US-UK Advanced Materials for Low Emission Power Plant

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

Dr Barry F McGhee
Doosan Babcock Energy Limited
Department: R&D - *Material & Fuels*

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

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)

Background

- 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; SO_2/SO_3, HCl, CO_2

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

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

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

Objectives

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

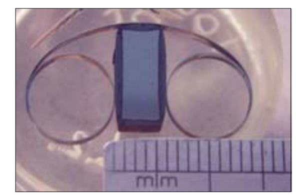
Laboratory-Scale Experimentation

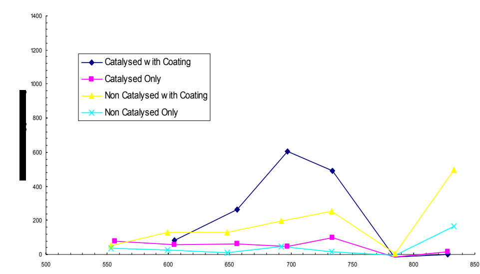
Work Programme

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 $Na_2SO_4/K_2SO_4/Fe_2O_3$ (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*

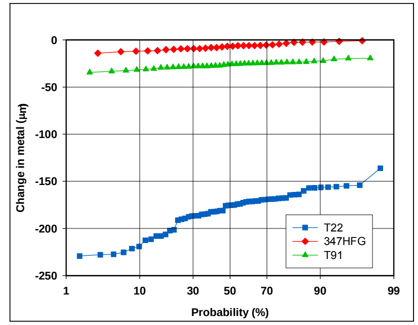


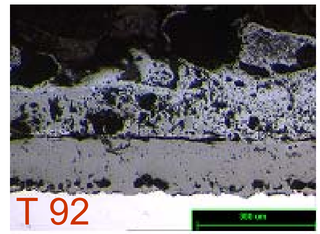


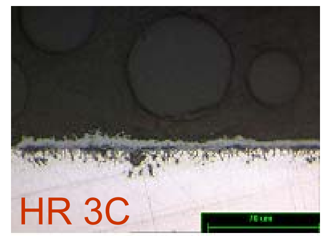
Work Programme – Laboratory-Scale Experimentation

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 ºF), for 1,000 hours
- 4 synthetic ash loadings
- Synthetic atmospheres:
  - *Conventional flue gas, Superheater/biomass co-fired, Low NOx evaporator, High CO_2*
- 6 tests completed
- Exposed specimens analysed by optical microscopy and SEM techniques
- Corrosion rate determined from dimensional metrology

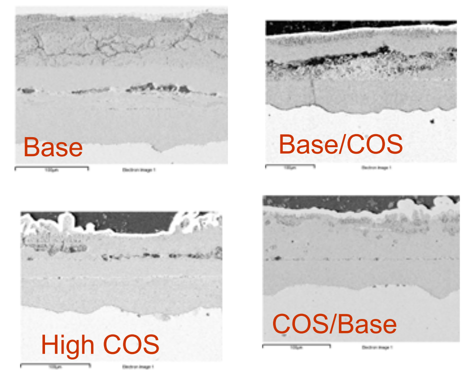






Task 2: Boiler Corrosion/ Corrosion Monitoring/ Co-Firing

Work Programme – Laboratory-Scale Experimentation



NPL Activities (Waterwall, Superheater/Reheater):

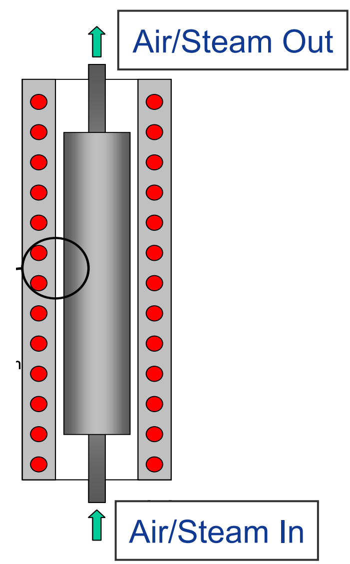
Two test approaches:

Fluctuating Atmosphere

- Coupons of 3 low grade alloy materials tested, 15Mo3, T22, T23
- Exposure temperatures 500 & 540 °C (932 &1,004 ºF), 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 ºC (842, 887 & 932 ºF) for up to 2,000 hours
- ΔT across tube wall 40 ºC (104 ºF)
- Electron Back Scattered Diffraction (EBSD) analysis conducted for oxide thickness and grain size distribution

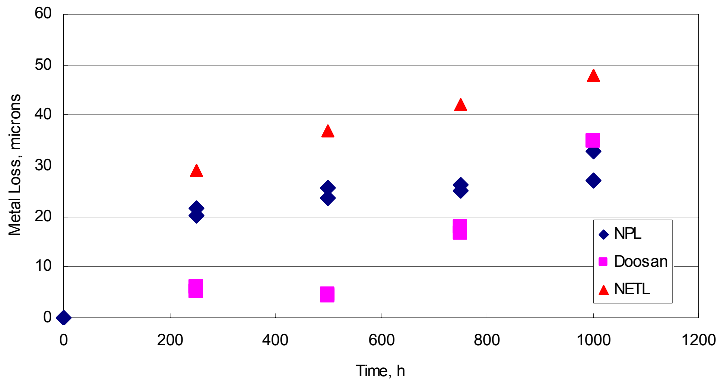


Work Programme – Laboratory-Scale Experimentation

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 $Na_2SO_4/K_2SO_4/Fe_2O_3$ (1.5 / 1.5 / 1 mole basis) employed
- Synthetic atmosphere:
  - 0.3 % SO_2 /6.0 % O_2 /14.6 % CO_2 /74.2 % N_2 /5.0 % H_2O
- Corrosion rate determined from dimensional metrology
- Detailed analysis completed as part of **Task 4** "Standardisation in High Temperature Corrosion Testing"

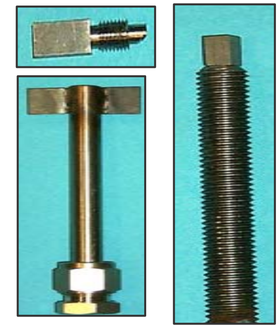


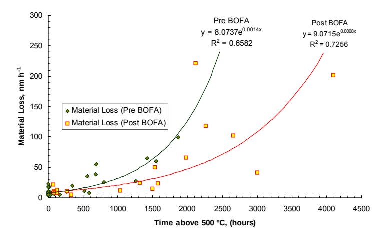
Corrosion Probe
Work Programme

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*



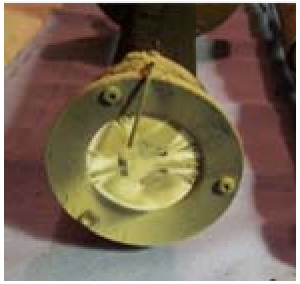


Work Programme – Corrosion Probe

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

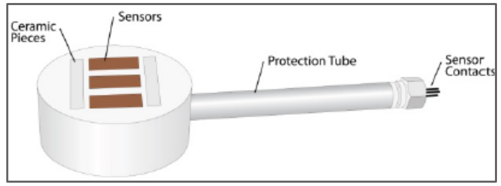
- Laboratory activities to establish signal response at temperature with known deposit and gas atmosphere and correlate results with material loss
  - *Corrosion rate monitoring accuracy directly assessed by comparison with sacrificial test pieces*



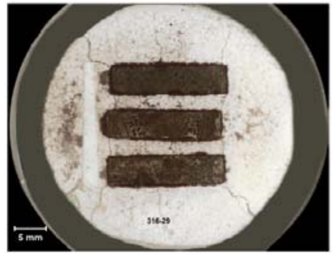
- Pilot plant activities to gauge performance in more realistic conditions;
  - *Coal & biomass fuels fired*,

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

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*

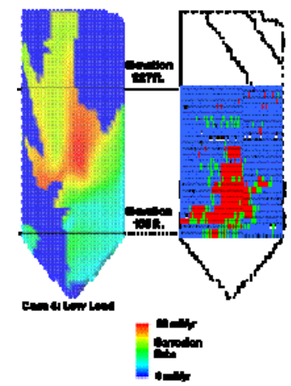
- Corrosion rate monitoring accuracy directly assessed by comparison with sensor material loss

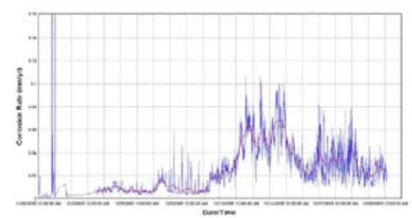
Task 2: Boiler Corrosion/ Corrosion Monitoring/ Co-Firing

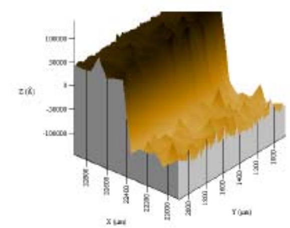
Work Programme – Corrosion Probe

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

U.S. DEPARTMENT OF ENERGY

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

DEPARTMENT OF ENERGY & CLIMATE CHANGE

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

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

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

Doosan Babcock Energy

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

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

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

bmcghee@doosanbabcock.com