Field measurements of NOx and mercury emissions from compression condensates at the Callide Oxyfuel Project

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The Callide Oxyfuel Project Retrofit

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

Courtesy of Yamada, IHI
APP Oxyfuel Course 2010
Oxyfuel research at UoN

• Part of Callide Oxyfuel Project Feasibility Study 2005-6
• Coal reactivity 2007-9
• Sulfur impacts 2009-11
  – Review, SO3 formation, catalytic impacts, ADP
• NOx in compression 2012-15
  – Effect of pressure residence time, capture in H2O
  – Laboratory compression system, mass balancing
• Hg in compression 2012-15
  – Impact of NOx + ∆P + ∆t
  – Mass balancing → Recovery methods
• Emissions from condensates (depressurised)
BACKGROUND - Liquid Sampling of Condensates
(from bench compressor)
presented at OCC3 SPAIN & published in IJGHGC

![Diagram of liquid sampling process]

- From 2nd or 3rd stage
- Condenser
- Gas / Liquid Separator
- Pressure Control
- Gas to 3rd stage or exit
- Needle valve

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

\[ \text{HNO}_2 + \text{HNO}_3 \]

\[ \text{HNO}_2(aq) \quad \text{HNO}_3^- \quad \text{stable ion gas} \]

\[ \text{H}_2\text{O} + \quad \text{"stable species"} \]

To gas analysers Air + "volatiles"
BACKGROUND - “Volatile” NOx and Hg measured from liquid condensates on depressurisation

\[
\text{NO}_2 / \text{NO} / \text{HNO}_2 \text{ (aq)} \rightarrow \text{NO}_x \text{ (G)} \quad \text{Hg}^0 \text{ (aq)} \rightarrow \text{Hg}^0 \text{ (G)}
\]

Slow process occurs over hours

3-10% of NOx in liquid volatile

< 1% of Hg in liquid volatile
Sampling locations at COP

CPU Trial 1
Gas
Slipstream to piston compressor

LOW SOx Slip stream

HIGH SOx Slip stream

CPU Trial 2
Condensates re-emissions
Preliminary Liquid Sampling on HP Scrubber

Depressurised sampling

Pressurised sampling
Callide Volatile Condensates – Preliminary Pressurised Sampling

Degassing Aftercooler Condensate sample 24bar
~0.37g/L NO3-

Residence time impact

Degassed immediately after sampling
Volatile NOx = 5.0%

Degassed ~ 6.5 hours after sampling
Volatile NOx = 1.7%
Experimental - Sampling

- Clear vessel to control liquid volume
- Pressure resistance
- 5LPM air as sweep gas
- 40m of PFA sampling tube
- Gas Analysers
  - NOx + Hg + CO2
- Long measurements
  - 8-12 hours
NOx emissions from degassing compression condensates

Intercooler
4 bar

Aftercooler
22 bar
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

![Graphs showing volatile NOx and Hg levels over sampling days from start-up.](image-url)
Conditions to favour “stable” condensates

Volatile of NOx species in liquids inversely proportional to concentration of NO3-

Higher pressure + NO2 needed for stable liquids

![Graph showing the relationship between volatile NOx and stable NO3- in liquid](image1)

![Graph showing the relationship between NO2 concentration and stable NO3- in liquid](image2)
Hg interaction with NOx in sampling lines

22bar condensate + shaking vessel for ↑ desorption

PFA Sampling lines used

Suggests highly reactive NOx (HNO2) + downstream issues

+ve peaks in Hg correspond with NOx peaks

-ve peaks in Hg correspond with NOx peaks

Hg rises with lower NOx + Hg0 check (only Hg2+)

Hg Concentration, ng/Nm³

NOx Concentration, ppm

Time
Meanwhile back in the lab...

UoN + Macquarie University (Prof Peter Nelson) study
Combined pressurised NOx with FTIR
Understanding the NOx balance in simplified conditions at 25 bar

**Diagram Flow**

- **Gas/liquid contact**
  - NO (g) → 6% NOx (g) (not captured)
  - 6% HNO₃ * (deposited)
  - 88% NOx (l)

- **Depressurise**
  - 9% NOx (g) as HONO*
    - 23% NO
    - 77% NO₂
  - 91% NOx (l)

- **Remarks**
  - Formed in downstream areas of wet gas but no liquid H₂O
  - Identified in molecular sieves
  - Contacted for ~1.5 hours

* Identified by FTIR
Quantified by NOx Analyser
Implications

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

• Stability of liquids enhanced by higher pressure, NO2 and liquid residence time
Publications


- Stanger, R., T Ting, T Wall, High pressure conversion of NOx and Hg and their capture as aqueous condensates in a laboratory piston-compressor simulating oxyfuel CO2 compression, International Journal of Greenhouse Gas Control 29, 2014


- 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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N2O Production with mixed SOx /NOx Capture at 5 bar

N2O ~ 11% NOx feed  N2O ~ 310 x CO2
at 25 bar N2O peak +5000ppm!

2 SLPM, 1000ppm SO2, 1000ppm NO, 5% O2, N2 bal
Overview

• Current work at UoN
• Experimental
• Results
• Key Findings
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
Research Needs in the COP CPU

• Australian context
  – Low Coal sulfur, no deSOx
  – Low Hg + Fabric Filter, no AC guard bed
  – No SCR/nSCR

• For a Australian retrofit
  – Caustic polishing at low pressure
  – CPU to passively remove NOx + Hg as condensates
  – Cold Box to remove remaining NOx from product CO2 and recycle
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.

• Program overall funding……across 2012 to 2020  ASK NOEL
ANLECR&D Research areas at COP to reduce cost and risk

Fabric Filter (not ESP) \(\Rightarrow\) NaOH Polishing (not FGD) \(\Rightarrow\) Compression (no AC bed)

- SO3 formation \(\Rightarrow\) acid dew point corrosion + temperature
- Hg capture \(\Rightarrow\) affected by oxy-conditions or carried to CPU

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

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

- Focused 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

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<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><strong>Hg^{Total gas} μg/m^3</strong></td>
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<td>Hg^{2+}</td>
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<td><strong>Hg^{Total gas} μg/m^3 Corrected to 12%CO_2</strong></td>
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<td>Hg^{Total gas} μg/m^3 Corrected to 12%CO_2</td>
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<td>0.45</td>
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* Highest point in transition corresponding to higher O2
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
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