only occurs at an appreciable rate in presence of NO$_2$ and a condensed phase
- Significant conversion can occur even with very small liquid phase volumes (i.e., very low L/G ratios)
  - Speculation that condensation creates a fine mist with large interfacial surface area, and that reaction is occurring at the interface
  - Speculation that reactions are accelerated at low pH

- Recognized need to develop internal capability to explore broader range of parameters and to increase rate of data generation
DOE/NETL Cooperative Agreement: Air Products’ Sour Compression PDU

- 1st campaign Jan 2010
- 2nd campaign April-May 2010

U.S. Department of Energy's National Energy Technology Laboratory under Award Number DE-NT0005309
DOE Project: Air Products’ Sour Compression PDU – Key Results

- For the overall process, total SO₂ removal was 20-100 % (based on gas compositions).
- For the overall process, total NOx removal was 60-90 % (based on gas compositions).
- The effects of variations in the SO₂/NOx feed ratio, column pressure, gas flowrate and liquid recirculation on the reactor performance were explored. Process performance was most sensitive to SO₂/NOx feed ratio, over the range of parameter values investigated.
- SO₂ was removed from the flue gas through both sulfite and sulfate mechanisms.
Sour Compression Modelling

• Concurrent with the technology demonstration projects, lab experiments and ASPEN modelling were carried out to develop a robust reaction model.

• Goals of modelling:
  - Single reaction model to describe reactions in compression train and in column
  - Use literature reactions and kinetics wherever possible
  - Same model can be used to describe lab data and to describe pilot data from multiple configurations / scales (Renfrew, Windsor, Schwarze Pumpe)

• Modelling timeline:
  - 2005: 1st reaction model developed from literature references (no data available at this time)
  - October 2009: research program with Imperial College initiated
  - September 2010: startup of Air Products lab reactor system
  - July 2011: Final version of reaction model developed from lab data
Sour Compression Model compared to experimental data

Compression Train Configuration

Model prediction vs Lab unit results

SO2 removal, NO conversion, N removal, N2O yield, NOx conversion vs 45° line

Column Configuration
50/50 Flue Gas Mix From Before and After OxPP FGD

![Graph showing SO2 levels over time with different lines for Inlet FGCC, Inlet K432, Inlet Column, and Exit Column.](image-url)
50/50 Flue Gas Mix From Before and After OxPP FGD
Control of condensate formation during compression

- Need to control where condensate forms
- Temperature – Pressure – composition profile needs to be understood to prevent condensation, as acids will form
- First set of diaphragm compressor valves incorrectly specified with incompatible material
  - Mode of operation caused condensation, hence acid formation
  - Not all stainless steels are equal!

What happens when the incorrect valve material is selected:

And what happens when the correct valve material is selected:
Path to from Lab to Demo

160 kW$_{th}$ oxy-coal combustion unit

15 MW$_{th}$ oxy-coal pilot plant

30 MW$_{th}$ oxy-coal pilot plant

Imperial College
London

DOOSAN
Doosan Babcock Energy
Renfrew, Scotland

VATTENFALL
Schwarze Pumpe, Germany

DOE Project
Host: Alstom, Windsor, CT

1 MW$_{th}$ slip stream

0.3 MW$_{th}$ slip stream

Batch

6 kW$_{th}$ slip stream

Cylinder fed bench rig
LICONOX™ Process

Recycle to burner

To CO₂ liquefaction

CaO

H₂O

NOₓ Scrubber

N₂

NH₃

H₂O

purge

Flue gas

FGD

Oxidation

Gypsum production

Gypsum

air

H₂O
Removal of nitrogen oxides - LICONOX™
Experiments done at the Oxyfuel Pilot Plant

Aim: integration of the alkali wash DeNOx in the CO₂ plant

Advantages: ≈ low process temperature
≈ small volume flow
≈ low dust content
≈ high conversion rate
≈ simple design

pressure: 5-18 bar
temperature: 25-60°C
flow rate: 200-700 Nm³/h
pH: 4-7
NOx-concentration: 100-800 ppmv
alkali wash agent: NH₃, NaOH
LICONOX™ - Results of Experiments at the Oxyfuel Pilot Plant

**Extended Kinetic Model**
- Consideration of NO₂ yield and influence onto NO conversion
- Determination of kinetic rate constants
- Nitrite selectivity forecast
- Good correlation between measured data and kinetic model

**Scale up Jänschwalde**
- Model based determination of NO/NO₂ profile
- Selection of DeNOx position
- Performance simulation based on kinetics for Jänschwalde feed flow
- Column height and diameter determination for NOx removal
**Extension of the DeNOx by Addition of a Reduction Stage**

Regeneration/Reduction of salt-loaded solution after reaction of nitrogen oxides with ammonia-water possible

**NO oxidation within the CO₂-plant:**

\[ \text{NO} + \frac{1}{2} \text{O}_2 \rightarrow \text{NO}_2 \]

**Alkali Wash:**

\[ \text{NO} + \text{NO}_2 + 2 \text{NH}_3 + \text{H}_2\text{O} \rightarrow 2 \text{NH}_4\text{NO}_2 \]
\[ 2 \text{NO}_2 + 2 \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{NO}_2 + \text{NH}_4\text{NO}_3 \]
\[ 2 \text{NO} + \text{O}_2 + 2 \text{NaOH} \rightarrow \text{NaNO}_2 + \text{NaNO}_3 + \text{H}_2\text{O} \]
\[ 2 \text{NO}_2 + 2 \text{NaOH} \rightarrow \text{NaNO}_2 + \text{NaNO}_3 + \text{H}_2\text{O} \]

**Regeneration/Reduction:**

\[ \text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2 \text{H}_2\text{O} \text{ (nitrite-breakup > 60°C)} \]

Possible reduction of salt-loaded solution:

- nitrogen oxides - reaction with \(\text{NH}_3\) \(\Rightarrow 100\% \text{ (basis)}\)
- nitrogen oxides - reaction with \(\text{NaOH}\) \(\Rightarrow \text{ca. 46}\%\)
- nitrogen oxides - reaction with \(\text{NH}_3\) and reduction stage \(\Rightarrow \text{ca. 23}\%\)
Technology Fundamentals
Near Zero Emissions CO₂ Processing Unit (CPU)

Sulphuric Acid Method

Activated Carbon Method

Activated Carbon Method

\[
\begin{align*}
SO₂ + \frac{1}{2}O₂ & \rightarrow SO₃ \\
NO + \frac{1}{2}O₂ & \rightarrow NO₂ \\
SO₃ + H₂O & \rightarrow H₂SO₄ \\
NO + H₂SO₄ & \rightarrow H₂SO₄ NO \\
3NO₂ + H₂O & \rightarrow 2HNO₃ + NO
\end{align*}
\]
Auto-Refrigerated Inerts Removal

- Removal of impurities minimises compression and transportation costs.
- O₂ can be removed for EOR-grade CO₂
- CO₂ capture rate of 90% with CO₂ purity >95%
- CO₂ capture rate depends on raw CO₂ purity which depends on air ingress
  - Increases from zero at 25mol% to 90% at 75mol%
  - Reducing air ingress increases CO₂ capture rate
Can we improve on ~90% CO₂ Capture?

Vent stream is at pressure and is CO₂ (and O₂) rich

Flue Gas
Vent
1.1 bar
~25% CO₂
~25% O₂
~50% N₂

1. Flue Gas Expander
2. Aluminium plate/fin exchanger
3. Flue Gas Heater
4. Driers
5. CO₂ product
~96% CO₂
~4% Inerts
-60°C dp

30 bar Raw CO₂
Saturated 30°C
75-85% CO₂
Autorefrigeration Process

- J-T expansion of purified LCO₂ for refrigeration
- Raw CO₂ partially liquefied by boiling product

Compared to NH₃ refrigeration:
- Simpler process
- Lower CAPEX
- Higher CO₂ recovery
- Lower power

US Pat. 7,666,251
Air Products Oxy-Fuel CO₂ Capture and Purification – with Air Products PRISM® Membrane

- Flue Gas Expander
- Aluminium plate/fin exchanger
- To Boiler
- Driers
- 30 bar Raw CO₂
  Saturated 30°C
  75-85% CO₂

CO₂ product
~96% CO₂
~4% Inerts
-60°C dp
Use of Membrane to recover CO₂ and O₂ at the vent

Vent: 7% CO₂
93% inerts (~10% O₂)

Product: 96% CO₂
4% inerts (~0.75% O₂)
Concept 6 for the purification stage

Application for requirement of high CO₂ recovery rates
- maximum 99%

- installation of a pressure swing adsorption unit
- CO₂-rich fraction for regeneration and fed back into process before pre-compression
- CO₂-lean fraction could be fed to the ASU
Increasing of the recovery rate by PSA

Advantage:
possible: CO₂ recovery rate 99 %
energy saving in ASU

disadvantage:
higher spec. energy consumption (approx. 106%)

Air

ASU

Compression → Coldbox

95% O₂ (N₂, Ar)

Recycle

Lignite Drying → Boiler → Dust filter → Desulphurisation

Flue gas cooling

CO₂-Compression → DeNOx → Drying → cryogenic separation → Final compression → Pipeline CO₂ >100 bar → Storage

CO₂ rich

Ventgas 15-20 bar

PSA

CO₂ rich/ lean gas for regeneration of adsorber

O₂, N₂, Ar (500 ppmv CO₂) > 6.5 bar a

Linde-KCA Dresden GmbH
VPSA (Vacuum Pressure Swing Adsorption) for Recovering CO₂ from Cold Box Vent

- CO₂ –rich
  - Cold box Vent

- CO₂ –lean vent
  - CO₂ –rich recycle

- Feed
  - Cold Box
  - CO₂

Diagram shows CO₂ recovery percentage under varying air ingress percentages. The graph indicates a decrease in CO₂ recovery as air ingress increases.

Legend:
- Cold box
- Cold box + VPSA
Modern power plants are capture ready

Oxyfuel technology is ready for demonstration
Vattenfall - Janschwalde (PC -250MWe) - ??
KEPCO/KOSEP - Yongdong (PC - 100MWe)
FutureGen2 - Illinois (PC - 100MWe)
Endesa/CIUDEN - El Bierzo (CFB - 300MWe) - ???

3 Newly announced oxyfuel projects in China.
Drax Power Plant Oxyfuel in UK

By 2014-2018
Demonstration of 50–300MWe full scale power plant.

2008
World’s FIRST 30 MWt full chain demonstration at Schwarze Pumpe Pilot Plant

2007
B&W CEDF (30MWt) large scale burner testing started

2003 - 2005
Vattenfall (ENCAP ++) CS Energy / IHI Callide Project

1998 – 2001
CANMET US DOE Project / B&W / Air Liquide

1990 - 1995
EC Joule Thermie Project
- IFRF / Doosan Babcock / Int'l Combustion
- NEDO / IHI / Jcoal Project

1980’s
ANL/Battelle/EERC completed the first industrial scale pilot plant

By the end of 2010/2011,
Users (i.e. Power Plant Operators) will have 6 burner manufacturers fully demonstrating “Utility Size Large Scale Burners” which should give a high level of confidence toward demonstration

Updated by S. Santos (01/12/10)
Thank you

Website:  http://www.ieaghg.org