Challenges in Understanding the Fate of Mercury during Oxyfuel Combustion

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MEC7 Workshop
DLCS, Strathclyde University
18th June 2010
IEA Greenhouse Gas R&D Programme

- A collaborative research programme founded in 1991
- We are the sister organisation of IEA Clean Coal Centre
- Aim: Provide members with definitive information on the role that technology can play in reducing greenhouse gas emissions.
- Producing information that is:
  - Objective, trustworthy, independent
  - Policy relevant but NOT policy prescriptive
  - Reviewed by external Expert Reviewers
  - Subject to review of policy implications by Members
- Funding approx 3 million €/year
Contracting Parties and Sponsors
Acknowledgement

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Special Workshop on Oxyfuel Combustion

SO$_2$/SO$_3$/Hg/Corrossion Issues in Oxyfuel Combustion Boiler

London, UK
25$^{th}$ – 26$^{th}$ January 2011

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Area of Discussions:

1) Fundamental Experimental work on SO$_2$/SO$_3$/Hg emission from oxyfuel combustion boiler
2) SO$_2$/SO$_3$/Hg/Cl measurement techniques under oxyfuel combustion conditions
3) Impact of Sulphur species to the Flue Gas Processing Units (ESP/FF, FGD, Direct Contact Cooler, Wet Scrubbers)
4) Boiler Corrosion issue – under oxyfuel combustion conditions
5) Modelling work on SO$_2$/SO$_3$/Hg from oxyfuel boilers
6) Experience from large scale demonstration/pilot plant projects
Presentation Outline

• **Objective of this Presentation**
• **Brief Introduction**
  • Oxyfuel combustion of power plant with CO$_2$ capture
  • Why we need to understand the fate of Hg during combustion?
• **Review of Literature – Where are we in our understanding of fate of Hg during oxyfuel combustion.**
• **Where are the challenges.**
Objectives of this Presentation

- **To provide awareness the impact / risk of ignoring Hg in any Oxy-Coal Combustion Power Plant with CO\textsubscript{2} Capture Power Plant**

- **To initiate discussion on the issue of Mercury in Oxy-Coal Combustion Power Plant with CO\textsubscript{2} Capture**

- **To initiate a review on the different factors to reconsider on the design of coal power plant in the perspective of Hg.**
Oxy-PC Combustion Fired Power Plants with CO$_2$ Capture
Oxy-Coal Combustion Power Plant with CCS...
Where Can You Extract the Recycled Flue Gas (RFG) (For Practical application using low S coal)
Updated by S. Santos (17/06/2010)
Today... There are 3 Major Full Scale PC Burner Testing Facilities Worldwide Retrofitted for Oxyfuel

- Babcock and Wilcox (B&W) 30MWth CEDF
  - Barberton, Ohio, USA
  - Wall Fired Burner Development

- Doosan Babcock – 40MWth in 90MWth MBTF
  - Renfrew, Scotland, UK
  - Wall Fired Burner Development

- Alstom Power Plant Lab. – 15MWth in 30MWth BSF
  - Windsor, Connecticut, USA
  - Start of Operation: Nov. 2009
  - T-Fired Burner Development

Courtesy of Alstom, B&W and Doosan Babcock
The Oxyfuel pilot plant
Why it is important to understand the fate of mercury during Oxyfuel Combustion?

Why Mercury is an operational issue to Oxyfuel Combustion Power Plant?

Case 1: Moomba Gas Plant
Case 2: Skikda Gas Processing Plant
Case 1: Moomba Gas Plant Accident caused by Mercury

- **Moomba Gas Processing Plant**, owned by Santos, is the main supplier of natural gas to South Australia and New South Wales
  - Liquids separated from raw natural gas via 2 trains of LRP (Liquids Recovery Plant)
  - Liquids (condensate and LPG) sent to Port Bonython for export (about 650Km south of Moomba)
- **A New Year BANG! About 02.43 in the morning, 1st January 2004 – an explosion & fire occurred at Train A of the LRP section.**
  - The fire incident also damaged Train B.
- **Effect: liquids production interrupted for 8 months**
Failure Location

- Failure occurred at the base (6 o’clock) of the gas nozzle
- Evidence of de-lamination consistent with Liquid Metal Embrittlement (LME) caused by mercury in contact with aluminium
Case 2: Skikda Gas Processing Plant Accident

- **Skikda Gas Processing Plant is owned by Sonatrach in Algeria.**
- **About 18.40 on 19th January 2004 (just about 3 weeks after Moomba Gas Processing incident), an explosion occurred in Train “40”**.
- **Consequence:**
  - 3 out of the 6 NG liquefaction trains were destroyed and 2, which were not operating at the time, were damaged. The administration building and the maintenance workshop, and other buildings, were completely destroyed.
  - Sadly, 27 person killed and 80 people injured.
  - Adjacent oil refinery and power plant were shut down due to the blast for at least a month.
Skikda Gas Processing Accident
Incident Report

• The Report concludes that the explosion was the consequence of a catastrophic failure in one of the cold boxes of Unit “40”, which led to a vapour cloud explosion of either LNG or refrigerant. The most probable source of ignition was the boiler at the north end of Unit “40”.

• Although (unlike the Moomba Gas Plant incident) – the report noted that it is not absolutely proven if Liquid Metal Embrittlement is the main cause of the failure – nonetheless, it was accepted that this was the most likely probable cause of the failure.

• Train “40” is the only NG Liquefaction train that doesn’t have mercury removal system!
Discussion Points
CO₂ Compression and Purification System – Inerts removal and compression to 110 bar

Flue Gas Vent
1.1 bar
20°C
25% CO₂
75% inerts

Flue Gas Expander

Aluminium plate/fin exchanger

Flue Gas Heater

Driers

30 bar Raw CO₂
Saturated 30°C
76% CO₂ 24% Inerts

CO₂ product
110 bar
96% CO₂
4% Inerts
-60°C dp
Statement of Fact:

• For oxyfuel combustion – Mercury is not an environmental issue alone but also an operational issue particularly to the CO$_2$ processing unit.

• The issue of Mercury to oxyfuel combustion is not about concentration – but it is about where Mercury could accumulate within the CO$_2$ processing unit!
Discussion Points
(Oxyfuel Boiler)

Where we are in the understanding of:
- NOx Chemistry during combustion
- SO2/SO3/Dew Point
- Chlorine issue (Halogen issue)
- Carbon in Ash
- Brief review of some results presented regarding Hg under oxyfuel condition
## Coal Combustion under CO₂ Atmosphere

<table>
<thead>
<tr>
<th>Item</th>
<th>Combustion with air</th>
<th>Combustion with oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Windbox</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>21%</td>
<td>21~30%</td>
</tr>
<tr>
<td>N₂</td>
<td>79%</td>
<td>(0)~10%</td>
</tr>
<tr>
<td>CO₂</td>
<td>0%</td>
<td>40~50%</td>
</tr>
<tr>
<td>H₂O</td>
<td>Small</td>
<td>10~20%</td>
</tr>
<tr>
<td>Others</td>
<td>—</td>
<td>NOx, SO₂...</td>
</tr>
<tr>
<td><strong>Flue gas</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>3~4%</td>
<td>3~4%</td>
</tr>
<tr>
<td>N₂</td>
<td>70~75%</td>
<td>(0)~10%</td>
</tr>
<tr>
<td>CO₂</td>
<td>12~14%</td>
<td>60~70%</td>
</tr>
<tr>
<td>H₂O</td>
<td>10~15%</td>
<td>20~25%</td>
</tr>
<tr>
<td>Others</td>
<td>NOx, SO₂...</td>
<td>NOx, SO₂...</td>
</tr>
</tbody>
</table>

(Wet % base)
NOx Emissions

- We have quite a good confidence in knowing the trend of these emissions
NOx Results from IFRF study (APG4)
SO$_2$ Emissions

- Highly dependent on how sulphur is captured in ash...

- *without the removal of SO$_2$ in the secondary RFG*, it should noted that about ~30% reduction could be achieved (on mass per unit energy input basis – especially for bituminous coal)
SO\textsubscript{2} Emissions
(Results from IFRF)
SO$_3$ Emissions

(Results from ANL-EERC, IVD Stuttgart, Callide/IHI Aiolo)
Correlation of SO₃-Moisture and Acid Dew Point
(Result from Stuttgart University – IFK)
SO₂ captured along the convective part (down to 450°C) by different inlet concentrations

<table>
<thead>
<tr>
<th>Coal Type</th>
<th>Iron Content in the Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>“KK”</td>
<td>~2-3%</td>
</tr>
<tr>
<td>“EN”</td>
<td>~17-18%</td>
</tr>
<tr>
<td>“LA”</td>
<td>~22-23%</td>
</tr>
<tr>
<td>“RH”</td>
<td>~16-17%</td>
</tr>
</tbody>
</table>

### Coal Type and Ash Composition

<table>
<thead>
<tr>
<th>Coal Type</th>
<th>Ash [wt, mass%]</th>
<th>CaO [wt, mass%]</th>
<th>Ca/S molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Klein Kopje (KK)</td>
<td>19.29</td>
<td>7.8</td>
<td>2.98</td>
</tr>
<tr>
<td>Ensdorf (EN)</td>
<td>7.29</td>
<td>10.50</td>
<td>1.03</td>
</tr>
<tr>
<td>Lausitz (EN)</td>
<td>4.79</td>
<td>23.78</td>
<td>3.17</td>
</tr>
<tr>
<td>Rhenish (RH)</td>
<td>4.07</td>
<td>35.10</td>
<td>3.96</td>
</tr>
</tbody>
</table>
Chlorine / Bromine Chemistry

- This could be a big challenge to Oxyfuel Combustion because we hardly know anything about it under oxyfuel combustion condition.

- But ... What we currently know shows the possible impact of Chlorine and Sulphur to boiler corrosion.
CORROSION - Low-S/Low-Cl

Temperature (°C)

95%ile Parabolic Rate (cm²/s)

El Cerrejon Oxy-Fuel

- T22
- T91
- E1250
- TP347HFG
- HR3C
- San25
- IN740
CORROSION - High-S/High-Cl

Thoresby Oxy-Fuel

Temperature (°C)

95\%ile Parabolic Rate (cm²/s⁻¹)

- T22
- T91
- E1250
- TP347HFG
- HR3C
- San25
- IN740
Addition of Calcium Chloride or Calcium Bromide to enhance oxidation of Hg may probably be a none starter under oxyfuel combustion conditions!!!

I could be a “villain” to a lot of commercial interests to this type of Hg reduction control technology!

But will the addition of other Calcium/Magnesium compounds enhance Hg removal???
Carbon in Ash

- This could be dependent to the burner design and combustion regime.

- It is expected that a lower Carbon in Ash during oxyfuel combustion conditions
Would the capture of SO$_2$ / SO$_3$ in the ash enhanced by lower carbon in ash?

Marrier and Dibbs (1974) Thermochimica Act (Vol. 8)
Review of Literature

- Assessing all the published worked relevant to Mercury and oxyfuel combustion

- Aim: My attempt to establish what we know...
Mercury

Speciation

• Hg measured by on-line analyzer
• Hg data taken when firing lignite
• Hg in flue gas (air firing) was $\approx 13.5 \mu g/m^3$
• Hg concentration in flue gas increase in oxy mode corresponded to removal of $N_2$.
• Oxidized (ionic) Hg increased from 25% to 30%
  ➢ Increases removal (less elemental Hg)
• Oxidized Hg removed in WFGD

CONCLUSIONS:

1. Hg oxidation may improve with oxycombustion
2. Hg removal is expected to be the same as for air firing
Experimental Results from Guo et. al. (2009)

Thermal Degradation of 3 Chinese Coal

Fig. 1. The RRT and VY of JC anthracite under N₂, CO₂, and air atmospheres.

Fig. 2. The RRT and VY of DT bituminous coal under N₂, CO₂, and air atmospheres.

Fig. 3. The RRT and VY of HLH lignite under N₂, CO₂, and air atmospheres.
Suriyawong et. al. (2005)

Mercury Concentration in the Combustor

- Total mercury
- Oxidized mercury
- Elemental mercury

Mercury concentration (ng/m³)

Air (79% N₂ + 21% O₂)  75% CO₂ + 25% O₂  80% CO₂ + 20% O₂
List of Literature


List of Literature


Discussion Points
(CO$_2$ Processing Unit)
CO₂ Compression and Purification System – Inerts removal and compression to 110 bar

- Flue Gas Vent
  1.1 bar
  20°C
  25% CO₂
  75% inerts

- Flue Gas Expander

- Flue Gas Heater
  Aluminium plate/fin exchanger
  -55°C

- Driers
  CO₂ product
  110 bar
  96% CO₂
  4% Inerts
  -60°C dp

- 30 bar Raw CO₂
  Saturated 30°C
  76% CO₂ 24% Inerts
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:
  - \( \text{NO} + \frac{1}{2} \text{O}_2 = \text{NO}_2 \) (1) Slow
  - \( 2 \text{NO}_2 = \text{N}_2\text{O}_4 \) (2) Fast
  - \( 2 \text{NO}_2 + \text{H}_2\text{O} = \text{HNO}_2 + \text{HNO}_3 \) (3) Slow
  - \( 3 \text{HNO}_2 = \text{HNO}_3 + 2 \text{NO} + \text{H}_2\text{O} \) (4) Fast
  - \( \text{NO}_2 + \text{SO}_2 = \text{NO} + \text{SO}_3 \) (5) Fast
  - \( \text{SO}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 \) (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

30 bar cw

Water

Dilute HNO₃

cw
Mercury behaviour and distribution in the process

We need to understand: how much mercury exists, in what form, and at which locations in the process. A guard bed downstream of the dryers will remove elemental Hg to prevent attack on the Aluminium heat exchangers.
NG Industry Practice

- Activated Carbon bed is generally employed. This is expected to be applied to oxy-combustion oxy-PC as well.
- It is important to be aware with regard to short term performance drop of the activated carbon bed during shut down or process upset.
- Competing reaction of Hg and Sulphur species
**CO₂ Compression and Purification System – Inerts removal and compression to 110 bar**

- **Flue Gas Vent**
  - 1.1 bar
  - 20°C
  - 25% CO₂
  - 75% Inerts

- **Flue Gas Expander**
  - Saturated 30°C
  - 76% CO₂ 24% Inerts

- **Flue Gas Heater**
  - -55°C

- **Aluminium plate/fin exchanger**
  - -60°C dp

- **Driers**
  - 30 bar Raw CO₂

- **CO₂ product**
  - 110 bar
  - 96% CO₂
  - 4% Inerts
  - -60°C dp
What is the Feasibility and Effectiveness of Cold Trapping of Hg as final polishing process? (Figure from US Patent 4982050)

- Hg is heavier than the gas at temperature colder than $-10^\circ$C (solid at $-40^\circ$C)
Summary and Conclusions

• For any oxy-combustion process, the removal of mercury from the CO$_2$ rich flue gas is a necessary to protect key components in the CO$_2$ clean up and processing unit.

• Damage cause by Mercury to any aluminium based equipment is a Random Event!!!
Understanding Failure Mechanisms

- **Statement from ALPEMA:**
  In general, mercury will not react with aluminium unless it is allowed to exist in contact with the heat exchanger in its liquid state and there is water present. If these conditions exist within a heat exchanger, then mercury contamination can result in problems. This attack is most severe when coupled with another corrosion process.

- **Currently, the common practice of NG Processing means reducing the mercury to less than 0.01 μg/Nm3.**

- **QUESTION: Is the 0.01 μg/Nm³ to be used as well in the oxy-coal combustion power plant?**
Summary and Conclusions

• What is the speciation of Hg in an oxy-coal combustion cases?
  • Together with this challenge is how we measure the speciation under oxyfuel combustion condition?

• How we deal with the impact of:
  • Higher concentration of NOx, SOx, HCl, HBr, CO2, etc...
Role of Chlorine and its Chemistry

- What is the role of Coal Chlorine and its Chemistry to the heterogeneous and gas phase oxidation of Hg under oxyfuel condition.

- $SO_2(g) + Cl_2(g) + H_2O(g) \leftrightarrow 2HCl(g) + SO_3(g)$
Impact of SO$_3$ on Hg Removal Efficiency of the Activated Carbon

Air Fired Case (CODEN Study)

Oxy Fired Case
Mercury Management in the CO2 Processing Plant

- I don’t see any technical barrier in removing Hg. This has been done in LNG industry. The consideration of cost is the main question!

- There are 3 levels where Hg (both elemental and ionic) could be captured in the CO$_2$ processing plant.
  - Compression stage
  - Moisture Removal stage
  - Activated Carbon Guard bed
1st Announcement

2nd Oxyfuel Combustion Conference
12th - 16th September 2011
Queensland, Australia
CS Energy/IHI Burner Testing Programme at Callide A Power Station

• **Callide A Project** – *would be the world’s 1st oxyfuel retrofitted power station. (Would be the largest demonstration of the technology by 2011!)*
  - First oxyfuel pilot plant that will actually produce electricity.
  - Installation of new IHI 2x ~30MWth Wall Fired Burners (with operation of 4 burners at full load)
    - A unique position to provide information related to the burner – burner interaction

• **Project Scope** (4 years operation):
  - Oxygen plant (nominal 2 x 330 tpd ASUs)
  - Boiler refurbishment and oxy-fuel retrofit (1 x 30 MWe Unit)
  - CO$_2$ compression & purification (75 tpd process plant from a 20% side stream)
  - Road transport and geological storage (~ 30 tpd liquid CO$_2$)

Courtesy of CS Energy, IHI
Interest to receive updates - Please Register at:

www.ieaghg.org/index.php/?create-an-account.html

Conference Dates:
- 12th Sept. 2011  Asia Pacific Programme - Oxyfuel Working Group Capacity Building Course
- 12th–15th Sept. 2011  2nd Oxyfuel Combustion Conference
- 16th Sept. 2011  Facility Visit to Callide Power Station

Dates to Remember:
- 15th Sept. 2010  Call for papers opens
- 15th Dec. 2010  Deadline for Abstract Submission
- 15th Feb. 2011  Conference Registration opens
- 15th Apr. 2011  Notification of Acceptance for Oral / Poster Presentations
- 15th May 2011  Early Bird Registration Deadline
- 12th – 16th Sept. 2011  2nd International Oxyfuel Combustion Conference