Utilities Perspective on Requirements for Oxy-fuel Combustion Power Plant

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INTRODUCTION

- E.ON conventional plant
- CCS approaches: Pre (IGCC), Post (MEA) and Oxy-fuel
- Oxy-fuel plant build / operation
- E.ON pilot scale oxy-fuel fired corrosion testing
- Summary
E.ON SE – International Energy Company

- Nuclear, coal & CCGT 40GW capacity in Europe plus 14GW outside Europe
- 10GW renewables hydro, wind, biomass, solar

- European coal capacity 17.5GW:
  (Germany 8.6, UK 2, Sweden 0.7, France 2.7, Benelux 1.7, Italy 0.9, Spain 0.9)
- Outside Europe coal capacity 3GW
  (Russia 1.5, Brazil 1.0, Turkey 0.4)
E.ON Power Plant Operating Conditions

- Subcritical plant: SHTR 165bar, 540 - 568°C; RHTR 40bar, 540 - 568°C
- Supercritical plant: SHTR 262bar, 540 - 568°C; RHTR 70bar, 540 - 568°C
- New build supercritical plant:
  SHTR 285bar, 600°C; RHTR 60bar, 620°C
E.ON Power Plant New Build: Maasvlakte 3

- 1100MW_{electrical}
- ~46% efficient
- 360t/h hard coal, biomass co-firing capability
- 2950 t/h steam 600°C 285bar and 620°C 60bar
- Furnace 105m tall x 24m wide x 17m deep
- Project costs: €1.6bn (without CCS!)

- 100Khours min design life

- Economiser: 16Mo3
- Furnace walls: T24
- SHTR / RHTR: T24, VM12, HR3C, Super304H
CCS Interests

- Post combustion
  - Pilot scale amine scrubbing Wilhelmshaven PS, Germany
    70 tonnes/day CO2 capture and release
  - Demonstration scale amine scrubbing Maasvlakte, Netherlands
    250 MW slipstream from new 1GW power plant (1.1 Mt CO2/yr)
    Rotterdam Capture and Storage Demonstration (ROAD) project
    LP steam tapping installed for solvent regeneration.
- Pre-combustion
  - ~370MW IGCC project study (inactive), Killingholme, UK
- Oxy-fuel projects
  - 1MW_{thermal} pilot scale combustion test facility, Ratcliffe, UK
Pressure Parts Construction Materials

- Code approved materials:
- BS EN 12952 Water-tube boilers and auxiliary installations – Part 2: Materials for pressure parts of boilers and accessories, Annex A
- ASME Boiler Pressure Vessel Code Cases
- Economisers: Ferritic steels:
  - Carbon steel, 16Mo3
- Furnace: Ferritic and bainitic steels, nickel based alloys
  - Carbon steel, 16Mo3, T11, T22, T23, T24, IN617
- Note ASME forbids use of austenitics
- SHTRs & RHTRS: Ferritic, bainitic, austenitic steels and nickel based alloys
  - Carbon steel, 16Mo3, T11, T22, T23, T24
  - T91, VM12
  - E1250, 300 serries austenitics, Sanicro25, HR3C
  - IN617, IN740
Oxy-Fuel Plant Build

- Minimise CAPEX
- Boiler design similar to traditional plants
- Vendor performance guarantees
  - Efficiency
  - Component life
Oxy-Fuel Plant Build

- Plant configuration options
  - (1) dirty (hot) recycle: higher efficiency, aggressive boiler environment, lower air-fuel operating loads, cheap
  - (2) clean (cold) recycle: lower efficiency, benign boiler environment, higher air-fuel operating loads, expensive
Oxy-Fuel Plant Safety / Environmental Implications

- Power plants operate at high temperatures and pressures – significant safety implications
- Require to minimise any additional safety implications associated with new / additional processes.
- Minimise other discharges to the environment (water / ground)
Oxy-Fuel Plant Operational Requirements

- Ideally oxy-fuel plants constrained on-load / base load, but:
- Will plant be flexible?
  - Respond to constraints imposed by renewables such as wind
- Fuel diet
  - World traded coals – wide ranging compositions / firing characteristics
  - Biomass additions?
- How long will it take to start?
  - Can it 2-shift if not required at night
- Can it operate in air-fuel mode for long periods?
  - What if oxygen plant is unavailable
  - Increased output at times of peak demand
- Required to be reliable – generate on demand
- Maximise plant efficiency – more MWs per tonne of coal
- Minimise costs
Boiler Tube Life / Inspection Interval

- Typical boiler statutory insurance interval 4 years
- Expected tube lives required to be multiples of 4 years or ~30,000 hours for a base load plant
- Predictable corrosion, erosion & creep degradation rates – enables planned replacements
- No / minimal forced outages due to tube leaks between major inspections
Acid Dewpoint Considerations

- Mills, ducts, gas mixing, heat exchangers
- $\text{H}_2\text{SO}_4$ dewpoint variation Verhoff & Banchero Correlation
- Hydrochloric acid dewpoint much lower, not significant

\[
T_{\text{dew}}=1000 / \left(2.276 - 0.0294 \ln(P_{\text{H}_2\text{O}}) - 0.0858 \ln(P_{\text{SO}_3}) + 0.0062 \ln(P_{\text{H}_2\text{O}} \times P_{\text{SO}_3})\right)
\]
Flue Gas Desulphurisation

- Large full flow / size clean recycle or small part flow dirty recycle?
- Established use of protective coatings and high alloy corrosion resistant materials:
  - Flake filled vinyl esters
  - Rubber lining
  - Polypropylene
  - SiC filled epoxy
  - GRP
  - Stainless steels
  - Nickel based alloys
  - Titanium

- Oxidation sparging sulphite to sulphate external to FGD?
Acknowledgement Funding Pilot Scale Testing

- Technology Strategy Board / BERR
- Technology Programme Project H0639C: Modelling fireside corrosion of heat exchanger materials in advanced energy systems
- Technology Programme Project TP11/LCE/6/I/AE188L: Impact of high concentrations of \( \text{SO}_2 \) and \( \text{SO}_3 \) in carbon capture applications and its mitigation
- OxyCoal 2 Project
- Technology Programme Project TP11/MFE/6/I/AA140E: Advanced surface protection enabling carbon abatement technologies (ASPECT)
Pilot Scale Combustion Test Facility – 1MW\textsubscript{th}
Typical Test Conditions

- Nominal 50 hours duration
- 0.85MWth, 15% - 20% over fire gas, back end $O_2$ 1% - 3%
- Dirty recycle – cyclone ash removal only
  - Primary recycle gas $O_2 \sim 1\%$ (dried)
  - Secondary / tertiary / over fire enrichment $\sim 24\% O_2$
- or
  - Primary recycle gas $O_2 \sim 21\%$ (dried)
  - Secondary / tertiary / over fire enrichment $\sim 35\% O_2$

- Furnace alloys: 15Mo3, T23, T91, HR3C, IN671
- Superheater alloys: T22, T91, E1250, Super304H, TP347HFG, HR3C, Sanicro25, IN740
## Pilot Scale Test Coals

<table>
<thead>
<tr>
<th>Coal</th>
<th>%S</th>
<th>%Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hard / Black Coal</td>
<td>%S</td>
<td>%Cl</td>
</tr>
<tr>
<td>El Cerrejon (Columbian)</td>
<td>0.62</td>
<td>0.02</td>
</tr>
<tr>
<td>Thoresby (UK)</td>
<td>1.61</td>
<td>0.45</td>
</tr>
<tr>
<td>Daw Mill (UK)</td>
<td>1.46</td>
<td>0.18</td>
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<tr>
<td>Harworth (UK)</td>
<td>2.43</td>
<td>0.29</td>
</tr>
<tr>
<td>Williamson (USA)</td>
<td>1.66</td>
<td>0.34</td>
</tr>
<tr>
<td>Cutacre (UK)/ El Cerrejon</td>
<td>3.36</td>
<td>0.02</td>
</tr>
<tr>
<td>Thoresby / Cutacre</td>
<td>2.21</td>
<td>0.52</td>
</tr>
</tbody>
</table>

### Air-fuel Gas

- 0.1%Cl: 80ppm
- 1%S: 1000–1200ppm

### Oxy-fuel Gas

- 0.1%Cl: ~400ppm
- 1%S: ~5000 – 6000ppm
Precision Metrology Corrosion Probes

- Metal losses determined using digital image analysis on polished cross sections
- Optical / electron microscopy characterisation of damage & mechanisms

Furnace wall: single specimen
air cooled

SHTR / RHTR: multiple specimens
air cooled
Boiler Fireside Corrosion

- Furnace section
- Superheater / Reheater section

[Image of corroded boiler tubes and graph showing corrosion rate vs. metal temperature]
Furnace Wall Corrosion

- Low S, low Cl coals – low wastage rates, not affected by oxy-fuel firing
- High S, Higher Cl coals – higher wastage rates but no systematic worsening due to oxy-fuel firing
- Pyrosulphates - speculated to be a furnace wall corrosion mechanism
- Not normally encountered when air-firing coal
- Oxy-firing - potential for increased $\text{SO}_3$ stabilising pyrosulphates

$$(\text{Na,K})_2\text{SO}_4 + \text{SO}_3 = (\text{Na,K})_2\text{S}_2\text{O}_7 – \text{molten } <400^\circ\text{C}$$

- Could lead to:
  - Molten salt scale fluxing
  - Enhanced sulphidation
Superheater / Reheater Corrosion

- Low temperature stages – ferritic steels
  low oxidation rates
- High temperature stages – austenitic steels
  high sulphatic corrosion rates
- Above 540°C steam temperature
  \((\text{Na},\text{K})_3\text{Fe(SO}_4\text{)}_3\) molten ash, scale fluxing
Superheater / Reheater Corrosion

- CEGB PE8 corrosion rate model
  - Austenitic alloys
  - Air fired
  - %Cl indicator of alkali release
  - Alkali metals relatively inert

- Oxy-fuel
  Higher SO$_2$ / SO$_3$ concentration
  Increased flux alkali sulphate

\[ r = A \times B \left( \frac{T_e}{G} \right)^m \left( \frac{T_m - C}{M} \right)^n (\%Cl - D) \]
Superheater / Reheater Corrosion: Oxy-Fuel Firing

- T22 ferritic steel data compared to air-fired wastage rates
- Low Cl coals rates within expected air-fired range
- Medium / high Cl coals rates at top end or above air-fired range

![Graph showing 95%ile Parabolic Wastage Rate vs Surface Metal Temperature for different coal types and locations.]

- El Cerrejon
- Thoresby
- Daw Mill
- Harworth
- Williamson
- Cutacre-El Cerrejon

- Low Cl coals rates within expected air-fired range
- Medium / high Cl coals rates at top end or above air-fired range
Superheater / Reheater Corrosion: Oxy-Fuel Firing

- Austenitic data compared to T22 air-fired wastage rates
- Low Cl coals negligible corrosion
- Medium / high Cl coals rates increase with Cl content
- Fuel chemistry (%Cl) major variable
- Wastage rates reduce as alloying content increases
- Heat flux minor variable
Superheater / Reheater Corrosion: Oxy-Fuel Firing

- Pilot scale tests – attack still due to usual (molten) sulphatic mechanism
- Additional potential risk – carburisation austenitic stainless steels
  
  High CO\textsubscript{2} environment: C + Cr = Cr\textsubscript{x}C\textsubscript{y}
  
  Tube surface Cr depleted – reduced corrosion resistance
  
  Exposures to short to quantify risk
Options to Manage Oxy-Fuel Fireside Corrosion

- Good combustion control – oxidising conditions at furnace wall
- Coal (fuel) selection: low S and Cl
- FGD in oxy-fuel recycle loop – minimise SO$_2$ and Cl in environment
- Tube alloy selection – use of higher alloyed materials
- Protective coatings - weld overlays or sprayed coatings
  - Very good resistance required to justify additional cost
Summary

- Oxy-fuel and air-fuel boilers and operating conditions ideally similar.
- Tubing alloy selection “restricted” by code approved materials.
- Plant required to be flexible to meet demands imposed by renewables.
- Output, efficiency, costs and risks all need to be managed / optimised.
- Excessive furnace fireside corrosion results from poor combustion. Furnace wall corrosion when oxy-fuel firing not obviously worse than air-fuel firing coal. Unproven potential for pyrosulphate attack.
- Superheater / reheater fireside corrosion due to molten sulphates regardless of air or oxy-fuel firing. Increased wastage rates especially for austenitic materials due to greater flux of alkali sulphate. Unquantified risk of austenitic steels carburisation and reduction in corrosion resistance with long term exposure.
- Corrosion control: combustion control, fuel selection, FGD in recycle loop & alloy / coating selection