Oxyfuel Combustion Technologies for Coal Fired Power Plants with CCS

Current State of Development of the CO₂ Processing Unit

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Cheltenham, UK

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What is our remit?

Our Remit Covers:
- All Greenhouse Gases – Focus on CO2
- Fossil Fuels & BioCCS
- Power Sector and Major Industrial sectors
What do we do?

Our Core Activities Are:

- Assessing Mitigation Options – Focus our R&D CCS
- Tracking Capture Technology Developments/Costs
- Monitoring Geological Storage Performance
- Providing Members and Policy Audience with Independent Technical Input
CO$_2$ Processing Unit

- CO$_2$ processing unit
- SCGH
- Oxy-CFB
- Coal
- CaCO$_3$
- Steam turbine island
- Steam
- Condensates
- Particulate control
- Sulphur control
- Flue gas cooler
- CO$_2$ processing unit
- CO$_2$
- Fluidisation RFG w/o O$_2$
- Fluidisation RFG w/ O$_2$
- Overfire “air” RFG
- Air separation unit
- Air
- N$_2$
- O$_2$
- Bottom ash
- Fly ash
- Fly ash
Simplified PFD of the CPU

Flue Gas from FGC → Flue Gas Compressor → Flue Gas Pre-treatment (DeSOx and/or DeNOx) → Flue Gas Drying → Mercury Removal

CO2 to transport & storage → Product CO2 Compressor → Cold Box → CPU Vent Gas

Warm Part of the CPU

Cold Part of the CPU
Focus of Presentation

- **Flue Gas Compressor & Pretreatment**
  - Air Products
  - Linde
  - Praxair
  - Air Liquide

- **Cold Part of the CPU**
  - Fundamentals of Cryogenic Purification
  - Auto-refrigeration

- **Additional CO₂ recovery from Vent**
Overview of Development of CPU over the last 10 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.

- **Development of the use of impure CO$_2$ as refrigerant driven mostly by reducing energy penalty.**

- **Work on further recovery of CO$_2$ in the vent of CPU.**
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.
### Updated NO\textsubscript{x} - SO\textsubscript{x} Reaction Network

#### Stoichiometry

<table>
<thead>
<tr>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 NO + O\textsubscript{2} → 2 NO\textsubscript{2}</td>
</tr>
<tr>
<td>2 NO\textsubscript{2} → N\textsubscript{2}O\textsubscript{4}</td>
</tr>
<tr>
<td>N\textsubscript{2}O\textsubscript{4} + H\textsubscript{2}O → HNO\textsubscript{3} + HNO\textsubscript{2}</td>
</tr>
<tr>
<td>2 HNO\textsubscript{2} → NO + NO\textsubscript{2} + H\textsubscript{2}O</td>
</tr>
<tr>
<td>4 HNO\textsubscript{2} → 2 NO + N\textsubscript{2}O\textsubscript{4} + 2 H\textsubscript{2}O</td>
</tr>
<tr>
<td>SO\textsubscript{2} + H\textsubscript{2}O → H\textsubscript{2}SO\textsubscript{3}</td>
</tr>
<tr>
<td>2 HNO\textsubscript{2} + 2 SO\textsubscript{2} + H\textsubscript{2}O → 2 H\textsubscript{2}SO\textsubscript{4} + N\textsubscript{2}O</td>
</tr>
<tr>
<td>2 HNO\textsubscript{2} + 2 H\textsubscript{2}SO\textsubscript{3} → 2 H\textsubscript{2}SO\textsubscript{4} + N\textsubscript{2}O + H\textsubscript{2}O</td>
</tr>
<tr>
<td>2 HNO\textsubscript{2} + SO\textsubscript{2} → H\textsubscript{2}SO\textsubscript{4} + 2 NO</td>
</tr>
<tr>
<td>2 HNO\textsubscript{2} + H\textsubscript{2}SO\textsubscript{3} → H\textsubscript{2}O + H\textsubscript{2}SO\textsubscript{4} + 2 NO</td>
</tr>
<tr>
<td>2 NO\textsubscript{2} + H\textsubscript{2}O → HNO\textsubscript{3} + HNO\textsubscript{2}</td>
</tr>
</tbody>
</table>

#### Phase

- V
- L
- \(\downarrow\)

**Green** – propagates NO\textsubscript{x} redox cycle

**Red** – terminates NO\textsubscript{x} redox cycle

- NO + O\textsubscript{2} → NO\textsubscript{2} / N\textsubscript{2}O\textsubscript{4}
- HNO\textsubscript{2} + HNO\textsubscript{3}
- H\textsubscript{2}SO\textsubscript{4} + NO
- NO + NO\textsubscript{2} / N\textsubscript{2}O\textsubscript{4}

H\textsubscript{2}SO\textsubscript{4} + N\textsubscript{2}O
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

Dilute H₂SO₄
HNO₃
Hg

Water

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

BFW
Condensate

Dilute HNO₃
Path to from Lab to Demo

**160 kW_th oxy-coal combustion unit**

**30 MW_th oxy-coal pilot plant**

**DOE Project**
*Host: Alstom, Windsor, CT*

**Imperial College**
*Renfrew, Scotland*

**Doosan Babcock Energy**

**VATTENFALL**
*Schwarze Pumpe, Germany*

1 MW_th slip stream

0.3 MW_th slip stream

6 kW_th slip stream

Batch

Cylinder fed bench rig
LICONOX™ Process

Recycle to burner

CaO
H₂O

NOx Scrubber
N₂

Nitrite reduction
NH₃
H₂O

purge

Gypsum production
H₂O

Gypsum

FGD

Flue gas

air

Oxidation
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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>5-18 bar</td>
</tr>
<tr>
<td>Temperature</td>
<td>25-60°C</td>
</tr>
<tr>
<td>Flow rate</td>
<td>200-700 Nm³/h</td>
</tr>
<tr>
<td>pH</td>
<td>4-7</td>
</tr>
<tr>
<td>NOx-concentration</td>
<td>100-800 ppmv</td>
</tr>
<tr>
<td>Alkali wash agent</td>
<td>NH₃, NaOH</td>
</tr>
</tbody>
</table>

Linde-KCA Dresden GmbH

2nd Oxyfuel Combustion Conference, Yeppoon, AUS/15th September 2011
LICONOX™ - Results of Experiments at the Oyxfuel 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:**

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

possible reduction of salt-loaded solution:

- nitrogen oxides - reaction with NH₃
- nitrogen oxides - reaction with NaOH
- nitrogen oxides - reaction with NH₃ and reduction stage

⇒ 100% (basis)
⇒ ca. 46%
⇒ ca. 23%
Technology Fundamentals
Near Zero Emissions CO₂ Processing Unit (CPU)

Sulphuric Acid Method

Activated Carbon Method

$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$
$NO + \frac{1}{2}O_2 \rightarrow NO_2$
$NO_3 + H_2O \rightarrow HNO_3 + NO$
$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$
Low Pressure SO\textsubscript{2} Removal by NO\textsubscript{x}

**Second strategy for the 2\textsuperscript{nd} generation of CPUs:** use NO\textsubscript{2} directly (or indirectly as HNO2/HNO3/NO2-/NO3-/N2O4/…) as reagent for SO\textsubscript{2} removal at low pressure

NO\textsubscript{2} (pure or diluted) can be recovered from compressor coolers condensates, HP scrubbing, adsorber regeneration gas and/or distillation

Overall chemical reaction:

\[ \text{NO}_2 + \text{SO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{SO}_4 + \text{NO} \]
Process design: numerous options

- **Basic Process:**
  - Single flash, Single Column,
  - Dual flash, Flash-Column, Dual Columns
  - Triple flash, 2Flashes+Column, Flash+2Columns, Triple Column

- **External cooling or autorefrigerated cycle**

- **With/without Recycle of ventgas**

- **Expansion of HP-ventgas:**
  - inside/outside of coldbox
  - generator-expander or booster-expander
**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**
Fundamentals – Separation & Recovery of CO2
Impact of Operating Pressure to CO₂ Purity

Data adapted from EOn Engineering, Air Products, Air Liquide, Linde
Recovery Rate & Pressure

Data adapted from EOn Engineering, Air Products, Air Liquide, Linde
Recovery Rate & Feed Composition

Data adapted from Air Liquide
Recovery Rate, % CO₂ in Vent & Vapour Liquid Equilibria
(Data from TUHH)
Recovery Rate & Feed Composition
(Data from Air Products)

@ T = -55°C & P = 30 Bar

%CO₂ in the Feed (z_{CO₂})

%CO₂ in the Vent (y_{CO₂})

No Liquid Product
"Zero Recovery Rate"
Basic Scheme for Flash-Flash Arrangement (Auto-Refrigeration Cycle)

Data from Linde
Basic Scheme for Flash-Distillation Arrangement (Auto-Refrigeration Cycle)
Data from Linde

White et al (Air Products)  Shah et al (Praxair)
Recovery Rate vs Product CO2 Purity (Auto-Refrigeration Cycle) Data from Linde

**Flash-Flash Arrangement**

**Flash-Distillation Column Arrangement**
Capture Rate: Greater than 98% CO₂...
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)
Increasing of the recovery rate by PSA

Air → ASU → Compression → Coldbox → N₂, Ar

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

Disadvantage:
- higher spec. energy consumption (approx. 106%)

Recycle

Lignite Drying → Boiler → Dust filter → Desulphurisation → Reworking

CO₂ Compression → DeNOx → Drying → cryogenic separation → Final compression → Pipeline → Storage

CO₂ (90 % CO₂ (N₂, O₂, Ar) atm, p) → CO₂-plant → CO₂ rich

Storage

CO₂ rich/lean gas for regeneration of adsorber

O₂, N₂, Ar (500 ppmv CO₂) > 6.5 bar a
VPSA (Vacuum Pressure Swing Adsorption) for Recovering CO\textsubscript{2} from Cold Box Vent

![Diagram showing CO\textsubscript{2} recovery from Cold Box Vent with VPSA]

- CO\textsubscript{2} –rich recycle
- CO\textsubscript{2} –lean vent
- Cold box
- Feed
- CO\textsubscript{2}
- Cold box Vent
- VPSA

Graph:
- CO\textsubscript{2} Recovery, %
- Air Ingress, %
- Cold box + VPSA
- Cold box

Graph data:
- 0% CO\textsubscript{2} Recovery at 0% Air Ingress
- 100% CO\textsubscript{2} Recovery at 12% Air Ingress

Feed to Cold Box, VPSA, CO\textsubscript{2} –rich recycle, CO\textsubscript{2} –lean vent.
What’s the future landscape of Oxyfuel R&D for CO₂ Processing Unit

• **Specification of CO₂ is crucial to the engineering and design of the CPU**
• **We need large scale demonstration** – to validate the key results obtained from various pilot plant experience.
  • Selection of process configurations have several options
• **Further recovery of CO₂ from the vent will make oxyfuel more competitive if high recovery of CO₂ is required!**
• **Also for future R&D will require focus on:**
  • Flexibility of the CPU - this hinged on the CO₂ compressors and pumps performance.
  • Development of process controls
  • Integration with the boiler island and the CPU.
Oxyfuel Combustion with CCS is not only for Power Generation…

Cement Industry

Oil Refining Industry

H2 Production

Steel Industry

Helium recovery from natural CO2 source
Thank You

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