

KME-717

Boiler corrosion at lower temperatures – influence of lead, zinc and chlorides

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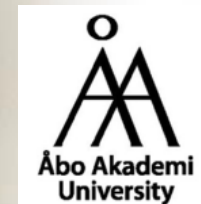
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Project goals

- To find out if lead, zinc and their chlorides causes serious corrosion problems in the temperature range 150-420°C in boilers firing used wood,
 - and if the attack is worsened by the use of additive that reduce alkali chloride corrosion on superheaters at higher temperatures.
- Based on the knowledge acquired by full-scale probe testing and the results of modelling and laboratory testing solutions for minimizing potential problems will be suggested.
- To investigate and describe the ongoing corrosion processes and make an attempt to explain the mechanisms behind them to some extent.

Three project parts

Thermodynamic calculations – Andritz

Field corrosion tests – Vattenfall, Swerea KIMAB

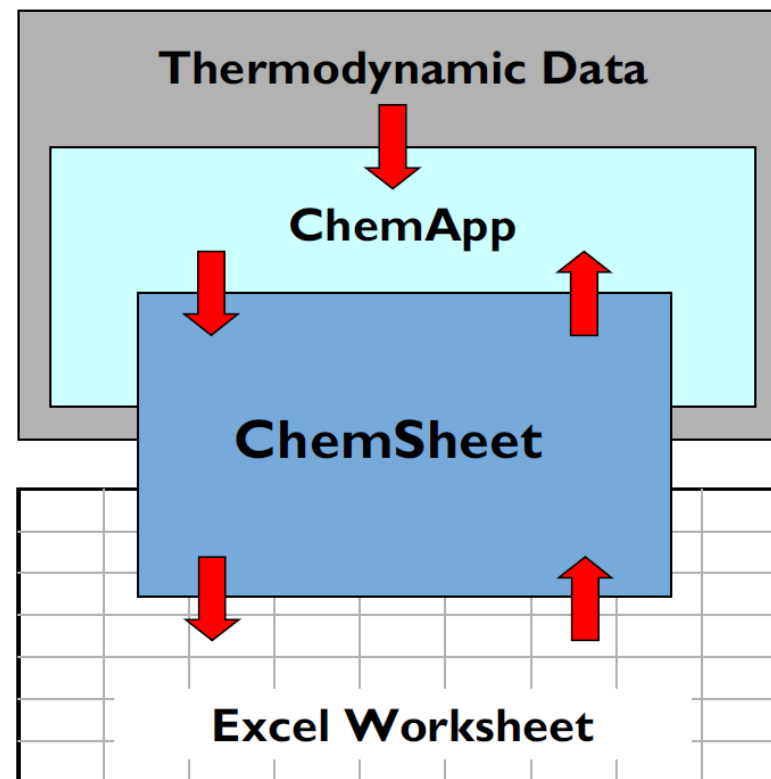
Laboratory corrosion tests – Åbo Akademi

RESULTS

Thermodynamic calculations – Andritz

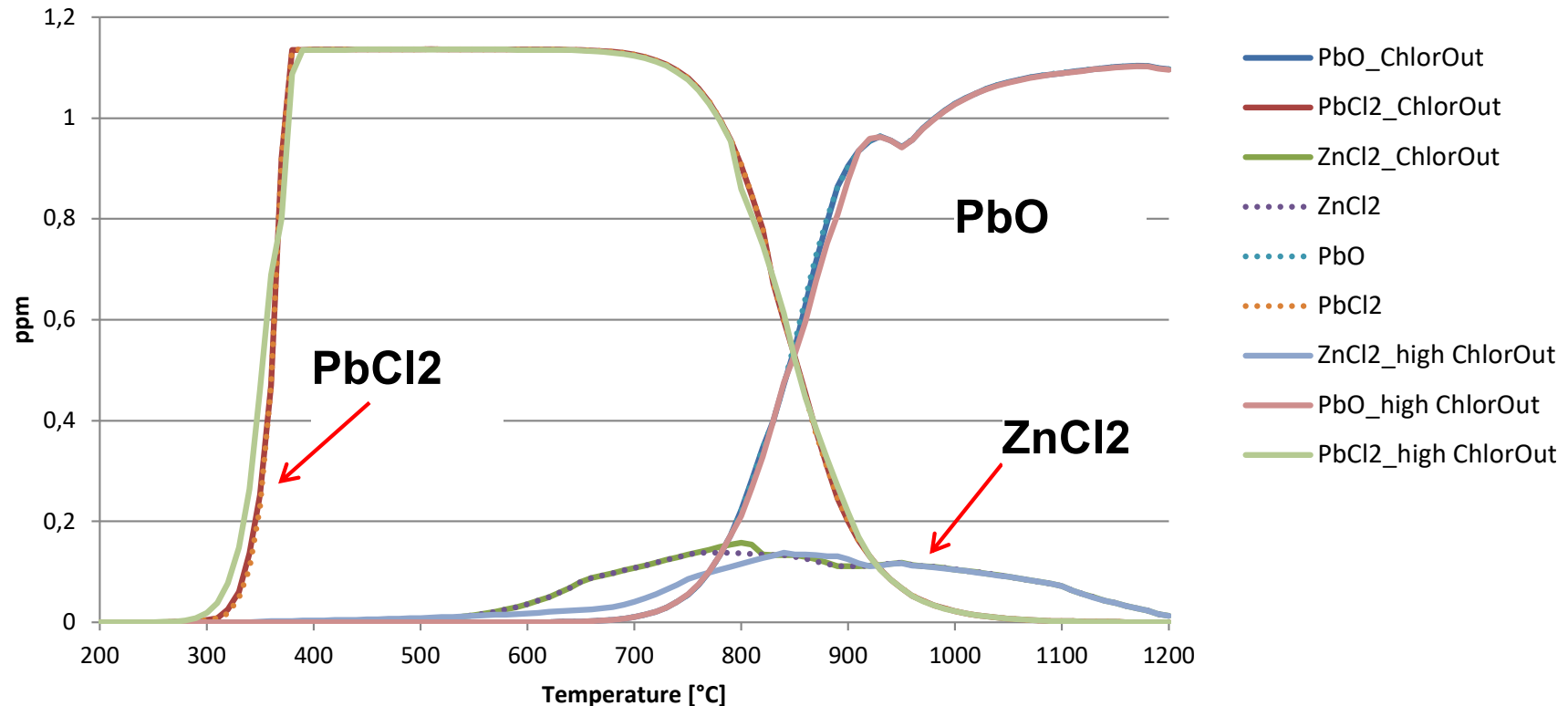
Chemsheet calculations by Andritz

- **Chemsheet** works as an add-in program of general thermodynamics in **Excel**.
- The thermochemical programming library **ChemApp** is used in combination with its application-specific thermochemical data
- ChemSheet is straightforward and requires no programming skills other than normal Excel use
- To the user, the process model can be just one Excel-file
- Andritz has a tailor-made database from Åbo Akademi University (“Andritz Melt”)



Chemsheet – results

Pb, Zn in gas phase, typical analysis



- Typical fuel in Jordbro results in PbCl₂ and ZnCl₂ at lower T and PbO at higher T
- No significant change in ZnCl₂/PbCl₂ with ChlorOut

Chemsheet – Final conclusions

- Temperature level very low for thermodynamic calculation in general
- No significant change in $\text{ZnCl}_2/\text{PbCl}_2$ with ChlorOut
- Zn and Pb sensitivity analysis
 - Zn at elevated levels ($0,273 \rightarrow 0,5 \rightarrow 2$ g/kg)
 - Pb at elevated levels ($0,067 \rightarrow 0,4 \rightarrow 1$ g/kg)
 - no significant difference in composition in temperature ranges of interest for this project

RESULTS

Field tests – Vattenfall, Swerea KIMAB

Jordbro P7

- BFB boiler
- Commissioned 2010
- 63 MW_{th}, 20 MW_{el}
- Steam data: 80 bar, 470°C
- Fuel 100% recycled (waste) wood
- ChlorOut (system with ammonium sulphate additive)



Performed tests

Test 1

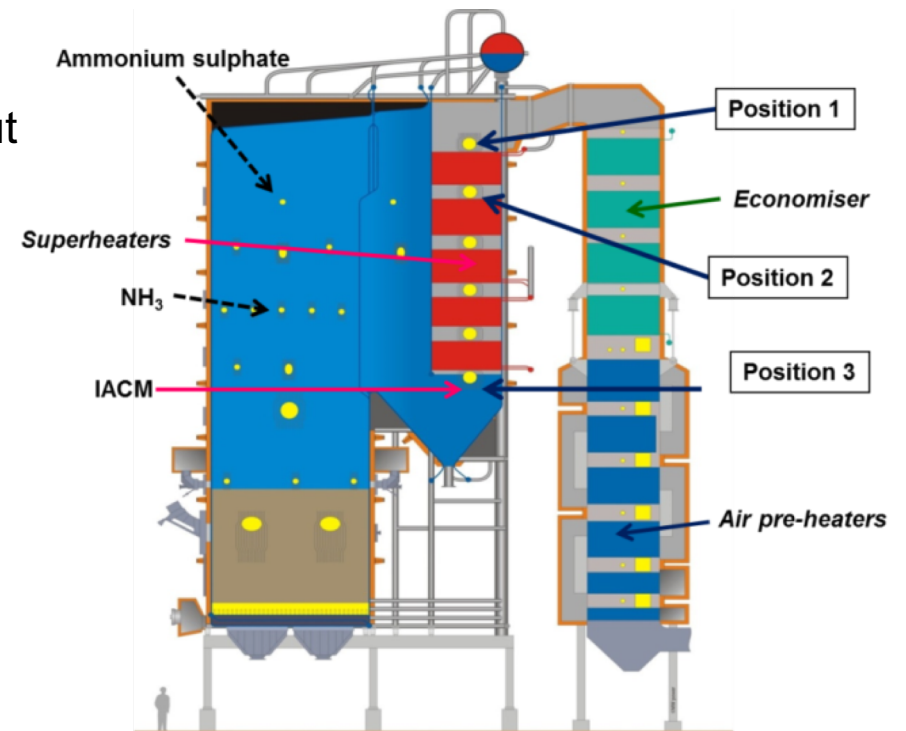
- 8h gradient probes with and without Chlor Out, 190-440 °C

Test 2

- 3 h deposit probes 250, 300, 350 °C with and without Chlor Out
- 6 weeks corrosion probe 250, 300 350 °C with Chlor Out

Test 3

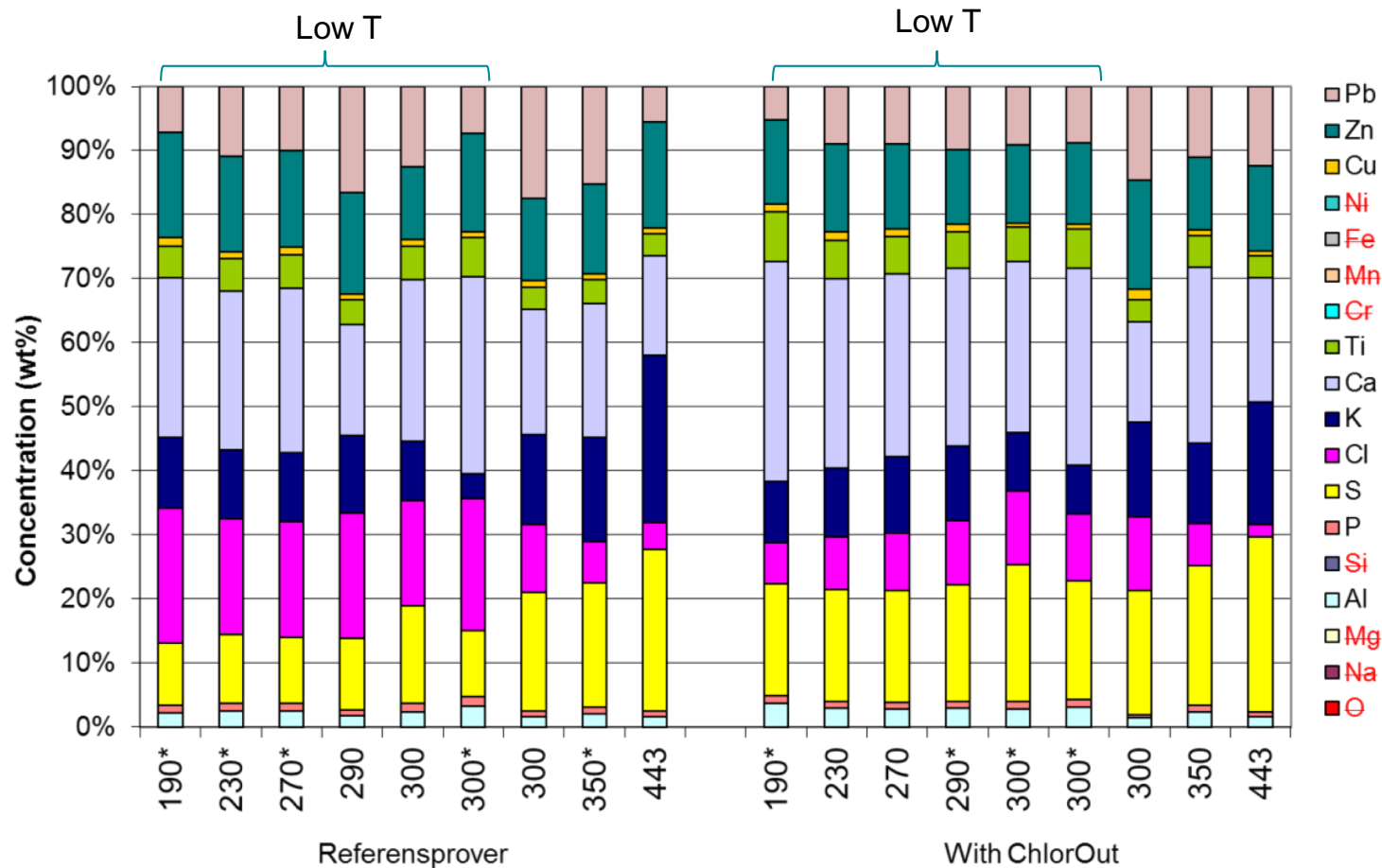
- 6 weeks corrosion probe at 300 °C with Chlor Out



Summary Test 1 (8 h)

- deposit analysis

- Less Cl when using ChlorOut
- No dramatic difference regarding Pb+Zn



Summary Test 2

(deposit probes and 6 week test)

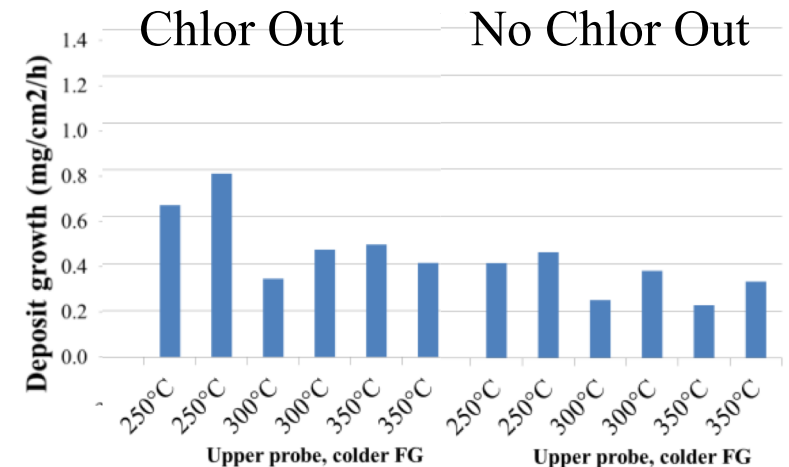
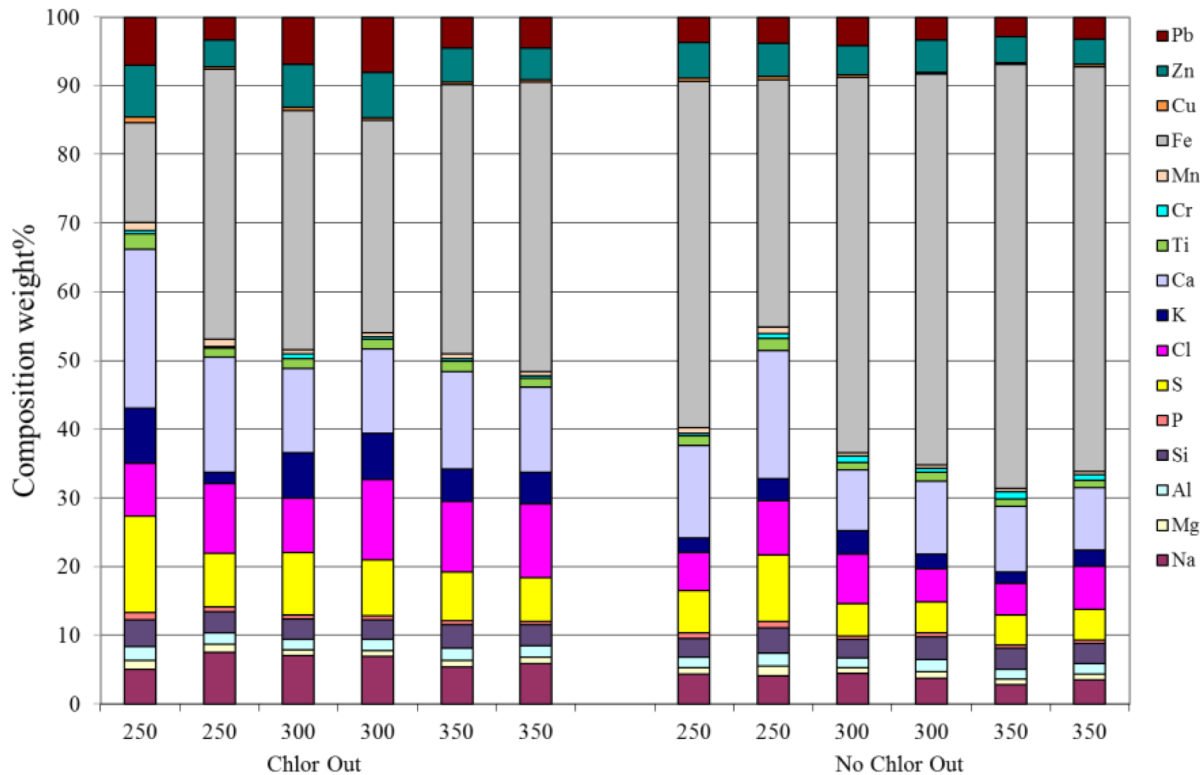
- Exposure in Jordbro
- Ring samples
- Temperatures: 250, 300 and 350 °C

Tested samples

- Deposit probes (3 h) before long run with Chlor Out
- Long run 6 weeks with Chlor Out
- Deposit probes (3 h) after long run both with and without Chlor Out

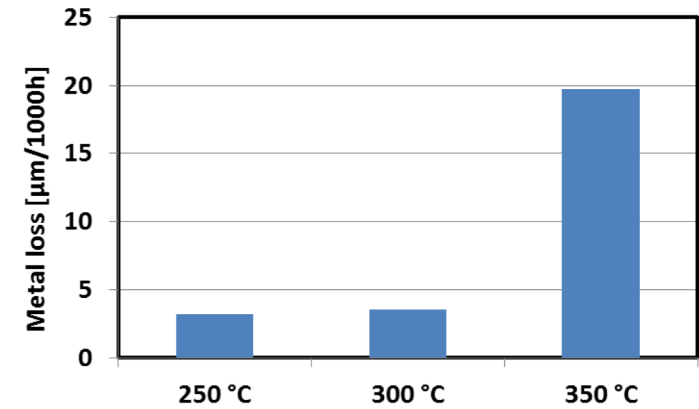
Deposit composition (upper probe, colder flue gas)

- Higher iron signals indicating thinner deposits without Chlorout.
- Indication of more Pb for 300 °C with ChlorOut.
- In general larger spread in Pb/Zn with ChlorOut



Corrosion probes 6 weeks, (upper probe, colder flue gas)

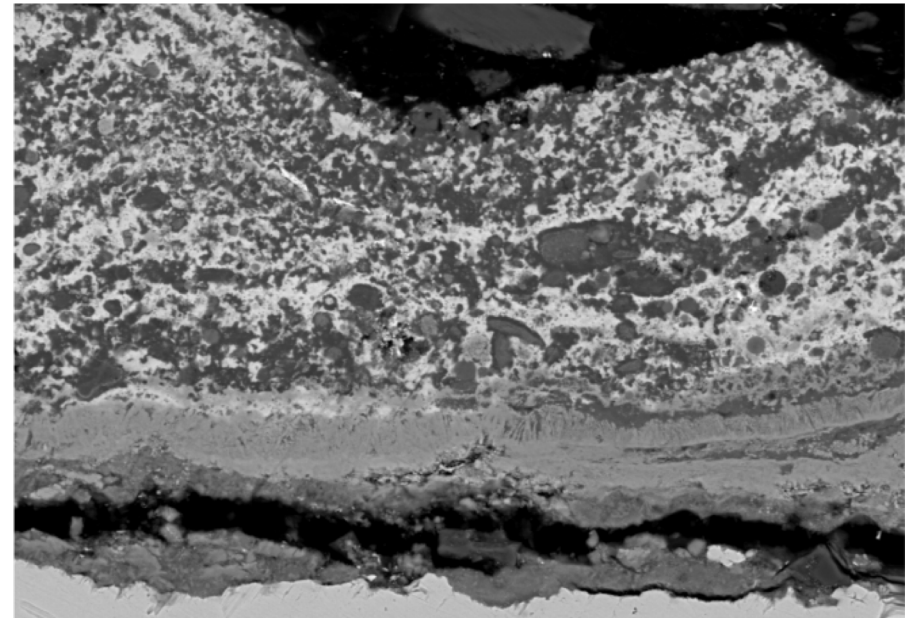
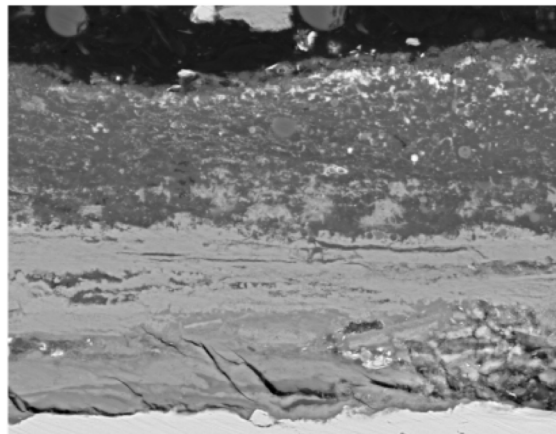
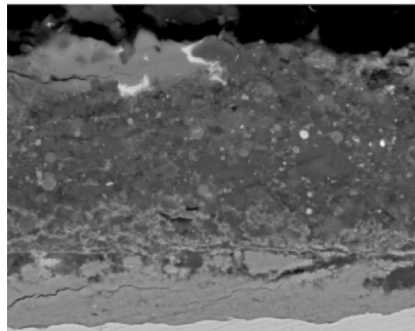
- Deposit and corrosion product layer increase in thickness with increased temperature.



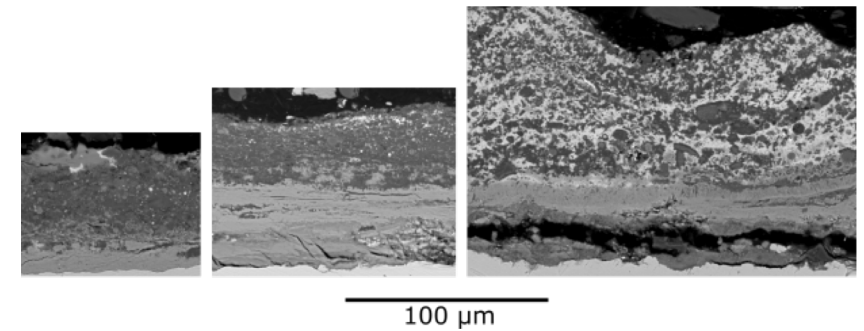
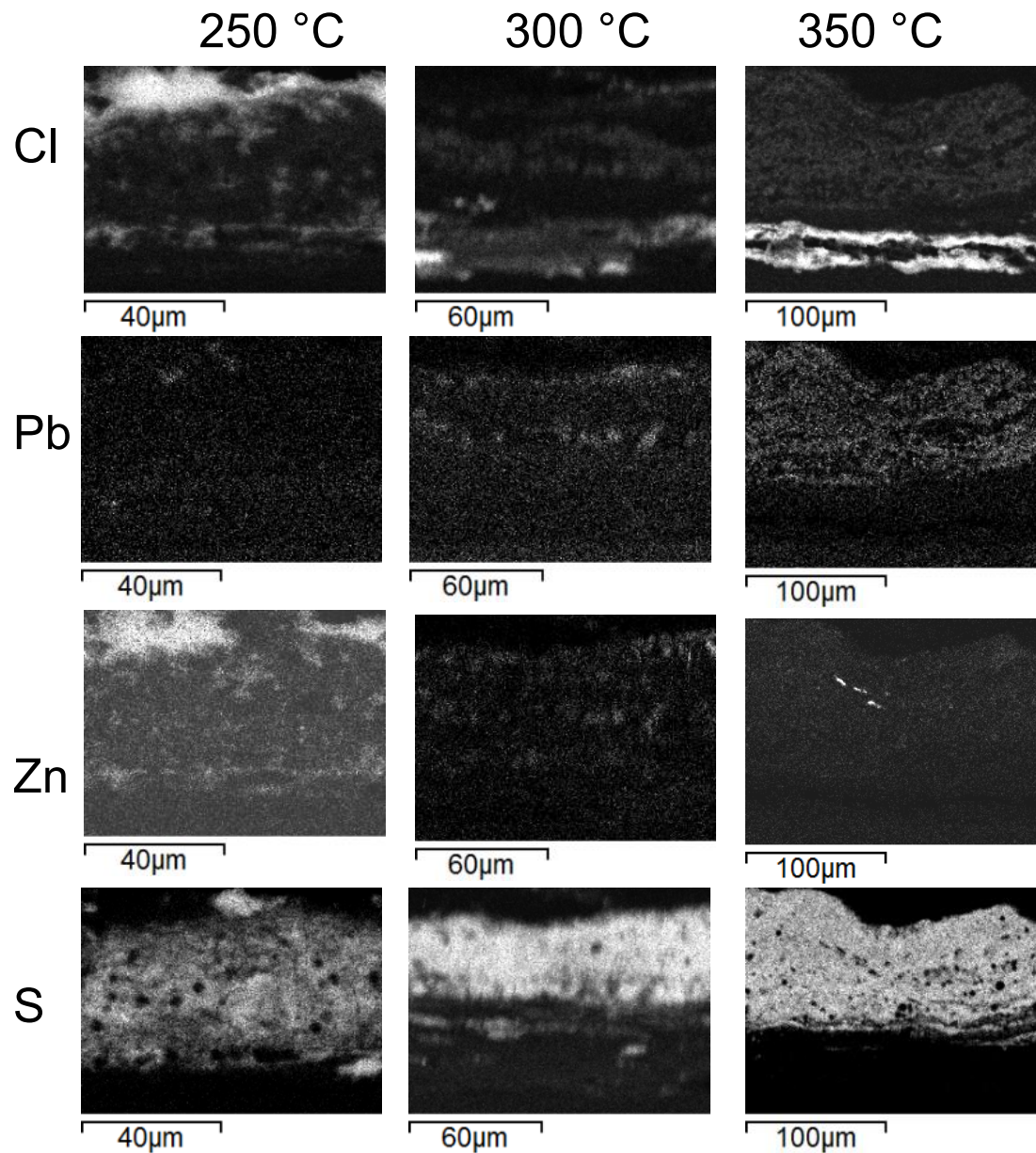
350 °C

300 °C

250 °C



100 µm



At 250 °C

- ZnCl_2 in deposit, a little iron chloride at interface

At 300 °C

- Pb/ ZnCl_2 in deposit, more iron chloride at interface

At 350 °C

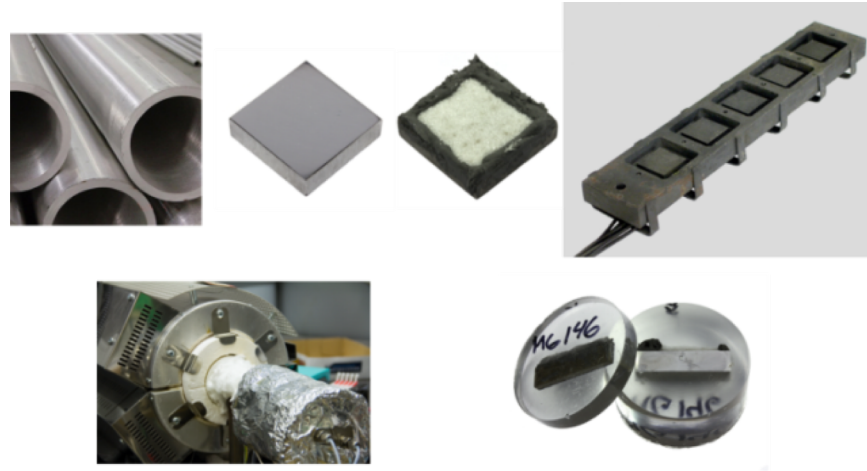
- Much Pb-compounds in deposit both in combination with S and Cl, much iron chloride at interface

Main conclusion – field exposures

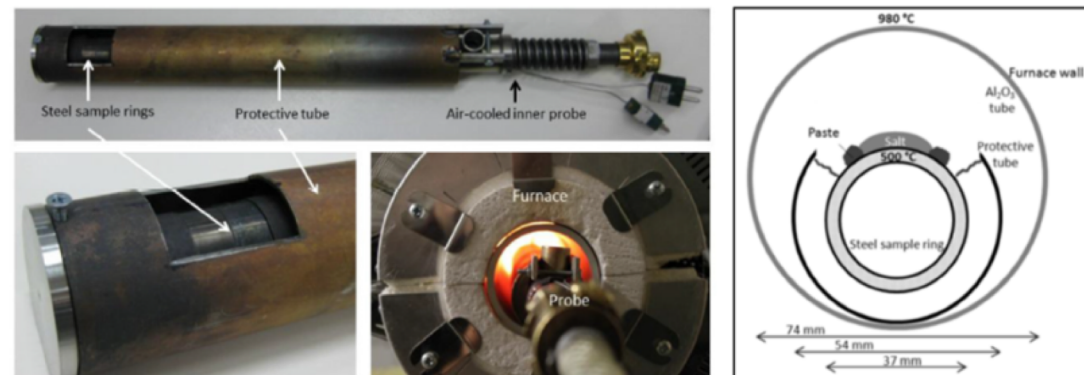
- The amount of Pb, Zn and Cl in the deposits from short exposures (3h and 8h) does not show that substantially more of these elements deposit at the surfaces at lower temperatures (for the investigated) when ChlorOut is used.
- Cross sections from short exposures do not show an increase in corrosion when ChlorOut is used.
- Increased corrosion with temperature for cold flue gas but not for hot
- At lower temperatures (250 °C and 300 °C) more corrosion is observed when the flue gas is hotter (lower probes).
- Pb-containing compounds in the deposit are increasing in amount with temperature. At 250 and 300 degrees in combination with chlorine and at 350 degrees in combination with sulphur.

Laboratory corrosion tests – Åbo Akademi

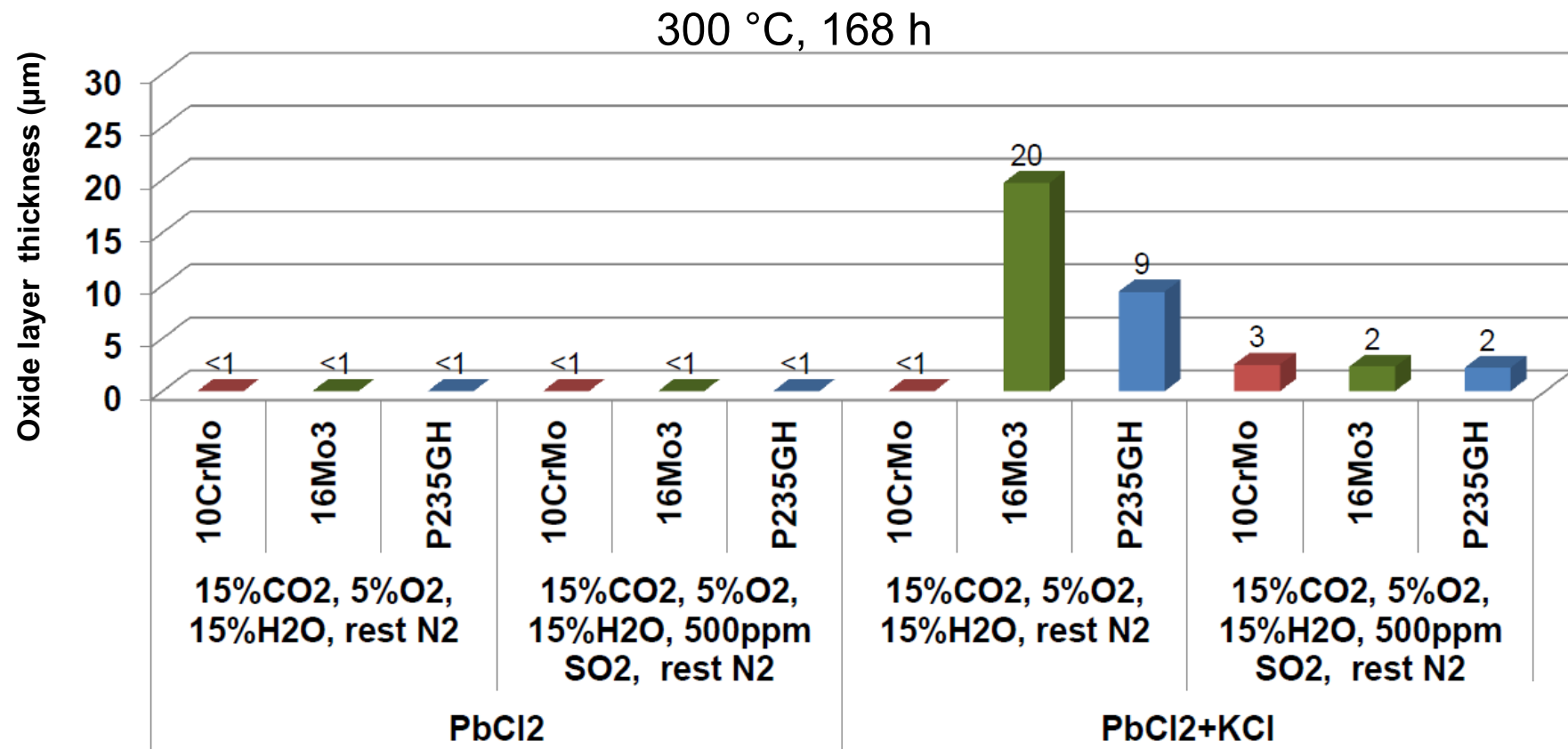
- Isothermal tests
 - Selected salt mixtures



- Gradient probe tests
 - Selected salt mixtures



Isothermal corrosion tests at Åbo Akademi University

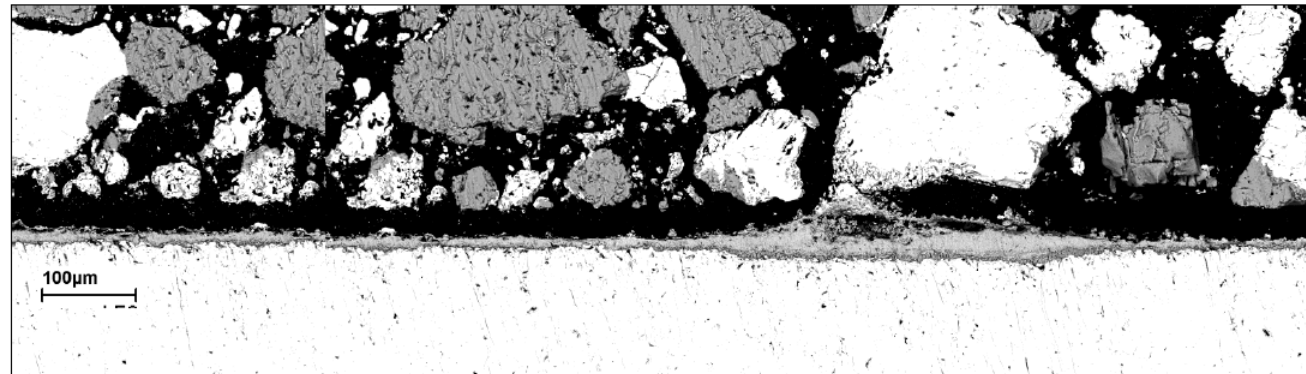


- Corrosion only in presence of mixed salt
- Corrosion decreases with SO₂ present

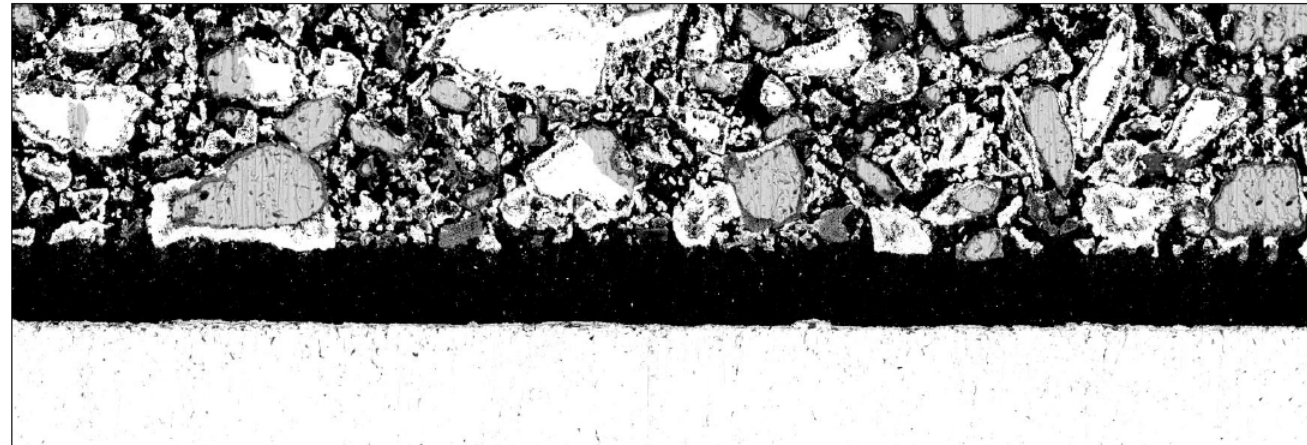
Isothermal corrosion tests at Åbo Akademi University

300 °C, 168 h

16Mo3 exposed with PbCl_2/KCl mixture in Gas 2 no SO_2)



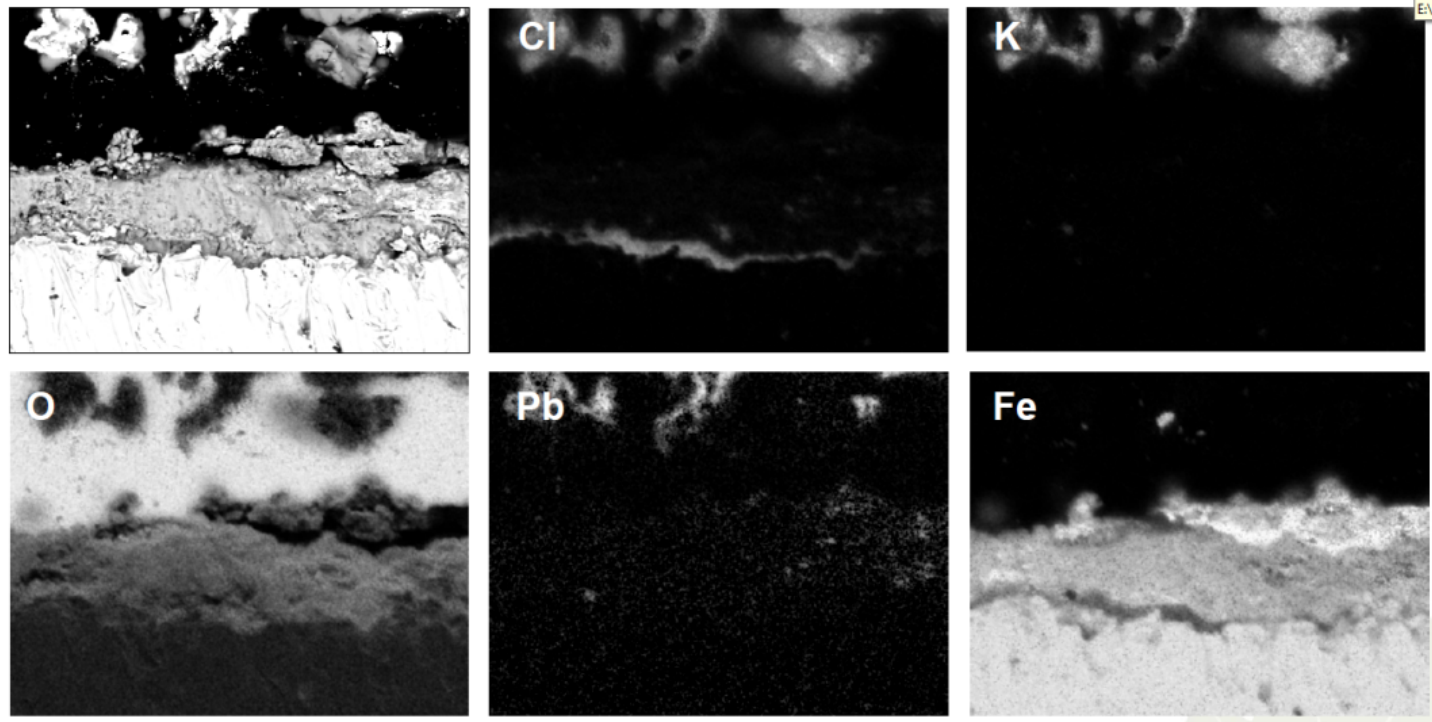
16Mo3 exposed with PbCl_2/KCl mixture in Gas 1 with 500 ppm SO_2)



Isothermal corrosion tests at Åbo Akademi University

300 °C, 168 h

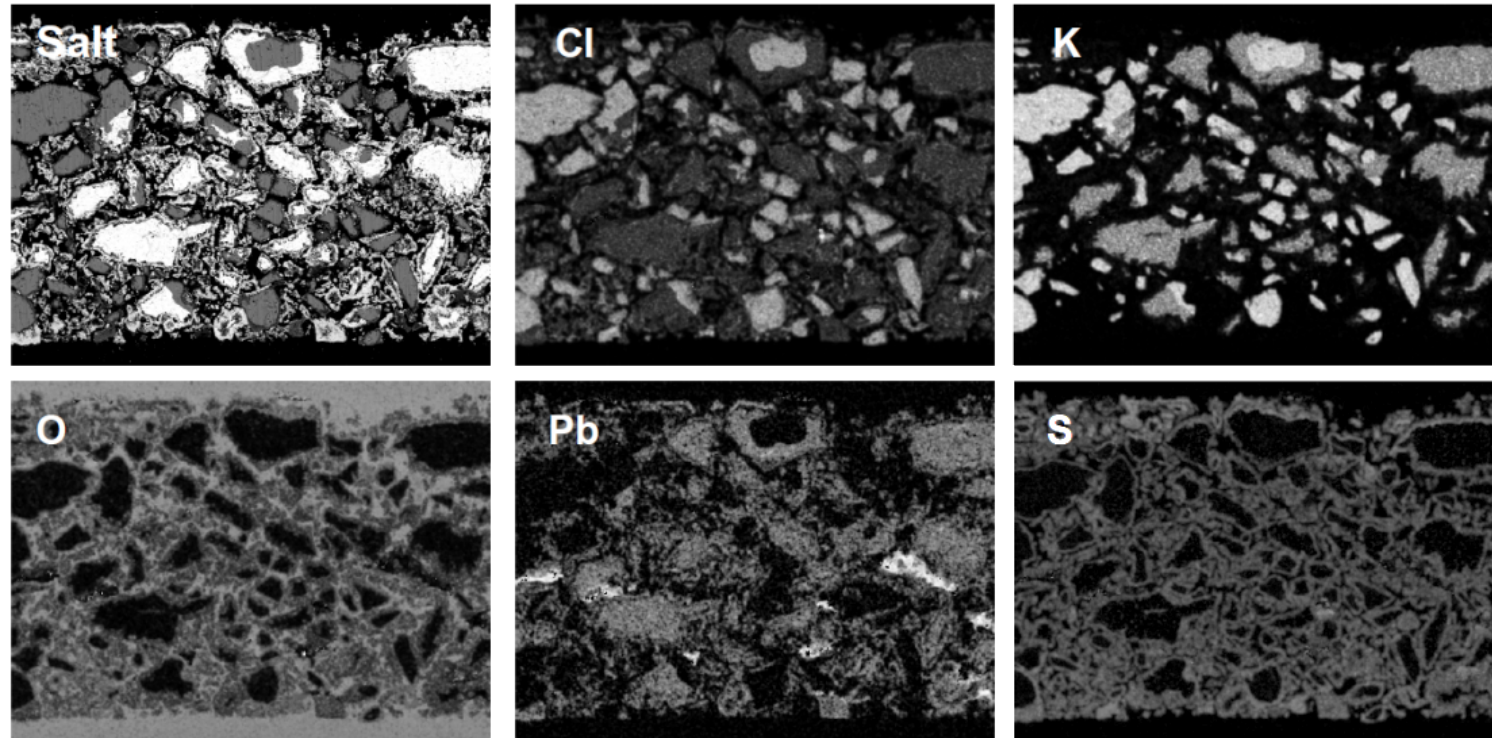
16Mo3 exposed with PbCl_2/KCl salt mixture in Gas 2 without SO_2)



Isothermal corrosion tests at Åbo Akademi University

300 °C, 168 h

PbCl₂/KCl salt mixture exposed in Gas 1 with 500 ppm SO₂)



Project outcome

- To find out if lead, zinc and their chlorides causes serious corrosion problems in the temperature range 150-420°C in boilers firing used wood,
 - and if the attack is worsened by the use of additive that reduce alkali chloride corrosion on superheaters at higher temperatures.



Results in this project show the presence of lead and zinc in deposits and corrosion products. Their presence does however not seem to increase when Chlor Out is used. The corrosion does not increase significant by use of the additive. (Note that long time tests only have been performed with and not without Chlor Out)

Project outcome

- Based on the knowledge acquired by full-scale probe testing and the results of modelling and laboratory testing solutions for minimizing potential problems will be suggested.



Based on the results in this project, the use of Chlor Out is not believed to increase the corrosion

- To investigate and describe the ongoing corrosion processes and make an attempt to explain the mechanisms behind them to some extent.



Indication that sulphation of Cl-containing salts decreases corrosion



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