Overview to ANLEC R&D support of the Callide Oxyfuel Project (COP)

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Overview

• What is ANLEC R&D?
• Research Program
• Oxyfuel related projects
• Callide Field Campaigns
• Key findings
ANLEC R&D
Australian National Low Emission Coal Research & Development

- Combined Federal Government Funding & Australian Coal Association
- Addresses:
  - The near term risk reduction and technology developments necessary for successful demonstration of LECT in Australia.
  - The delivery of skills, data and knowledge to assist key stakeholders understand the benefits and deployment risks of LECT's.
  - Support for, and investigation of, issues affecting the performance of the early demonstration projects.
Research Program to date

- Alternatives and Fundamentals
  - Step change in risk/cost reduction

- LECT Demonstration Support
  - Applied research associated with demo’s
  - Fundamental
  - Onsite testing
Oxyfuel related projects

- Alternatives and Fundamentals
  - OxyCFB scoping study
  - Membrane O2 separation
  - Adsorption based O2 separation
  - Chemical Looping O2 production

- Callide Oxyfuel Project Demonstration Support detailed here, including University of Newcastle and Macquarie University
  - Gas Quality Impacts I  SOx/NOx/Hg fundamentals
  - Gas Quality Impacts II  Fabric Filter + CPU liquids
  - Gas Quality Impacts III  Residual Hg in CPU (ongoing)
  - Trace Impurity Impacts  Hg/Ar/Se
The Callide Oxyfuel Project Retrofit

Courtesy of Yamada, IHI
APP Oxyfuel Course 2010

No deSOx / deNOx / de-Hg
All impurities sent to CPU

64-74% Hg captured in fly ash
~70% Hg$^{2+}$ in flue gas
To CPU
ANLECR&D Research areas at COP to reduce cost and risk

Fabric Filter (not ESP) \[→\] NaOH Polishing (not FGD) \[→\] Compression (no AC bed)

- SO3 formation \[→\] acid dew point corrosion + temperature
- Hg capture \[→\] affected by oxy-conditions or carried to CPU

- SO2 capture \[→\] pH and NaOH usage in high CO2
  \[→\] SO2/NOx reactions (N2O) in CPU
- Removal of Hg$^{2+}$?

- NOx capture in CPU \[→\] kinetic reaction to NO2 or emitted as NO
  \[→\] stability of condensates
- Hg capture in CPU \[→\] dependant on NOx
  \[→\] product identification and stability
  \[→\] risk to brazed Al-HEX cold box
Fabric Filter Field Campaign June 2014

- Focussed on SO3 + Hg
- Measurements during mode transitions
- More details given in other presentation and soon to be published
Fabric Filter Trial Outcomes

• SO3 levels below detection limit in transitions
• SO3 level 0.6 - 3.7ppm in steady state oxy-mode
• Hg affected by burner configuration

<table>
<thead>
<tr>
<th></th>
<th>AIR</th>
<th>OXY</th>
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<tbody>
<tr>
<td></td>
<td>Low NOx</td>
<td>Original</td>
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<tr>
<td>Hg_{Total gas}</td>
<td>0.07</td>
<td>0.53</td>
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<tr>
<td>µg/m^3</td>
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<tr>
<td>Hg^{2+}</td>
<td>0%</td>
<td>77%</td>
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<tr>
<td>Hg_{Total gas}</td>
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<td>0.45</td>
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<tr>
<td>µg/m^3 Corrected to 12%CO₂</td>
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* Highest point in transition corresponding to higher O2
Sampling locations at COP

CPU Trial 1
Gas
Slipstream to piston compressor

LOW SOx Slip stream

CPU Trial 2
Condensates re-emissions

HIGH SOx Slip stream
Bench Compressor Trial with COP Gas Slipstream September 2013

- Used real flue gas and piston compressor
- Focus on NOx and Hg removal by varying pressure
- Some SOx included
- Presented at OCC3 and now published
Gas Slipstream Compression Outcomes

- High capture rates with higher pressure (to 30bar)
- ~100% SOx ~80% NOx ~100% Hg
- NOx capture limited by kinetics + residence time
- Hg capture limited by amount of NO2
- Similar trends to laboratory measurements

![Graph showing NOx/SOx during compression, ppm against Pressure, bar.](image1)

![Graph showing Hg Captured % against Pressure, bar.](image2)
CPU Condensates Trial June 2014

- Focus on stability of compression condensates
-Measured re-emission of NOx and Hg after depressurising
-Long measurements (~8-12 hours)
-Specifically developed methodology
-Details given in other presentation and just published

![Graph showing NO and NO2 concentrations over time](image-url)
CPU Condensates Outcomes

- "Volatility" of condensates is time dependant (days)
- Captured Hg in liquids stable in steady state
- NOx re-emission measured as "NO2" most likely HNO2
- Similar trends to lab results

![Graph of Volatile NOx](image1)

![Graph of Volatile Hg](image2)
Hg “Hideout Study” and emission reduction from condensates (ongoing)

- Recovery methods for Hg species that are
  - Partially recoverable at 200°C
  - Partially soluble in 16M HNO3 / 8M HCl / 90°C
- Laboratory & COP internal surface analysis of CPU piping
- Investigate methods of emission reduction from condensates
Trace Impurities Trial December 2012

- Comprehensive sample program (4 weeks)
- Coal, Ash, Stack, CPU entry & Exit
- Based on standard methodologies
- Four Coal feeds (2 coals, 2 blends)
- Mercury (sorbent traps + continuous)
- Trace Metals (As, B, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, Se, Zn)
- Halide (HBr, HCl, Br, Cl, F)
- Particulates
- Presented at OCC3 Spain
Trace Impurity Outcomes

- Halides and Metals – variations in stack gas influenced by coal type and firing conditions (air or oxy)
- Significant removal in low pressure caustic scrubber (before CPU entry)
- Mercury “Steady State” Story
  - STACK
    - Higher concentration at stack in oxy-mode
    - similar to air-firing when corrected for CO2 (ie to 12%)
    - Higher amounts of Hg$^{2+}$ in oxy-firing
    - Less Hg fly ash capture due to lower UBC
  - CPU
    - Hg$^{2+}$ removed in caustic polishing before compression
    - Hg$^0$ insoluble and carried through to CPU
    - Removed in compression by NOx
    - Final CO2 product contains < 2ng/m$^3$
Key Findings

• Impurity control in CPU feasibility has been established
  – SOx removed by caustic polishing or compression
  – Halides / Trace Metals removed by caustic polishing
  – NOx / Hg removal linked + kinetically limited needs compression ($\Delta P$, $\Delta t$)

• Potential CPU emission points have been identified
  – Degassing compression condensates (HNO2)
  – Molecular Sieve regeneration (HNO3)
  – Both emission points easily recycled
Publications


- Ting, T., R. Stanger, and T. Wall, *Laboratory investigation of high pressure NO oxidation to NO2 and capture with liquid and gaseous water under oxy-fuel CO2 compression conditions*. International Journal of Greenhouse Gas Control, 18(0) 2013

Thanks for Listening

further questions?

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Further Research Needs

• Hg-NOx product identification
  • Different sections of compression
  • Higher temperature (<200°C directly after $\Delta P$, dry)
  • After cooling+ water condensation

• SO2-NOx combined capture in compression
  • Optimised
  • Formation of N2O minimised or accounted for

• CPU liquid product recovery