

Chlorine Rich Deposits and Superheater Corrosion in Co-Combustion

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BIO-ENERGY

ENLARGED PERSPECTIVES

Budapest ,16-17 October 2003

General Objectives for CORBI

- **The overall objective of the work is to improve understanding of corrosion mechanisms.**
- Corrosion mechanisms in waste and biomass combustion are not well understood due to the complex and variable ash behaviour and chemical nature of the fuel ashes.
- By increasing the understanding of corrosion mechanisms new superheater materials with higher corrosion resistance could be designed/selected for higher steam temperatures (480 °C → 550 °C).
- 50 °C raise in steam temperature would result about 10 % increase in power generation efficiency. In addition, significant savings in maintenance costs could be achieved due to longer durability of superheaters.

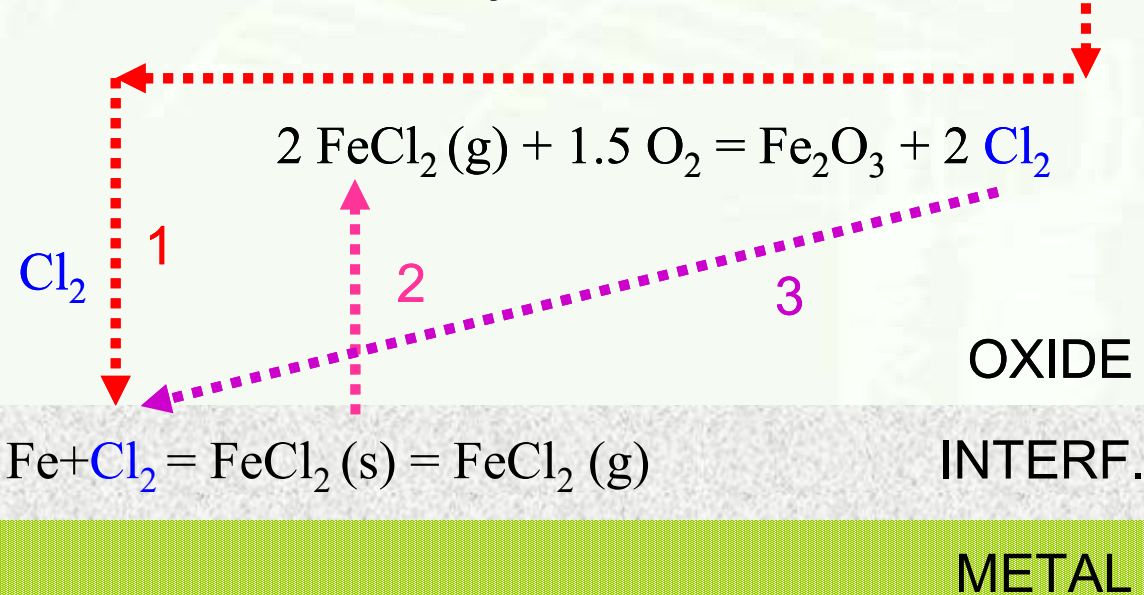
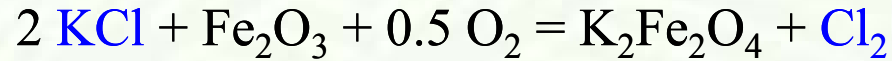
Description of the consortium

Partner	Role	Complementary
VTT - Processes - Industrial Systems	Deposit formation and corrosion monitoring in laboratory and full scale, expertise in co-firing and biomass-based fuels	Power plant and well-controlled laboratory scale fluidized bed combustion tests, analytics, measurements and theoretical analysis. Materials manufacturing and corrosion testing.
Max Planck Institute	Material research and development	Supply heat exchanger materials for laboratory and field tests of other partners, analytics, expertise in materials, local corrosion reactions
Vattenfall Utveckling Ab	Energy producer and supplier with expertise in operational experience and practice	Power plant tests (fluidized bed), deposit formation measurements and analytics
ENEL Produzione	Energy producer and supplier with expertise in operational experience and practice	Power plant and pilot-scale tests (pulverized fuel), deposit and corrosion measurements, theoretical analysis
Joint Research Center	RTD in support of EU policy, mainly in the area of clean and sustainable energy production, material research and development	Laboratory tests with biomass ash to discover information on corrosion phenomena, analytics, expertise in materials

Scientific and Technical Assessment

Max-Planck-Institut fuer Eisenforschung GmbH

ACTIVE OXIDATION

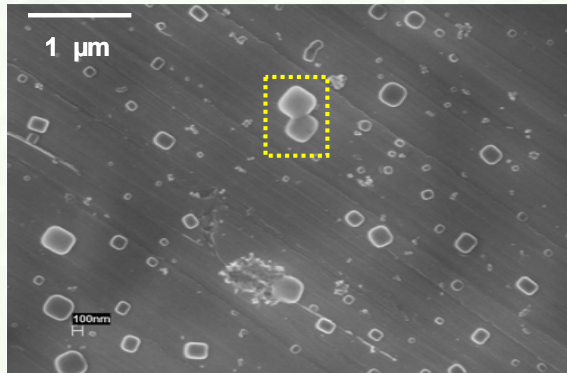


1. Formation and diffusion of Cl_2
2. Formation and outward diffusion of FeCl_2
3. Re-diffusion of Cl_2

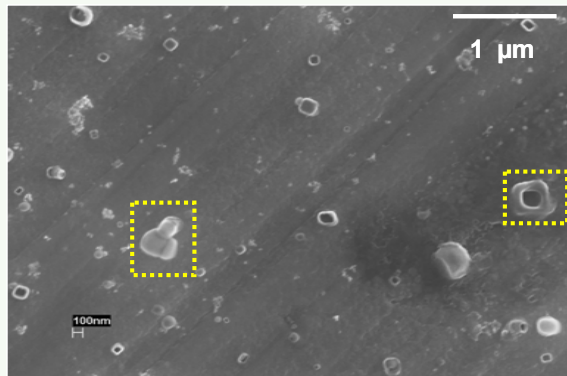
“ Cl_2 works as oxidation catalyst”

LOCAL REACTIONS

SEM images of KCl



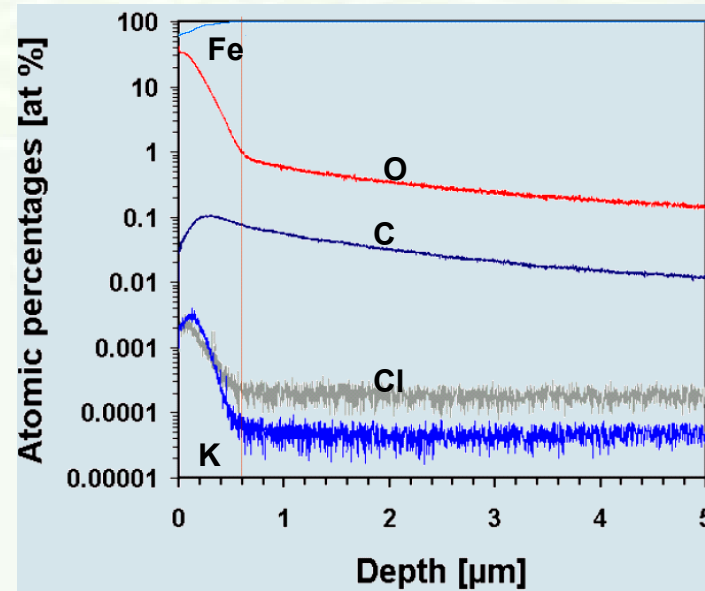
a) Non-oxidation: square form



b) Oxidation (Air, 300°C, 10 min.):
ring, agglomerate form

→ At 300°C local reactions of KCl and the metal surface occur

SNMS depth profile



Sample was:
1. pre-oxidized (300°C, 1h)
2. KCl deposited
3. oxidised (500°C, 10 min.)

- Max. concentration of K-Cl is up to 0.6 μm from the surface
- O- and C-concentration decreases from the surface to the inner layers
- Thickness of oxide scale is about 0.6 μm (~1 at %)
- ✓ Localized reactions are detectable betw. KCl and the oxide surface at 300°C
- ✓ Inward diffusion of chlorine into the oxide scale at 500°C

Scientific and Technical Assessment

Joint Research Centre, Institute of Energy

Experimental

Duration:

360 h

Temperatures:

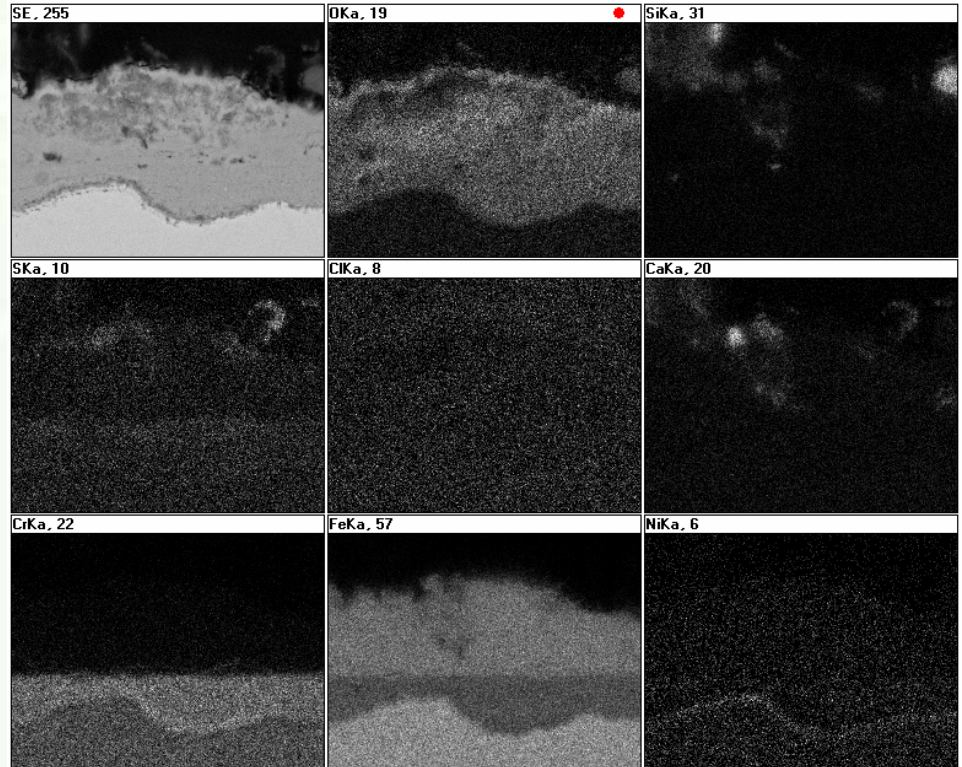
535°C isothermal (600°C)

Gas composition:

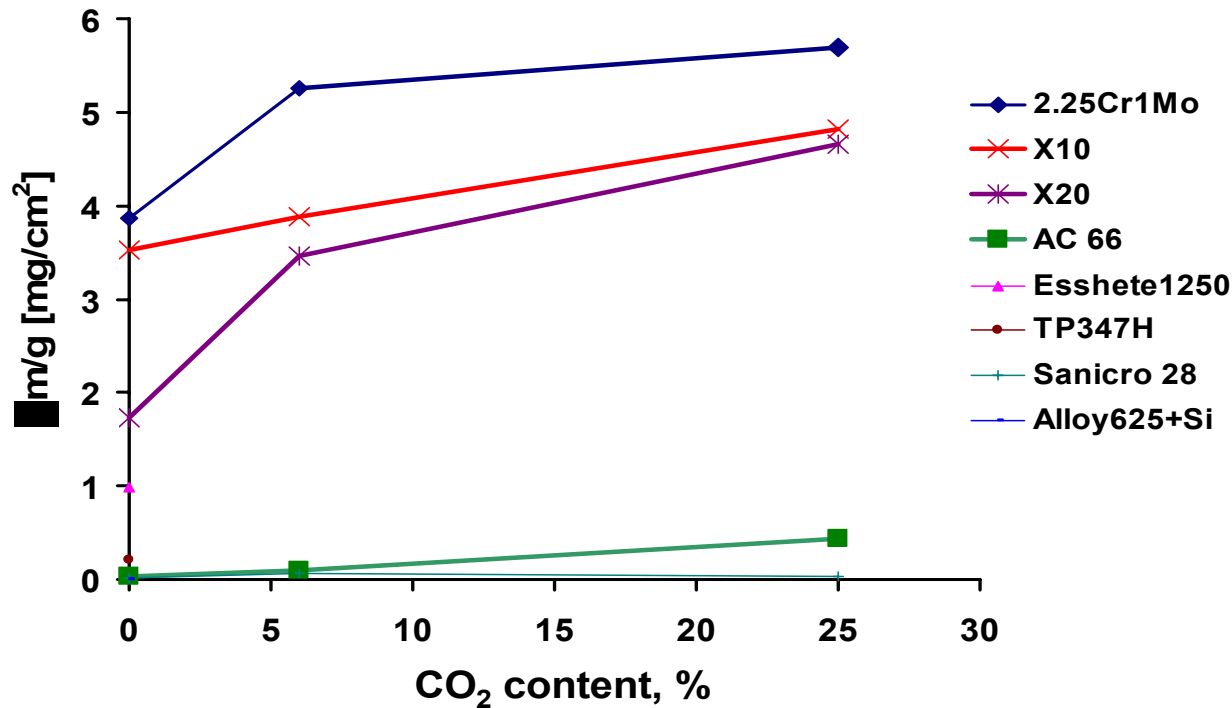
22% H_2O + 5% O_2 + $x\%$ CO_2 + N_2 ($x = 6, 15, 22$)

Deposits:

without and with cyclone -/filter ashes



Cross section and X-ray maps of the X20 steel with fly ash deposit oxidized in $N_2 - 5\%O_2 - 22\%H_2O + 25\%CO_2$ atmosphere at 535°C for 360 h



Weight mass change per unit area versus CO₂ content in corrosion atmosphere (535°C, 22H₂O+ 5%O₂ +xCO₂ + N₂)

Conclusions

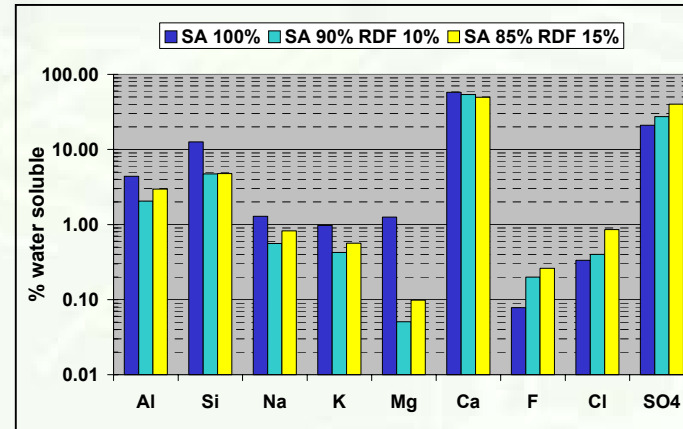
1. Corrosion rate, for the alloys without the deposit, increase with increasing CO₂ content, especially for the ferritic steels
2. Corrosion rate for samples with the deposit increase significantly and in this case the internal oxidation was observed

Scientific and Technical Assessment

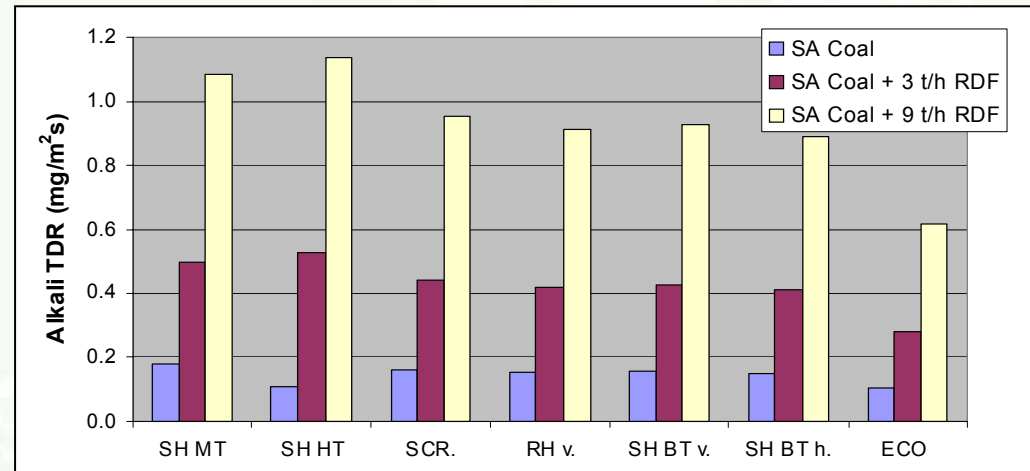
ENEL Produzione SpA

- ENEL objectives are to evaluate the impact of co-firing secondary fuel (RDF) with coal on boiler performance measuring the deposition tendency and the corrosion potential of the ash and to develop CFD tools aimed at simulating combustion chamber environment and predict ash deposition.

- Experimental campaign on pilot and full scale furnaces are aimed at measuring deposition tendency and deposit characteristics during RDF co-combustion in order to evaluate corrosion potential on superheater banks.



Water soluble fraction of the deposit: South African coal and RDF co-combustion, $T_{flue\ gas} = 1135^{\circ}C$

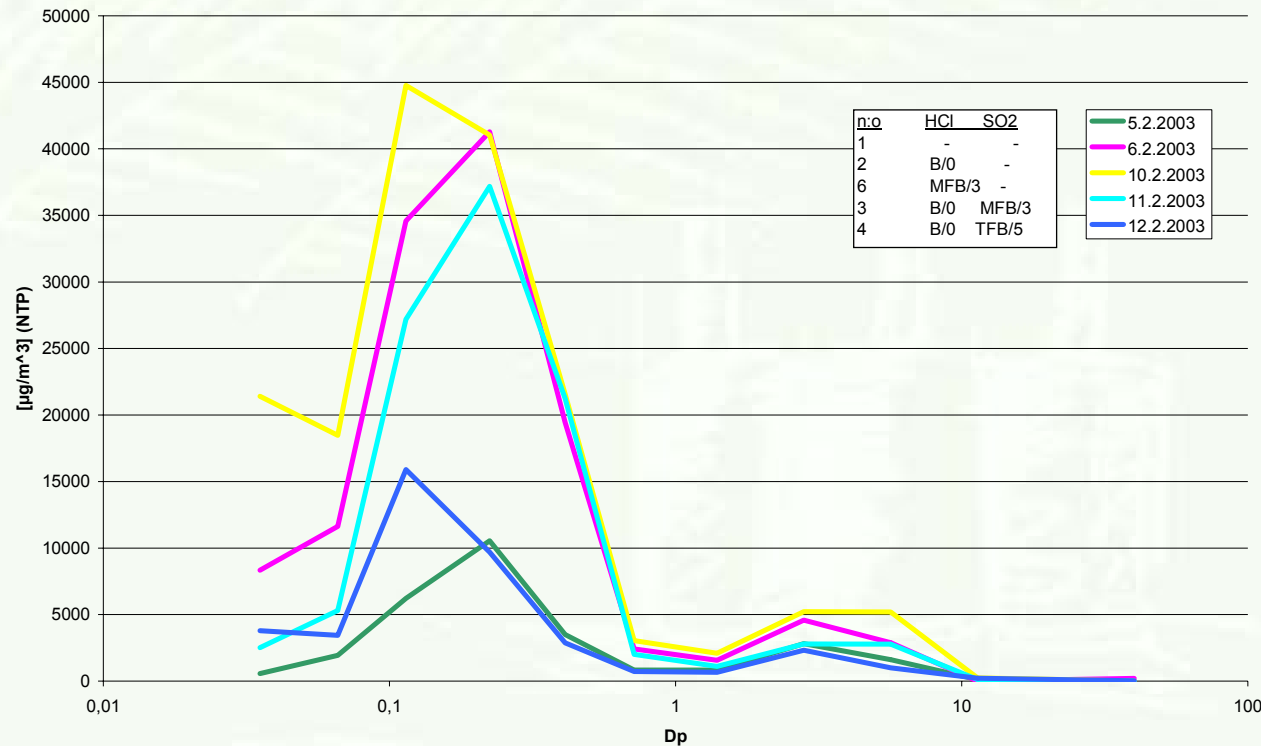


Total deposition rates (TDR) of alkali vapours calculated for the different sections of the convection pass and for different RDF shares in the fuel.

Scientific and Technical Assessment

Technical Research Centre of Finland (VTT)

- Two sets of laboratory-scale combustion tests with 40 kW fluidised bed reactor (CFB) have been carried out.
- The objectives were to obtain data on the formation rate, quality and components of deposits, and further, components' location in the deposit layer.
- The results contribute to understanding the mechanisms of deposit formation and corrosion



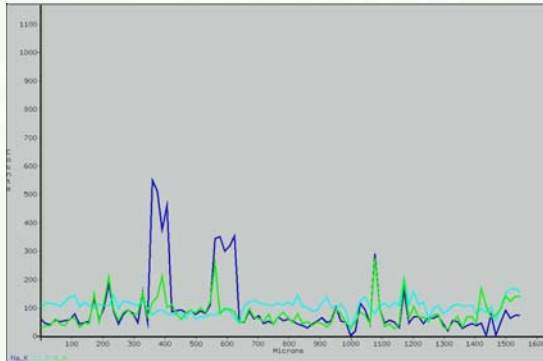
Chlorine in Hot Flue Gas in VTT's CFB-pilot, close to the Deposit Probe when using different HCl and SO₂ increment. SO₂ feed into the top of furnace (test 4) reduced most efficiently chlorine in the flue gas fines.

Scientific and Technical Assessment

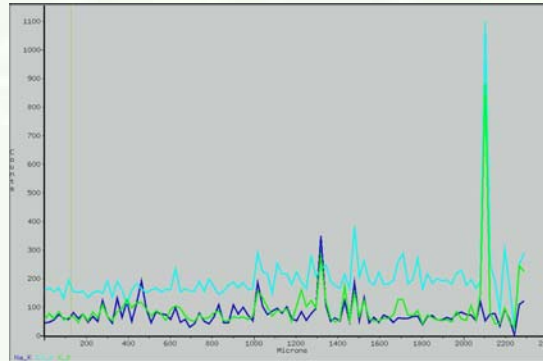
Technical Research Centre of Finland (VTT)

Line scans from deposit of material SAN28 (Na, Cl, K)

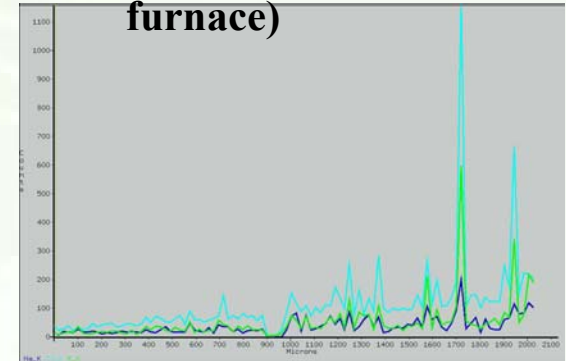
Test 1- no feed



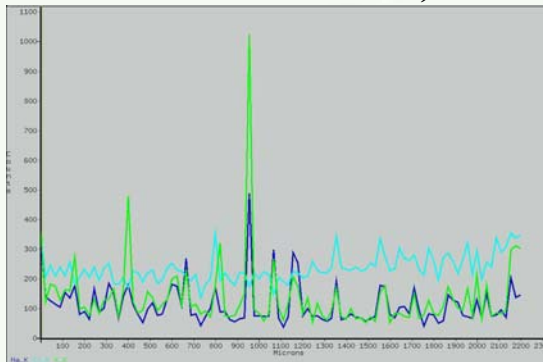
Test 2 - HCl feed into bed



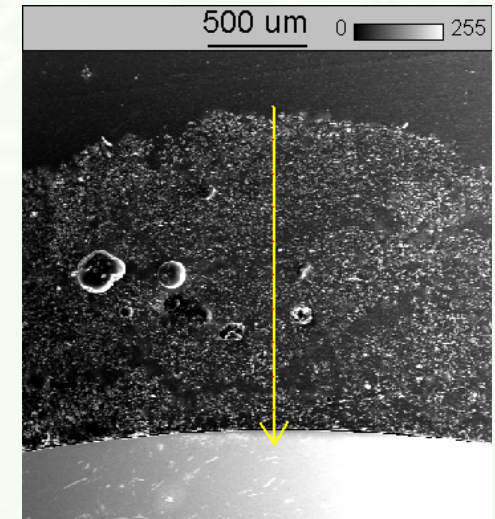
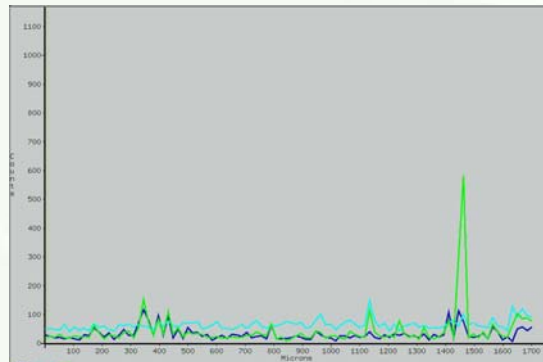
Test 6 - HCl feed (middle of furnace)



**Test 3 - HCl & SO₂ feed
(into bed & from middle of furnace)**



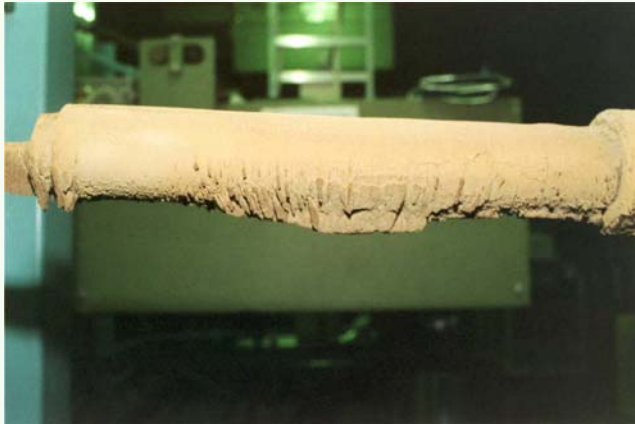
Test 4 - HCl & SO₂ feed (into bed & top of furnace)



Scientific and Technical Assessment

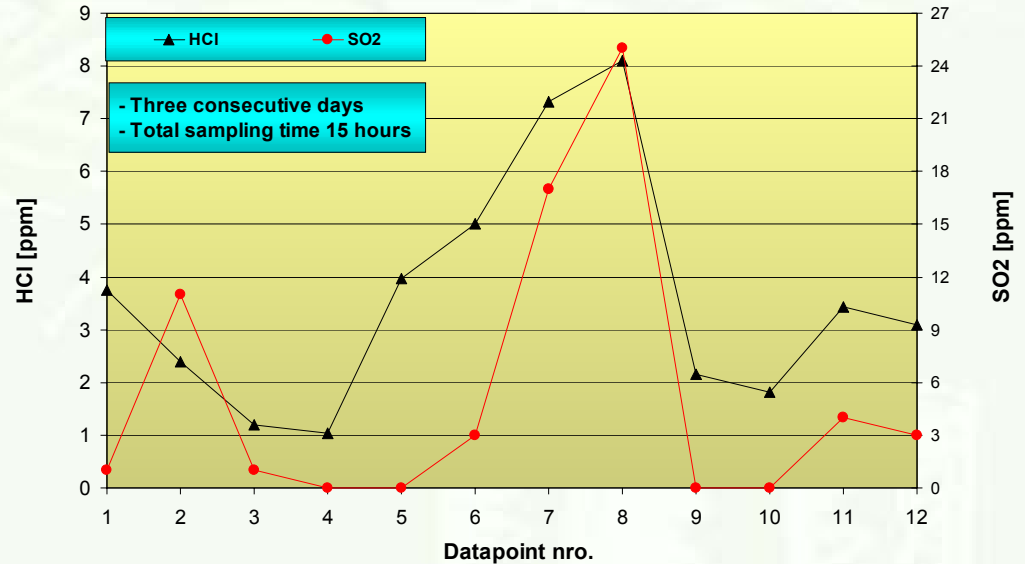
Technical Research Centre of Finland (VTT)

- Long- and short-term corrosion tests have been performed at Forssa BFB-plant and at Varkaus CFB-plant.

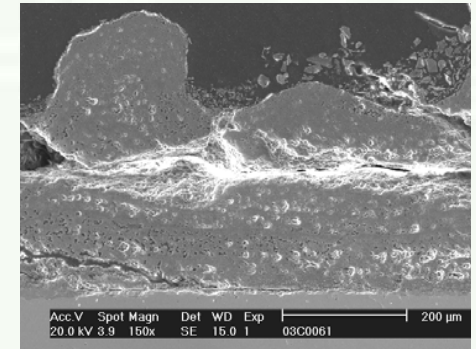
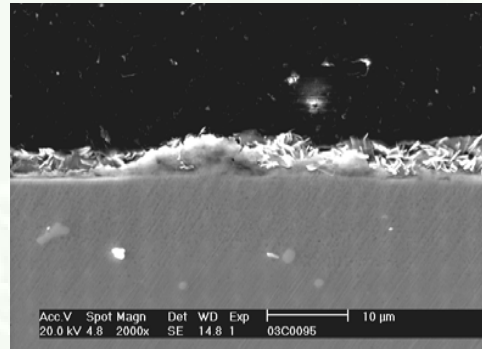


Deposit/corrosion probe after test period I in Forssa: Combustion of REF III with peat and wood based fuels (one week probing).

FLUE GAS CONCENTRATION (stack)



SO2 and HCl measurements at Varkaus plant.

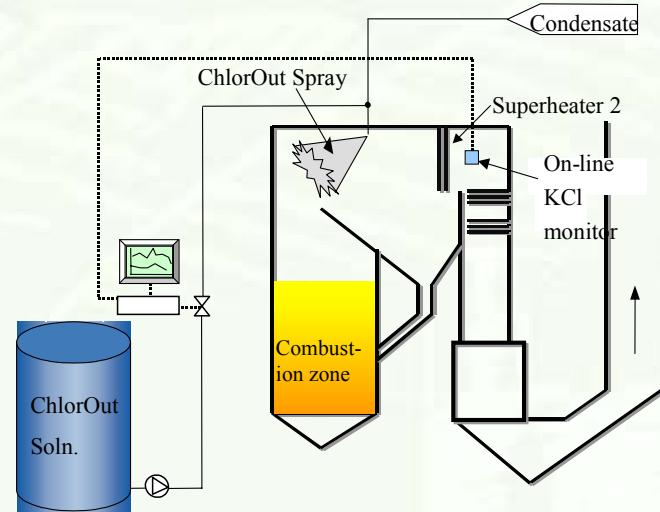


Cross sectional SEM-imaging of material samples exposed for 672 h at Varkaus. On the left AC 66 and on the right X20.

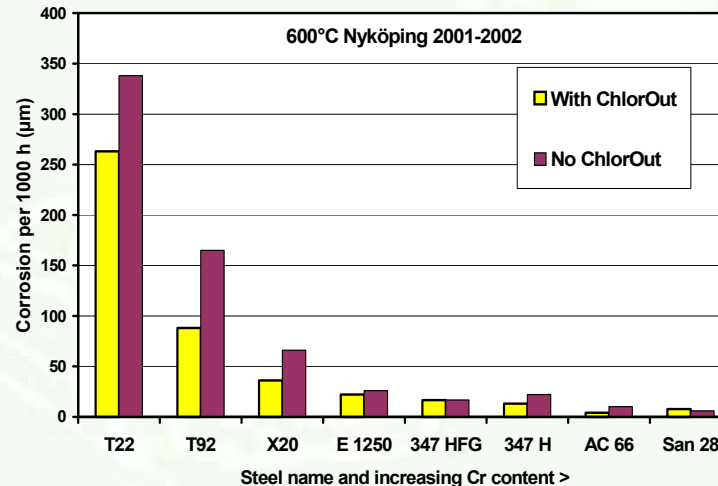
Scientific and Technical Assessment

Vattenfall Utveckling AB

- Vattenfall’s objective is to show that superheater corrosion in biomass-fired boilers can be reduced with the use of the “ChlorOut” additive and by the selection of the correct material.
- ChlorOut is a sulphate containing compound which is sprayed into flue gases with the aim of reducing corrosion and fouling.
- Tests performed in a 105 MW FB boiler in Nyköping showed that ChlorOut reduced the amount of alkali chlorides in the deposits and reduced the superheater corrosion rates by about 50%.



Schematic diagram of the ChlorOut system in Nyköping.



Corrosion per 1000 hours for some superheater steels.

Summary

- Laboratory tests are important for detailed corrosion mechanism studies. The objectives of the laboratory work are to contribute test data on candidate materials performance under various corrosive conditions.
- Pilot-scale reactors have been applied in studying the interaction of sulphur – chlorine – silicate species.
- Pilot-scale tests have been supported by large-scale power plant studies where biomass and waste combustion and their effect on boiler fouling and corrosion has been monitored.
- As an expected result wider range of waste and biofuels would be used in existing and new boilers in Europe.
- Project results contribute also to achieving the goals of the Kyoto Protocol as well as for higher operational reliability, cost savings, less shut-downs, higher boiler steam properties and efficiency of the power plants.
- Results will be utilized in practice for power plant operation, for boiler design, for defining limits for fuel mixture ratios, and for heat exchanger material selection.