Corrosion in an Oxyfuel boiler - First results from Vattenfalls 30MWth Oxyfuel Pilot Plant in Schwarze Pumpe

IEAGHG Special Workshop on SO2/SO3/Hg/Corrosion Issue under Oxyfuel Combustion Conditions, January 2011, London

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• Introduction

• Furnace measurements

• Material tests

• Future
The Oxyfuel Pilot Plant in Schwarze Pumpe (Germany)

- Boiler
- ESP
- Air separation unit
- FGD
- FGC
- CO₂ Plant
- Thermal capacity: 30 MWth
- CO₂ (liq.) production: 9 t/h
- CO₂ removal rate: > 90%
- Investment: 70 Mio.€

Schwarze Pumpe, location of the Oxyfuel pilot plant

Federal state of Brandenburg

Boiler

Air separation unit

FGD

FGC

CO₂-Plant

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Schwarze Pumpe, location of the Oxyfuel pilot plant

Federal state of Brandenburg
Plant overview - the Schwarze Pumpe OxPP

1. Pulverised Coal → Burner → Furnace
2. Alternative SCR → 2. Pass → FGD
3. 3. Pass → Ash → ESP → Hot Recirculation

Cold Recirculation:
- Sealgas <1,2 bar → Steam-HEx
- Sealgas 6 bar → Steam-HEx

Steam-HEx:
- Air

Air Recirculation:
- Vent gas → Fan 1 → FGD → Fan 2 → FG-Condenser

Steam-HEx:
- Oxygen

Nitrogen:
- ASU

VATTENFALL
Furnace measurements
Main focus for furnace measurements and operation points

• To quantify differences between air and oxyfuel operation and between different oxyfuel operation cases in pilot scale regarding
  - Combustion performance
  - Heat transfer
  - NO\textsubscript{x} formation

<table>
<thead>
<tr>
<th></th>
<th>AIR</th>
<th>OXY25</th>
<th>OXY30</th>
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<tbody>
<tr>
<td>Steam load [MW]</td>
<td>27,0</td>
<td>27,0</td>
<td>25,9</td>
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<td>Fuel load [MW]</td>
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<td>O\textsubscript{2} concentration in oxidant [%], wet</td>
<td>air</td>
<td>25,0</td>
<td>30,4</td>
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<tr>
<td>O\textsubscript{2} (in flue gas) [%], wet</td>
<td>2,8</td>
<td>3,4</td>
<td>3,2</td>
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</table>

• The fuel fired was a Lausitz Lignite, with about 6 % ash on dry bases, a water content of 10% and a lower heating value of approximately 21MJ/kg.
Flame shape - Temperature [°C] (FTIR)

AIR

OXY25

OXY30

T (mean) in °C TM332-Riso-nonext port 2 - 8

T (mean) in °C TM333-Riso-nonext port 2 - 8

T (mean) in °C TM334-Riso-nonext port 2 - 8

Bottom, Distance from right wall (cm)

Bottom, Distance from right wall (cm)

Bottom, Distance from right wall (cm)

Left wall, Distance from burner flange (cm)

Left wall, Distance from burner flange (cm)

Left wall, Distance from burner flange (cm)

600 800 1000 1200 1400 1600
Flame shape - CO [vol\%, wet basis] (FTIR)

AIR

OXY25

OXY30

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Material tests
Corrosion and Material testing in OxyFuel environment

- Are the corrosion rates and corrosion mechanism same as in conventional coal fired boilers?

- Exchange $\text{CO}_2 \leftrightarrow \text{N}_2$
- Carburisation
- Influence the heat transfer from flue gas to heat absorbing surfaces

- Risk of enrichment of corrosive species (recirculation)
- More corrosive flue gas and condensates will form
- Both oxyfuel- and air fired modes must be handled

- Higher power plant efficiency with super austenitic steels or Ni-based materials

- Specific objective: Materials for Demo Plant
Purpose

Identify useful materials for (screening):
- Super heater at 650°C metal temperature
- Super heater at 580°C metal temperature
- Super heater at 750°C metal temperature
- Economisers
- Water walls
- Low temperature corrosion (70 – 170°C)

- ESP, FGD, FGC, recirculation duct, etc

- Analysis of deposits formed on super heaters (ash formation)
- Identify differences between conventional coal firing and oxyfuel firing
Flue gas measurements after ESP (wet) for Oxyfuel

- $CO_2 \approx 65\%$ and $O_2 < 4\%$
- $SO_2 \approx 7000mg/m^3$ (Air $\approx 1600mg/m^3$)
- $H_2O \approx 27-29\%$ (Air $\approx 8\%$)
- $CO < 200mg/Nm^3$, $NO_x < 500mg/Nm^3$

Corrosive species $SO_2$ and $H_2O$ approx 4 times greater in oxyfuel.
- $SO_3$ in fly ash
  - Air $SO_3 \ 46 \pm 9 \ (mg/kg)$
  - Oxyfuel $SO_3 \ 77 \pm 18 \ (mg/kg)$
- Otherwise ash composition is similar
Deposit probes

- Deposit probes were exposed at different metal temperatures.
- Indication of increased deposition with higher temperatures, but this requires further investigation.
- Greater variation in the different oxyfuel modes than between air-firing and oxyfuel.
- Analysis of deposits with SEM-EDS reveals that the elemental composition is similar for both oxyfuel and air-firing deposits.

![Graph of deposition rates](image1)

![Graph of deposit composition](image2)
Deposit weight gain

Deposit growth L6/L8 at 580°C and 650°C, stainless steel

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<thead>
<tr>
<th>Test no.</th>
<th>Weight gain (g)</th>
<th>Level 6</th>
<th>Level 8</th>
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<tr>
<td>L6 02-03 OXY</td>
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<td>L6 02-16 OXY</td>
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<td>L6 03-12 OXY</td>
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<td>L8 01-27 AIR</td>
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<td>L8 01-29 AIR</td>
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<td>L8 02-03 OXY</td>
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<td>L8 02-10 OXY</td>
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<td>L8 02-16 OXY</td>
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<td>L8 03-11a OXY</td>
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<td>L8 03-11b OXY</td>
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- 580°C
- 650°C
- 760°C
Deposit under Oxyfuel

Deposit composition - oxyfuel, wind side

Test elemental composition [%]

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<tr>
<th>Test</th>
<th>0216</th>
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Oxyfuel deposit morphology

L 8 16 Feb. Windward side 650ºC. Substrate can be seen under deposit

L6 16 Feb. Windward side 650ºC. Thick deposit covering substrate
Corrosion probes after exposure in plant

Super heater probe (580°C) separated with isolators

Wall probe, flush mounted 4 coupons
Wall corrosion probe

Corrosion wall probe

Material name

Loss/thickness (µm) per 1000 h

2.7 Metal loss
2.7 oxide
3.7 oxide

10Cr
13Cr
15Mo3
1.4712
Sanicro 63 (Alloy 625), 347H FG and 253MA perform well at 580°C. 10Cr and T23 no good performance and X20 at the border.
AC66, TP 310, 304H and T92 showed no good performance at 600 C steam in oxyfuel.

Questions about Sanicro 63 and Alloy 625?
High temperature corrosion probes (e.g. 580C)

- No significant difference between the air-firing and the oxyfuel firing mode.
- SEM-EDS analysis revealed similar corrosion morphologies in air and oxyfuel, e.g. sulphur.
- There was no sign of increased carburisation due to the higher CO₂ concentration in the gas phase, maybe due to the similar oxygen content.
- Problems with carburisation could occur on the waterwalls due to low oxygen stoichiometry.
Low temperature gradient probe

Corrosion probes after exposure in plant
Low temperature corrosion probes

- 15Mo3 sustained corrosion over a wider temperature range in the oxyfuel mode.
- The deposits on the probes for oxyfuel firing were enriched in sulphur especially at 170 °C. Calculations show that the acid dewpoint due to the increased presence of SO₃ is about 30 °C higher in the oxyfuel mode.
- In addition the increase in water content from 9% to 30% also increases the dewpoint temperature.
Summary on material tests

- Strong indication of higher material wastage rate in OxyFuel
- Deposit composition and corrosion attack on high temperature components were similar
- The temperature range where low temperature components are susceptible to corrosion has increased due to oxyfuel firing probably due to increased susceptibility to SO3 dewpoint corrosion.
- There may be more ash deposition in the oxyfuel mode.

- Increased S-concentration in corrosion front
- Ni-based alloys may form non-protective NiO
- (Cu-containing alloys may form non-protective Cu-crystallites)
- Al-containing materials may form protective oxide (Al$_2$O$_3$) and is not getting carburised

- Carburisation (super austenitic steels, Ni-based) still under investigation
Future outlook
Roadmap for CCS

- **Concept-studies**
  - 2001: theoretic Investigations
  - 2004: Research, Basic principles, Combustion characteristics
  - 2008: Demonstration of the complete process chain, Interaction of components, Validation of test rig results, Investigation of scale up criteria
  - 2015: Verification und Optimisation of components, Reduction of risks, Verification of commercial availability (subsidies necessary)
  - >2020: Economic and competitive power plant concept

- Testrigs: 0.1 – 0.5 MW<sub>th</sub>
- Pilot plant: 30 MW<sub>th</sub>
- Demonstration plant: ≈ 300 MW
- Commer. plant: ≈ 1000 MW
Demo plant J änschwalde and potential storage sites

Separate new Oxyfuel block:
• 250 MW
• CO₂ removal > 90%
• 1.34 Mt/a separated CO₂

Retrofit Block F:
• PCC equivalent to 50 MW
• 0.39 Mt/a separated CO₂

Altmark:
EGR pilot project in cooperation with Gaz de France (pipeline 300 km)

Brandenburg (Birkholz or Neutrebbin):
Storage in deep saline aquifers (pipeline 50/140 km)