US-UK Advanced Materials for Low Emission Power Plant

Task 2: Boiler Corrosion/Corrosion Monitoring/Co-Firing

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Project Partners

**UK**

- Doosan Babcock Energy Limited *(Task Leader)*
- University of Cranfield
- National Physical Laboratory (NPL)

**US**

- National Energy Technology Laboratory (NETL) *(Task Leader)*
  - Covanta Energy
  - InterCorr International
  - Honeywell Process Solutions
- Reaction Engineering International (REI)
Excessive boiler tube corrosion has been a long term issue in coal-fired utility boilers. Measures introduced in the 1950s & 1960s in response to changes at that time have proven reasonably successful. However, a number of recent developments have changed this position:

- Primary NOx reduction technologies: Harsher furnace conditions (reduced sulphur species)
- Co-firing non-conventional fuels: Affected ash deposits (e.g. more corrosive, lower melting, lower sulphur and in some cases higher chlorine)
- Advanced design boilers: Higher steam temperature & pressure (material demands)
- Oxyfuel firing: Very high flue gas acid species; SO2/SO3, HCl, CO2
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Objectives

**General**

1. Review plant experience of furnace wall, superheater and reheater corrosion

**Laboratory Experimentation**

2. Further develop laboratory-scale characterisation of boiler tube corrosion processes and measurement of metal wastage rates relevant to in-furnace NOx reduction techniques and Oxyfuel firing

3. Expose candidate alloys in combustion rigs and laboratory assemblies in accurately controlled conditions reflecting current and Advanced Boiler Operations

4. Model extent and mechanisms of degradation involved and develop a predictive capability relevant to real plant performance
Corrosion Probe Development

5. Develop and apply probes and monitoring techniques to quantify corrosion in-situ for various plant situations, including biomass co-firing, waste incineration NOx reduction technologies and Oxyfuel firing.

6. Identify optimum monitoring techniques and data analysis approaches for quantifying type rate and mechanism of corrosion.
Work Programme

The work programme was focussed on two main topics:

• The development and performance of *laboratory-scale*, high temperature corrosion experiments

• The development, implementation and assessment of *corrosion probe techniques* for the measurement of corrosion in coal-fired utility boilers
Laboratory-Scale Experimentation

Work Programme

Pittsburgh Marriott – 14th May 2009

UK-US Collaboration on Fossil Energy R&D - Advanced Materials
Work Programme – Laboratory-Scale Experimentation

Doosan Babcock Activities (Superheater/Reheater):

- Coupons of 9 different materials tested: 9-25 Cr and some Ni alloys - Some of these are ASME coded

- Set temperatures between 550-820 °C (1,022-1,508 ºF), for 1,000 hours

- Synthetic ash Na₂SO₄/K₂SO₄/Fe₂O₃ (1.5 / 1.5 / 1 mole basis) employed in most tests

- Synthetic atmospheres: Conventional flue gas & high sulphur (Oxyfuel investigation)

- 7 tests completed

- Material loss measured to an accuracy of ≤ 10 µm - Equivalent to ≤ 10 nm h⁻¹/1,000 h

- Material wastage – temperature curves plotted using corrosion rate data
  - This allows for alloy corrosion rates in different environments to be directly compared and ranking of materials in particular conditions
Work Programme – Laboratory-Scale Experimentation

Cranfield University Activities (Waterwall, Superheater/Reheater):

- Coupons of 6 materials tested ranging from low grade ferritic to high Cr and high Ni alloys
- Exposure temperatures 425, 600 & 625 °C (797, 1,112, 1,157 °F), for 1,000 hours
- 4 synthetic ash loadings
- Synthetic atmospheres:
  - Conventional flue gas, Superheater/biomass co-fired, Low NOx evaporator, High CO₂
- 6 tests completed
- Exposed specimens analysed by optical microscopy and SEM techniques
- Corrosion rate determined from dimensional metrology
Work Programme – Laboratory-Scale Experimentation

**NPL Activities (Waterwall, Superheater/Reheater):**

Two test approaches:

**Fluctuating Atmosphere**
- Coupons of 3 low grade alloy materials tested, 15Mo3, T22, T23
- Exposure temperatures 500 & 540 °C (932 & 1,004 °F), for 4,000 hours duration
- Atmospheres: Base, High COS and 2x Base/COS, 2x COS/Base fluctuations
- Weight loss measurements made, SEM/EDX analysis conducted

**Heat Flux**
- 15Mo3 tube sections tested in a vertical tube furnace, internally cooled with air or steam
- Inner surface controlled at 3 positions to 450, 475 & 500 °C (842, 887 & 932 °F) for up to 2,000 hours
- $\Delta T$ across tube wall 40 °C (104 °F)
- Electron Back Scattered Diffraction (EBSD) analysis conducted for oxide thickness and grain size distribution
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Work Programme – Laboratory-Scale Experimentation

Doosan Babcock, Cranfield University, NPL and NETL
Inter-Laboratory Comparison “Round Robin Test Programme”

- Coupons of T22 (2 ¼ Cr - waterwall) and P92 (9 Cr - convective) material tested
- Exposure temperatures 425, & 675 °C (797, 1,247 °F), for 1,000 hours
  - Specimens removed every 250 hours
- Synthetic ash Na₂SO₄/K₂SO₄/Fe₂O₃ (1.5 / 1.5 / 1 mole basis) employed
- Synthetic atmosphere:
  - 0.3 % SO₂ / 6.0 % O₂ / 14.6 % CO₂ / 74.2 % N₂ / 5.0 % H₂O
- Corrosion rate determined from dimensional metrology
- Detailed analysis completed as part of Task 4
  “Standardisation in High Temperature Corrosion Testing”

![Graph showing metal loss over time for NPL, Doosan, and NETL](image)
Corrosion Probe

Work Programme
Work Programme – Corrosion Probe

Doosan Babcock Activities (Waterwall):

- Further development of probe system for membrane wall application
- Probes exposed for 6,700 & 9,400 hours in a commercial 660 MWe boiler
- Probe tip temperatures continuously monitored, local gas environment periodically assessed \((CO/O_2\) concentrations)
- Corrosion rate data correlated with temperature profile and local gas environment
- Host Unit was retrofitted with a Boosted Over-Fire Air (BOFA) system for NOx emission control prior to probe exposure campaign,
  - Data compared with results from the same locations prior to the Unit being converted
Work Programme – Corrosion Probe

Cranfield University Activities (Waterwall, Superheater/Reheater):

- Development of continuous corrosion monitoring system, based on electrochemical noise (ECN) measurement and heat flux
- 2 designs tested and evaluated – Tubular & Flat End
- Laboratory activities to establish signal response at temperature with known deposit and gas atmosphere and correlate results with material loss
  - Corrosion rate monitoring accuracy directly assessed by comparison with sacrificial test pieces
- Pilot plant activities to gauge performance in more realistic conditions;
  - Coal & biomass fuels fired,
Work Programme – Corrosion Probe

**NETL (Waterwall, Superheater/Reheater):**
Covanta Energy, Honeywell Process Solutions

- Development of electrochemical corrosion monitoring system, based on
  - Linear Polarisation Resistance, Electrochemical Noise, Harmonic Distortion Analysis

- Laboratory activities to establish corrosion rate using a SmartCET® monitoring system and recorded using FieldCET® software
  - Set temperatures with known deposit and gas atmosphere correlate results with material loss of sensor and sacrificial test pieces

- Field test activities to gauge performance in more realistic conditions;
  - Marion County Solid Waste to Energy Facility, Brooks, OR

- Corrosion rate monitoring accuracy directly assessed by comparison with sensor material loss
Work Programme – Corrosion Probe

REI (Waterwall, Superheater/Reheater):

• Development of continuous corrosion monitoring system, corrosion correlations and predictive models

• Field activities to assess response at temperature
  - Coal Fired Boiler, CFB Boiler (multi-fuel), Pilot Plant Test Facility

• Corrosion rate monitoring accuracy directly assessed by comparison with sacrificial probes and by profilometry,
  - Correlations between monitor data and sacrificial probe/profilometry

• Predictive models developed and validated
Laboratory-Scale Experimentation

Key Results
Key Results – Laboratory-Scale Experimentation

• Corrosion rate information for a number of current and candidate materials accumulated,
  - Temperatures: Sub critical to Ultra Supercritical
  - Conditions (gas/deposit): NOx emission control, Co-firing (coal with biomass), Oxyfuel

• Corrosion mechanism information,
  - Advanced conditions: Oxyfuel, NOx emission control – Potential effects identified
  - Heat Flux (steam/air oxidation): Oxide thickness and grain size effects – Finer grain structure produced

• Material Ranking,
  - Provision of corrosion rate data for conventional and new materials in service by comparing laboratory results with those of known performance

• Enhanced future experimental approach,
  - Fluctuating gas conditions has important effect on corrosion mechanism and may be an important consideration in future laboratory experimentation
Corrosion Probe Work Programme

Key Results
Key Results – Corrosion Probes

• Important information for furnace operating under BOFA regime:
  – Gas environment, indicated more reducing conditions – system was not deeply staged
  – Corrosion rate information over furnace waterwall tube temperature range
  – No excessive corrosion rate measured for the host side-wall locations

• Electrochemical corrosion probe signals were found to be sensitive to many factors:
  – Environment: Temperature, gas phase composition, ash composition, ash condition (solid/molten)
  – Alloy Composition, i.e. Alloy Type

• Electrochemical corrosion monitoring:
  – Specific correlation factors for individual materials required to obtain realistic corrosion rates
  – Strong correlations between system data and physically measured data reported in some instances

• Probe corrosion monitoring - General:
  – Applications and limitations of probe approaches understood
  – Data analysis techniques developed, limitations understood
Corrosion Review

Key Results
Task 2: Boiler Corrosion/Corrosion Monitoring/Co-Firing

Key Results – Corrosion Review

• Review of Corrosion in coal-fired utility plant prepared, containing:

  – Review of up-to-date, high temperature corrosion literature: 
    Waterwall, Superheater, Reheater

  – Information on corrosion mechanisms

  – Details of suitable diagnostic systems

  – Advice on remedial measures
Collaborative Benefits

Key Benefits
Key Benefits

**Beneficial effect from diverse laboratory experimentation**
- Access to a wider range of important corrosion rate data: materials, conditions
- Access to more, relevant mechanistic information

- Laboratory test procedures, discussed, compared and approaches to standardisation suggested *(Task 4)*
- Future test conditions and considerations identified, based on enhanced understanding – *Phase 2*

**Beneficial effect from sacrificial and diverse electrochemical probe activities**
- Access to more development and field experiences,
- Information on preferred approaches and methods provided

- Applications and limitations of the current technologies were established
- Key areas for future development were identified, founded on sound experience – *Phase 2*
Thank you for listening

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