Johan Gadolin
PROCESS CHEMISTRY CENTRE

Åbo Akademi University

Understanding Low Temperature Corrosion in BL Combustion

Nikolai DeMartini, Henri Holmblad, Emil Vainio

Background

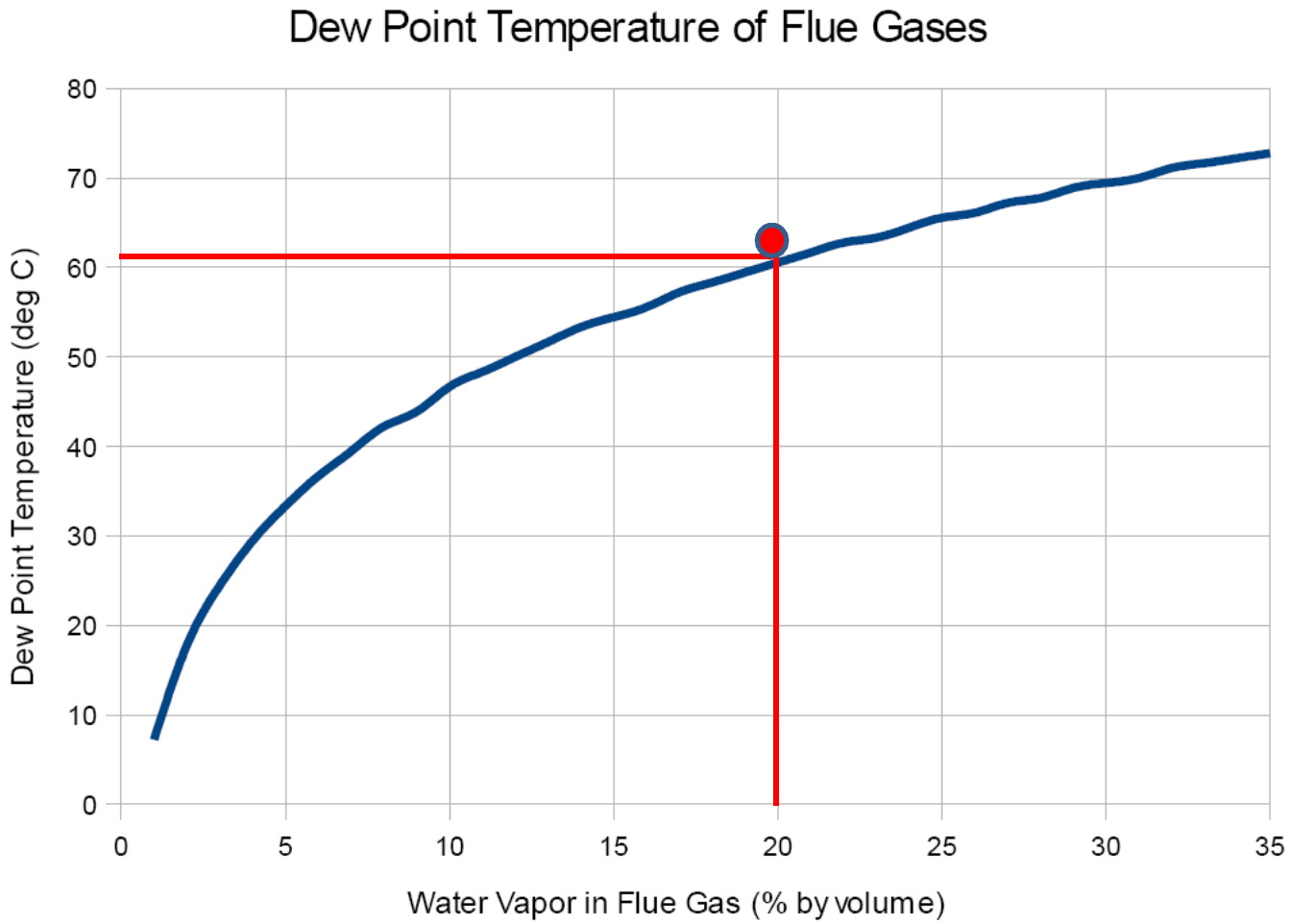
- This SKY project has funded the DI work of Henri Holmblad at ÅAU

Background

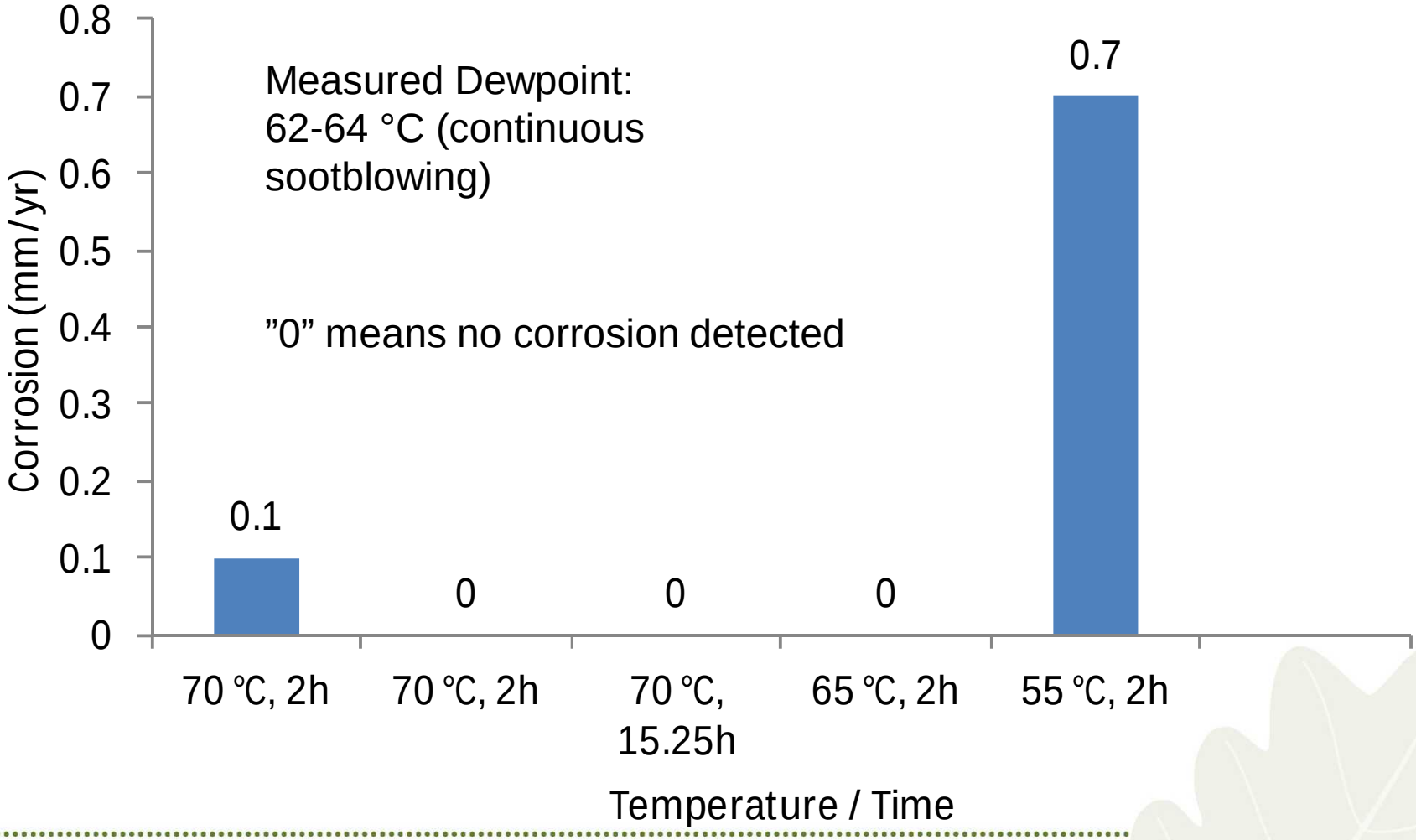
- Industrial interest in extracting more energy from flue gases
- Some historical industrial observation of low temperature corrosion – not well documented
- H_2SO_4 acid dewpoint previously thought to exist in recovery boilers

Background - dew point at Rauma

● = measured dew point

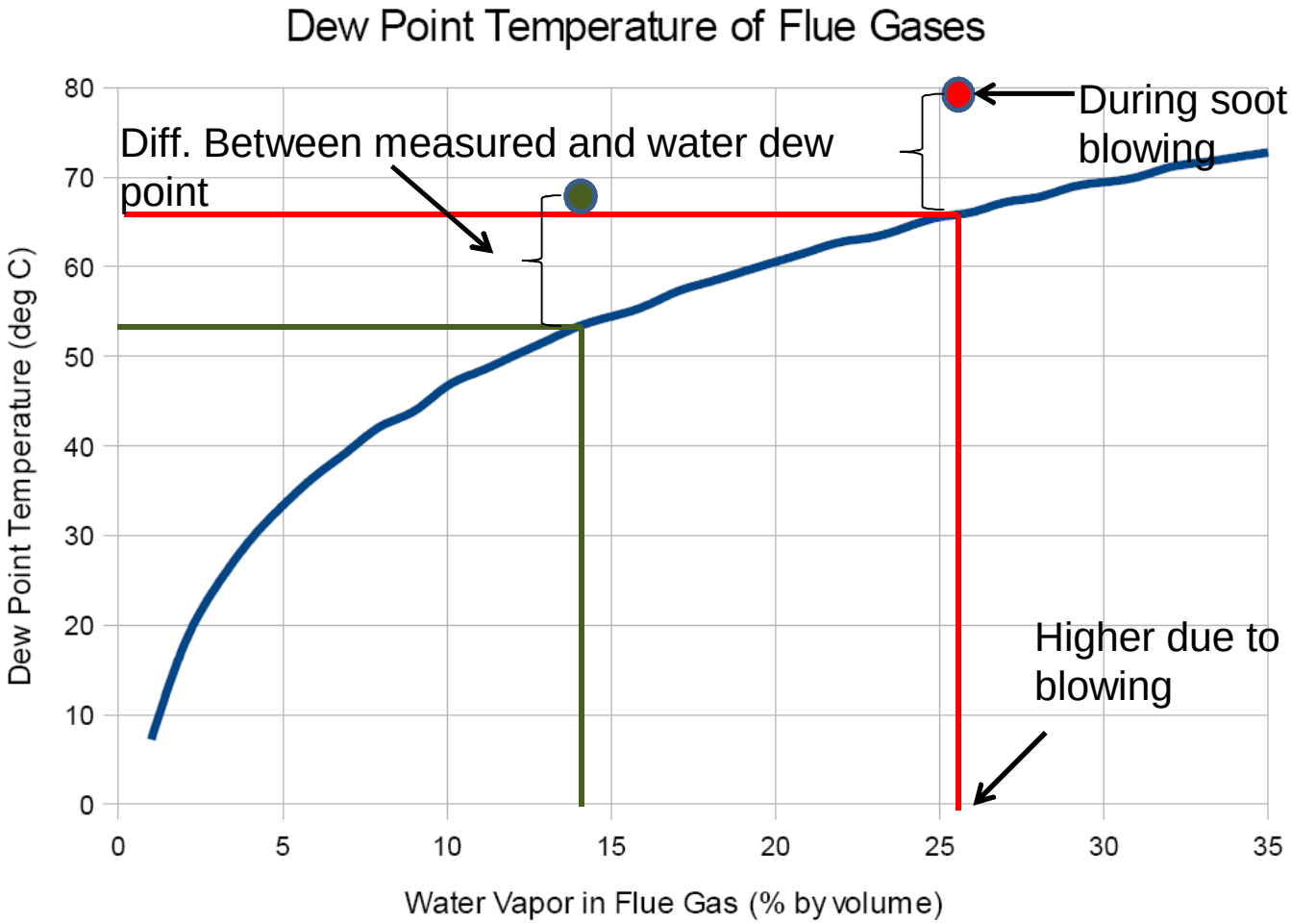


Background - corrosion probe results at Rauma

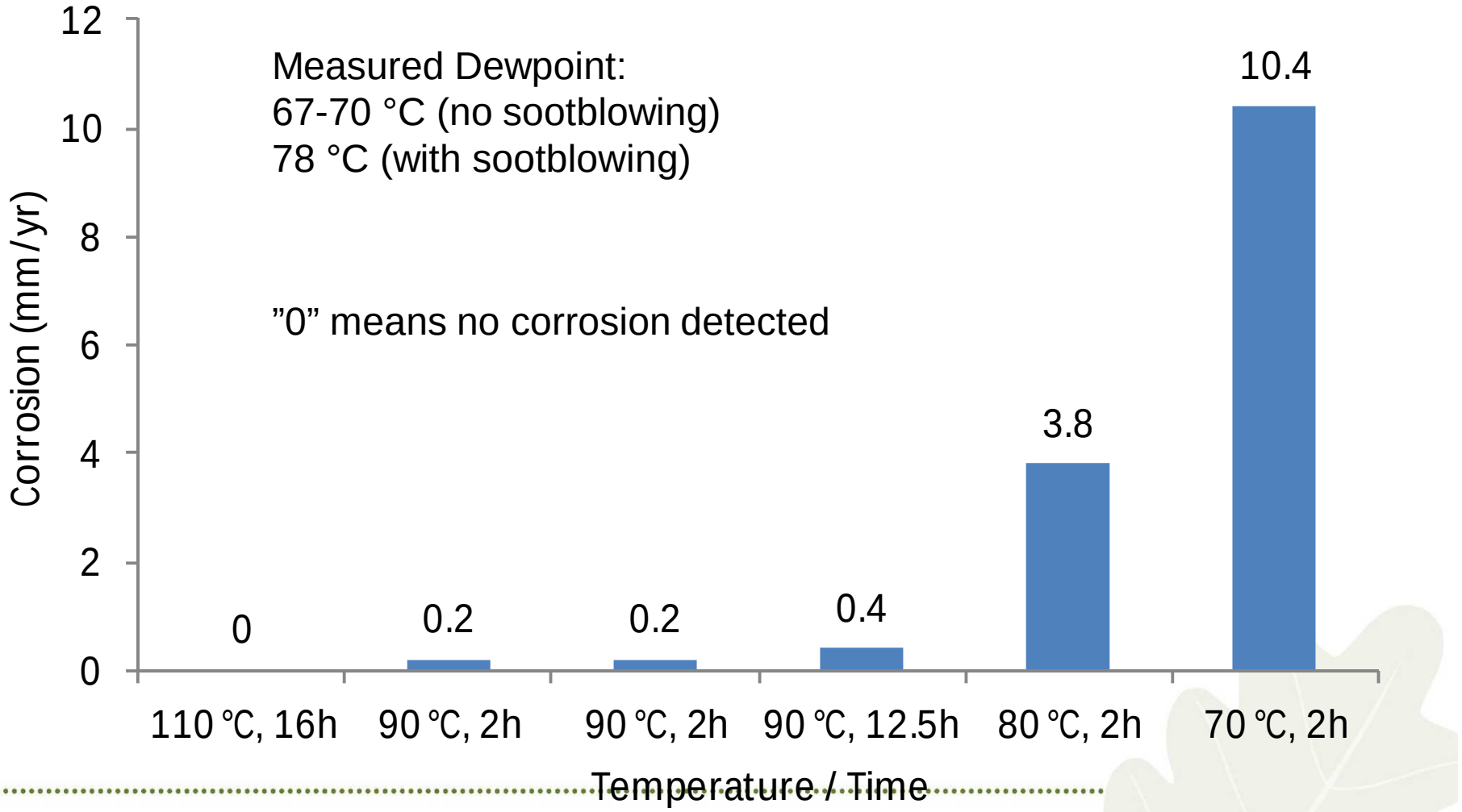


Background - dew point at Heinola

= measured dew point



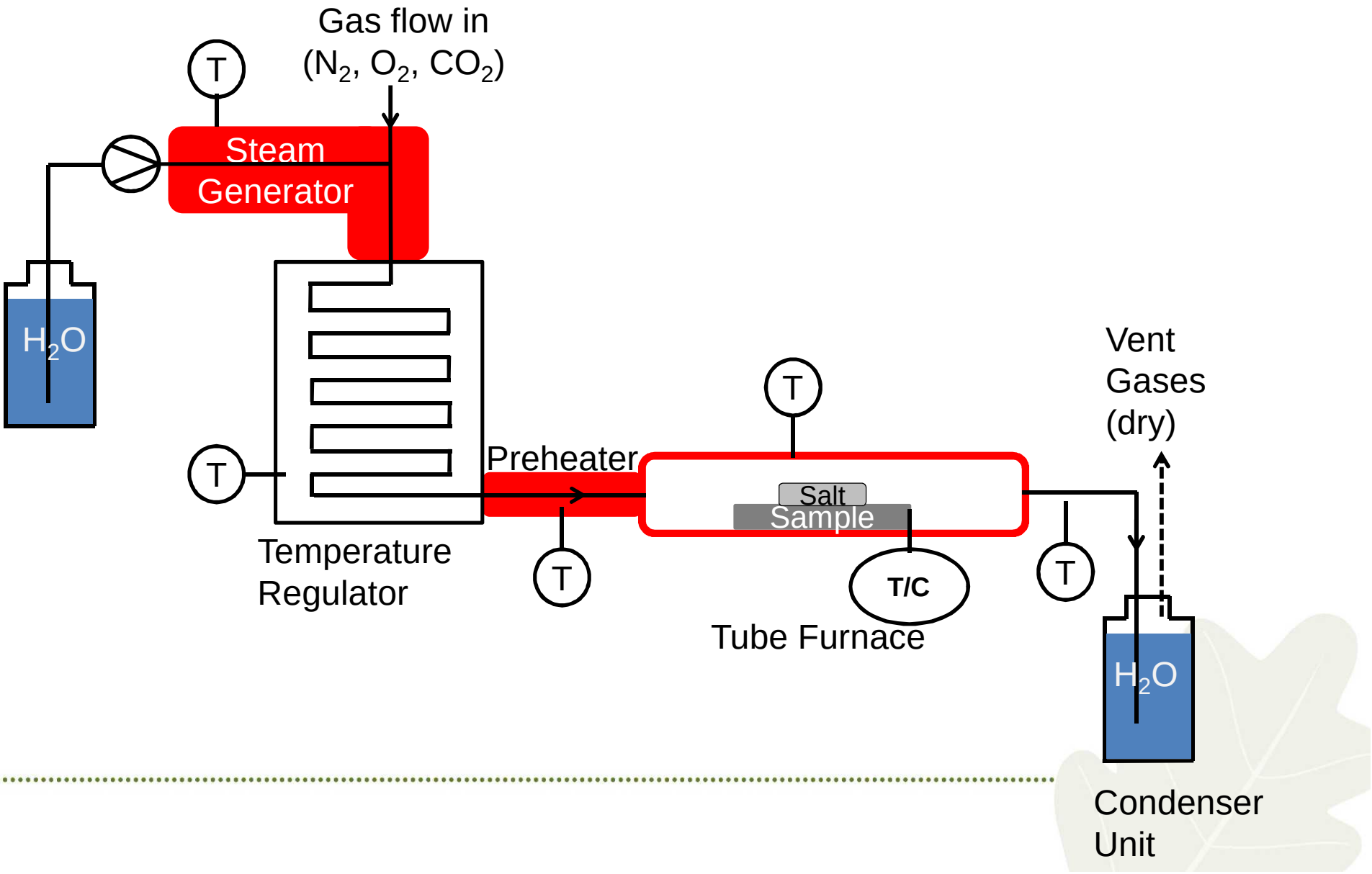
Background - corrosion probe results at Heinola



Objectives

- Hypothesis: hygroscopic salts absorb water, resulting in dew point corrosion
- Hygroscopic nature of salts in recovery boilers not yet understood
- This study – Start to map out at what temperatures/vol-% H_2O carbon steel corrodes

Experimental setup



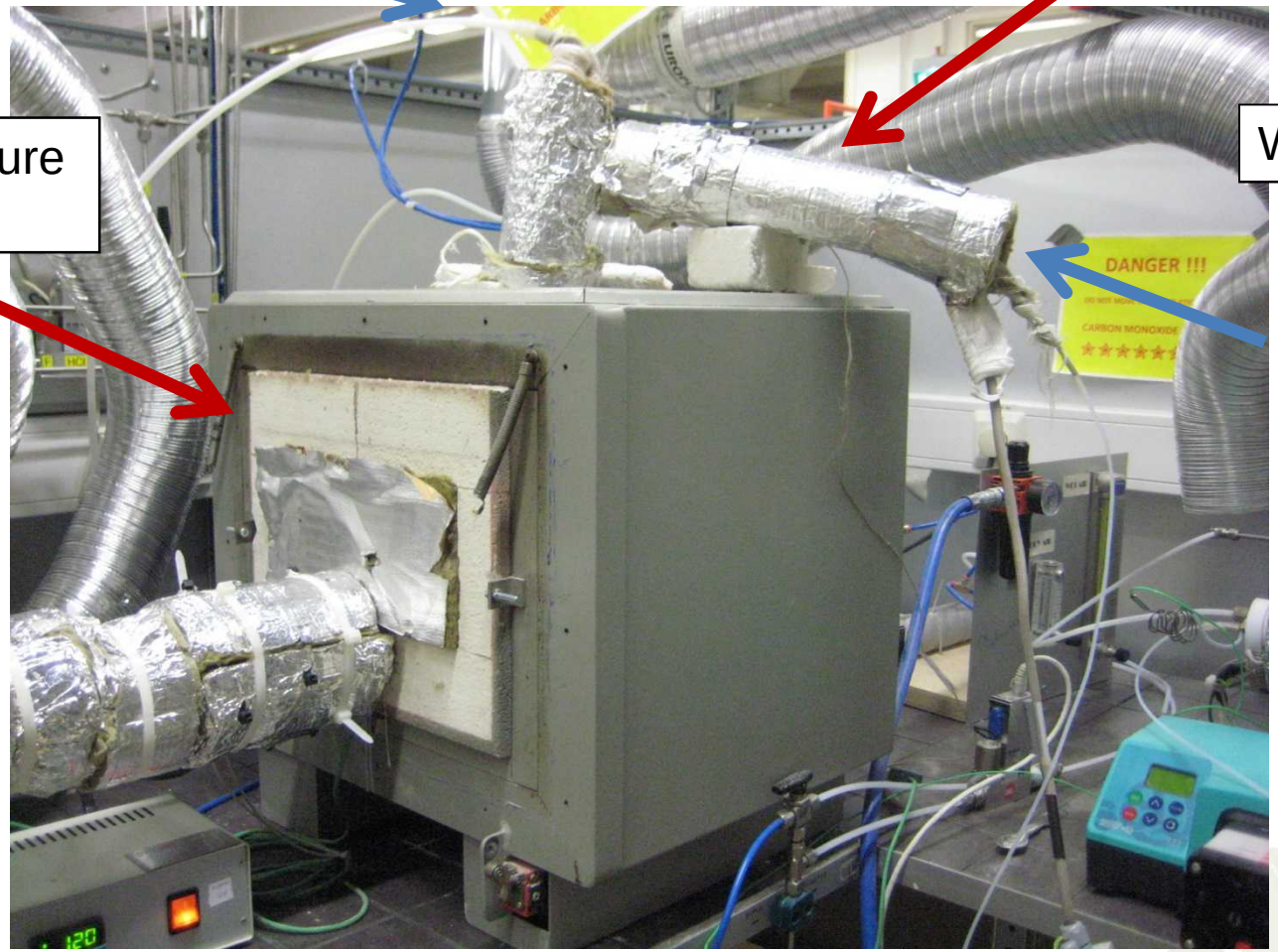
Experimental setup

Gases in

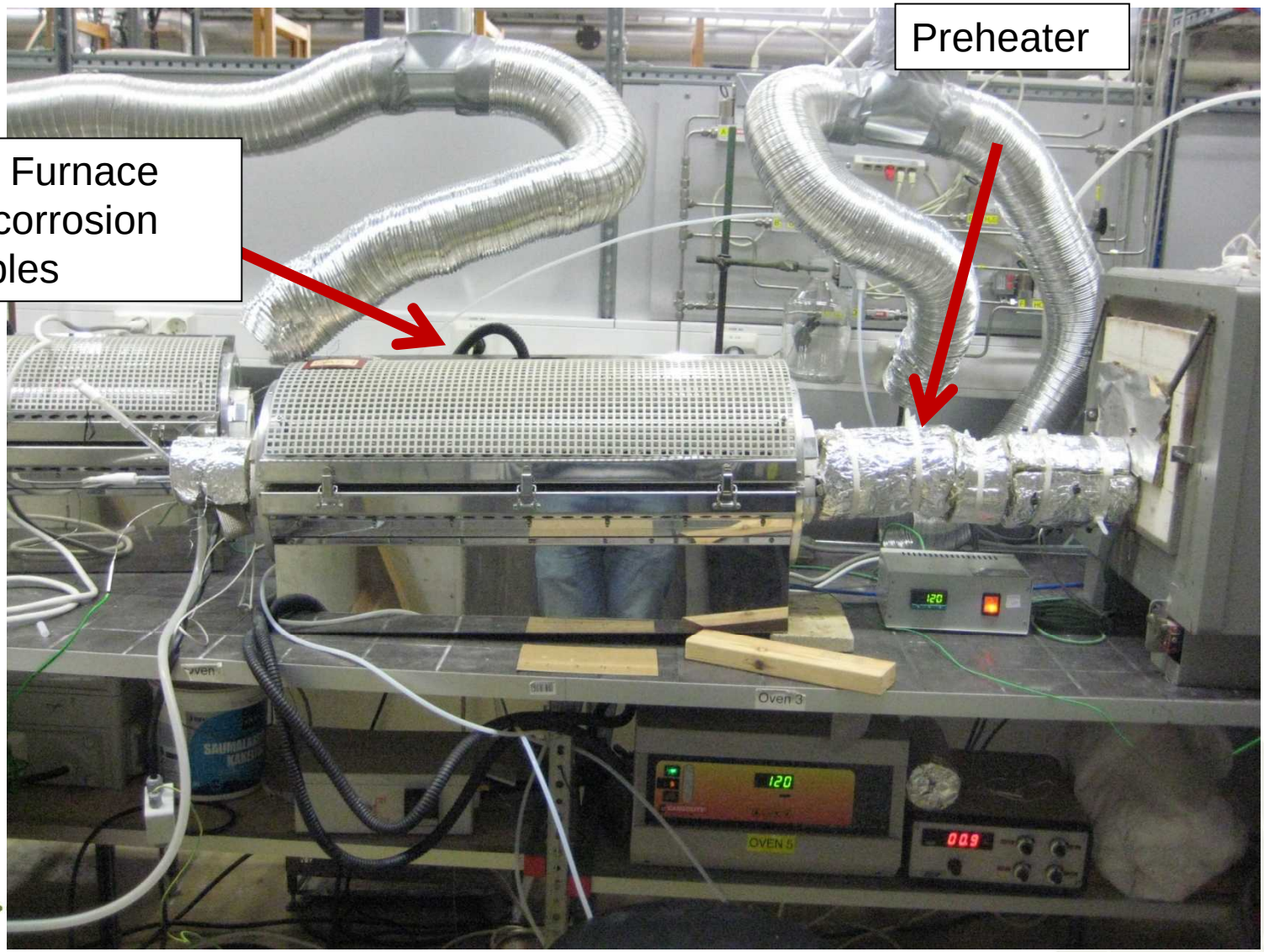
Steam Generator

Gas temperature regulator

Water in



Experimental setup



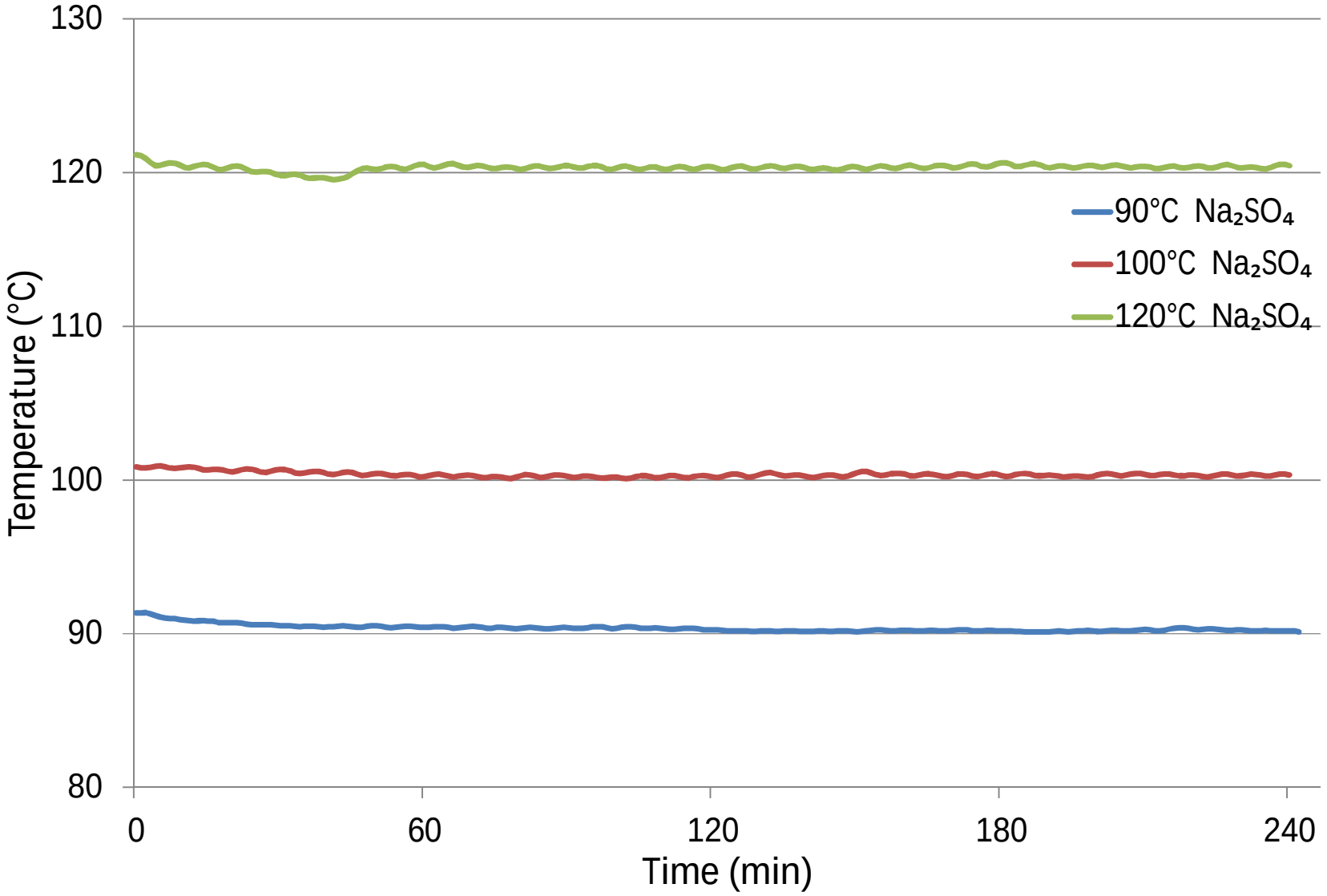
Experimental work

- corrosion sample:
  - 2x2 cm carbon steel coupon
  - 3-4 coupons per experiment
- ~0.1 g of salt on the coupon
- Ratio of dry gases during experimental runs: 15.5:3.5:1 N_2:CO_2:O_2
  - (31% N_2, 7% CO_2 & 2% O_2 at 60% H_2O)
- Corrosion determined by:
  - Visual inspection
  - (Weight loss)
  - (SEM analysis)

Experimental setup

Temparature

Na_2SO_4 4 h experiments



Experimental Plan 1

Salt	Temperature (°C)	H_2O (vol-%)	Time (h)
$NaHSO_4$	90	60	4
	100		
	110		
	120		
Na_2SO_4	90	60	4
	90		24
	100		4
	100		24
	110		24
	120		4

Salt Tests – Phase 2

Salt	H_2O (vol%)	Temp (°C)	Time (h)
Na_2SO_4	27	80	4
		90	4
	60	100	4
		100	24
		110	24
Na_2CO_3	80	90	4
		100	4
		110	24
		120	24
Na_2SO_4-Na_2CO_3 (90:10)	27	80	24
NaCl	80	110	24
		120	24
KCl	80	110	24
		110	4
		120	24

Precipitator Ash Tests – Phase 2

Salt	H_2O (vol%)	Temp (°C)	Time (h)
PA1	27	70	24
		80	24
		90	24
		100	24
		110	24
	60	100	4
		110	4
		120	4
	80	110	24
PA2	27	100	4
		110	4
	60	100	4
		110	4

$NaHSO_4$ tests – Phase 2

Salt	H_2O (vol%)	Temp (°C)	Time (h)
$NaHSO_4$	0	150	4
	27	80	4
		90	4
	60	120	4
		130	4
		140	4
		150	4

Precipitator Ash Composition

	Na (wt-%)	K (wt-%)	SO_4 (wt-%)	Cl (wt-%)	CO_3 (bal) (wt-%)
PA1	30.3	4.6	58.4	0.9	5.8
PA2	29.8	4.8	61.0	1.0	3.6

Results

Na_2SO_4

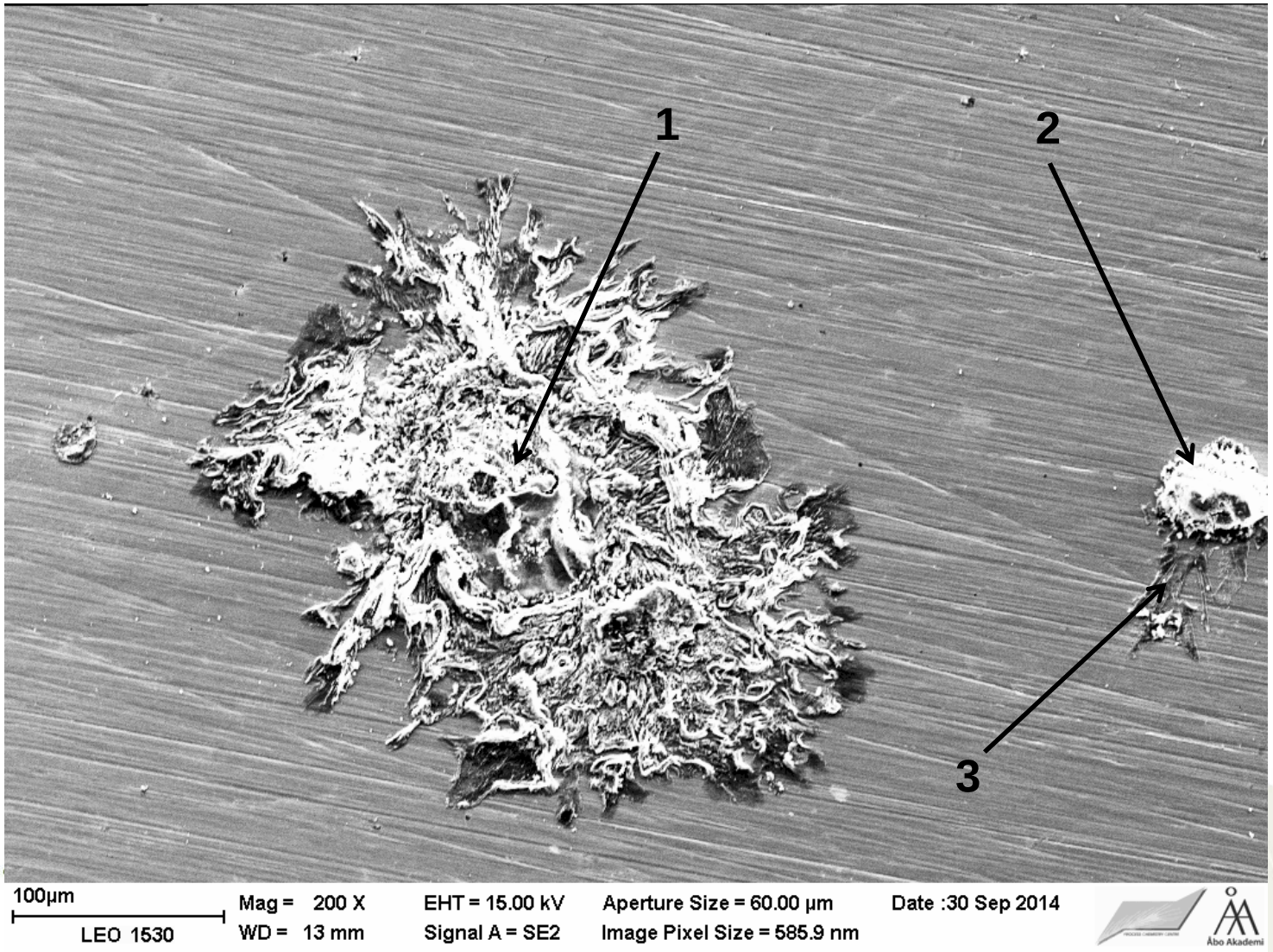
Salt: Na_2SO_4
Temperature: 90°C
H_2O: 60 vol-%
Exposure: 4h

Salt: Na_2SO_4
Temperature: 90°C
H_2O: 60 vol-%
Exposure: **24h**

Salt: Na_2SO_4
Temperature: 90°C
H_2O: 60 vol-%
Exposure: 4h

Top view

	WT%			
	Fe	S	Na	O
1	64.0	1.1	1.4	31.7
2	40.7	5.7	16.6	35.1
3	62.9	3.9	20.9	11.7

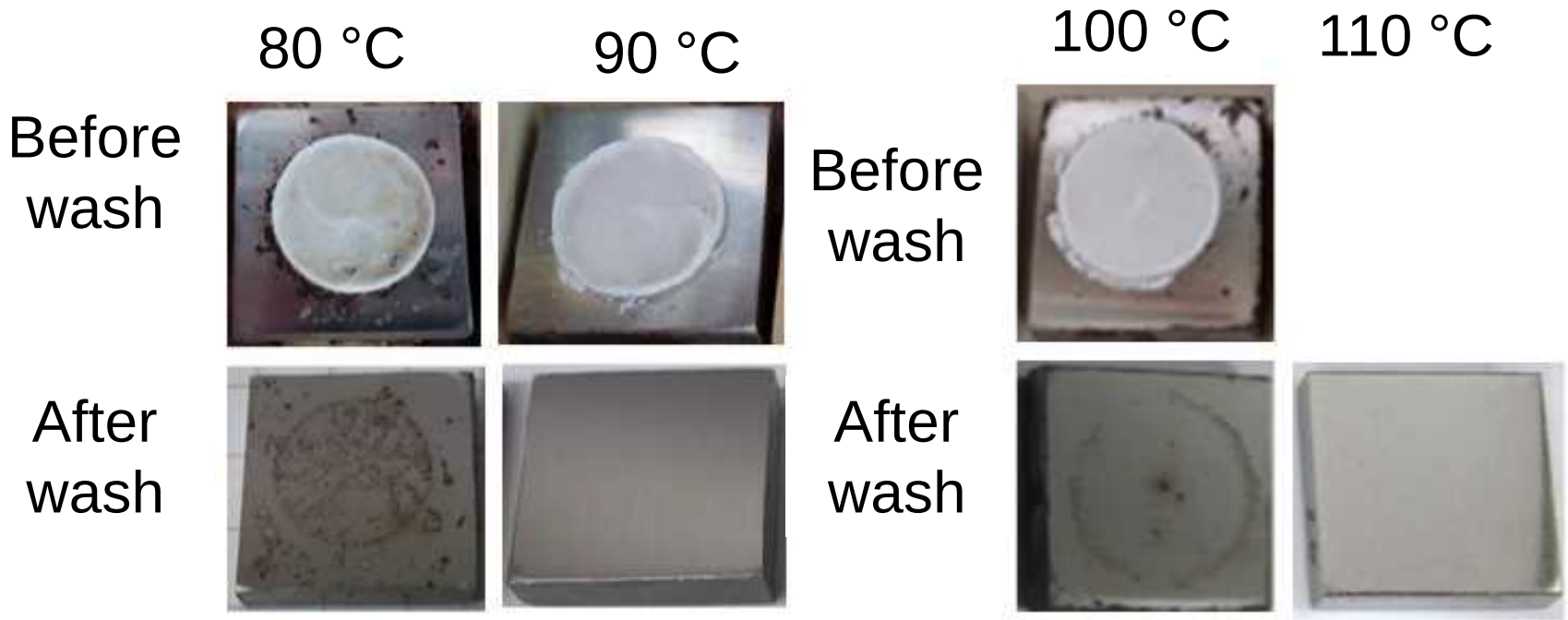


$NaHSO_4$ – Na_2SO_4 Comparison
(60 vol-% H_2O)

Na_2SO_4 – comparison of 27vol-% and 60 vol-% H_2O

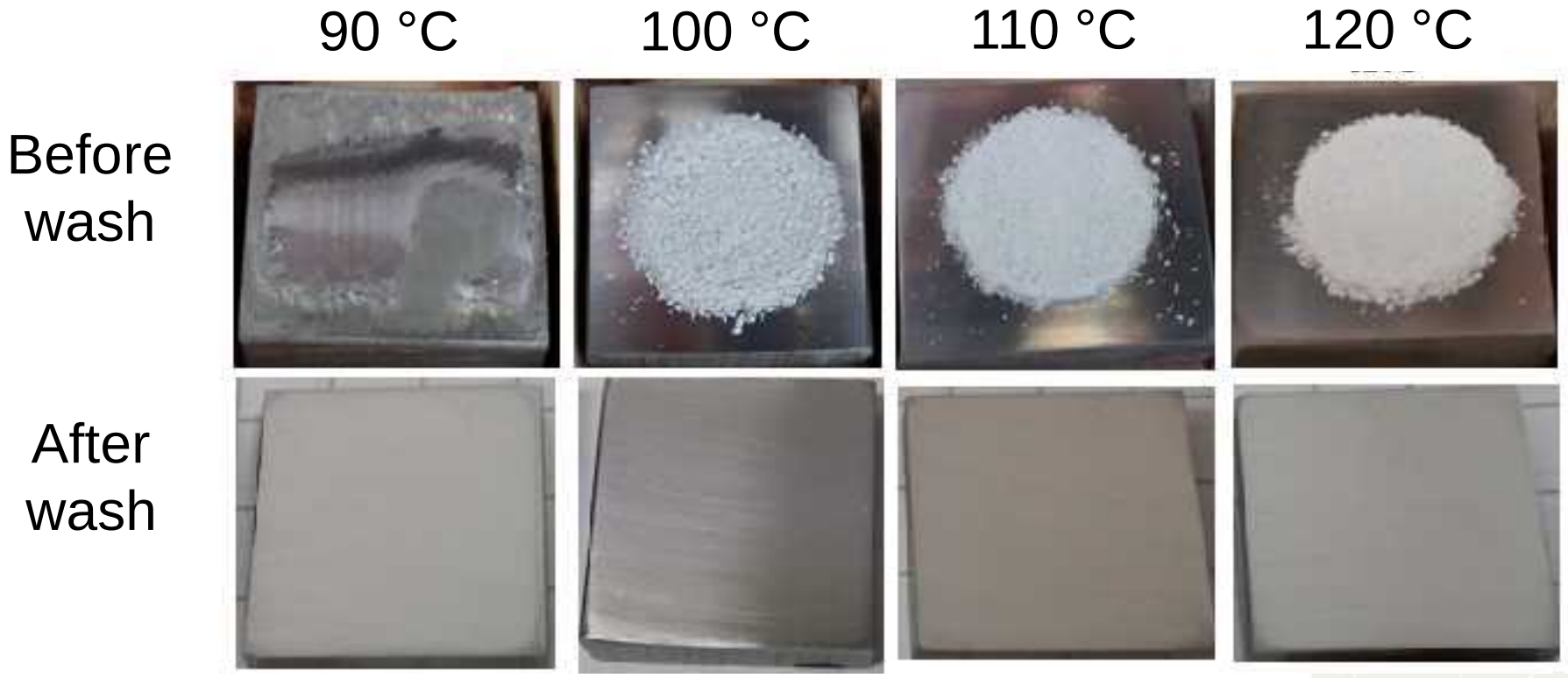
Na_2SO_4, 27 vol-% H_2O

Na_2SO_4, 60 vol-% H_2O



Na_2CO_3

Salt: Na_2CO_3
H_2O: 80 vol-%
Exposure: 4h (90 & 100 °C),
24h (110 & 120 °C)



Salt mixture

90% Na_2SO_4 – 10%Na_2CO_3

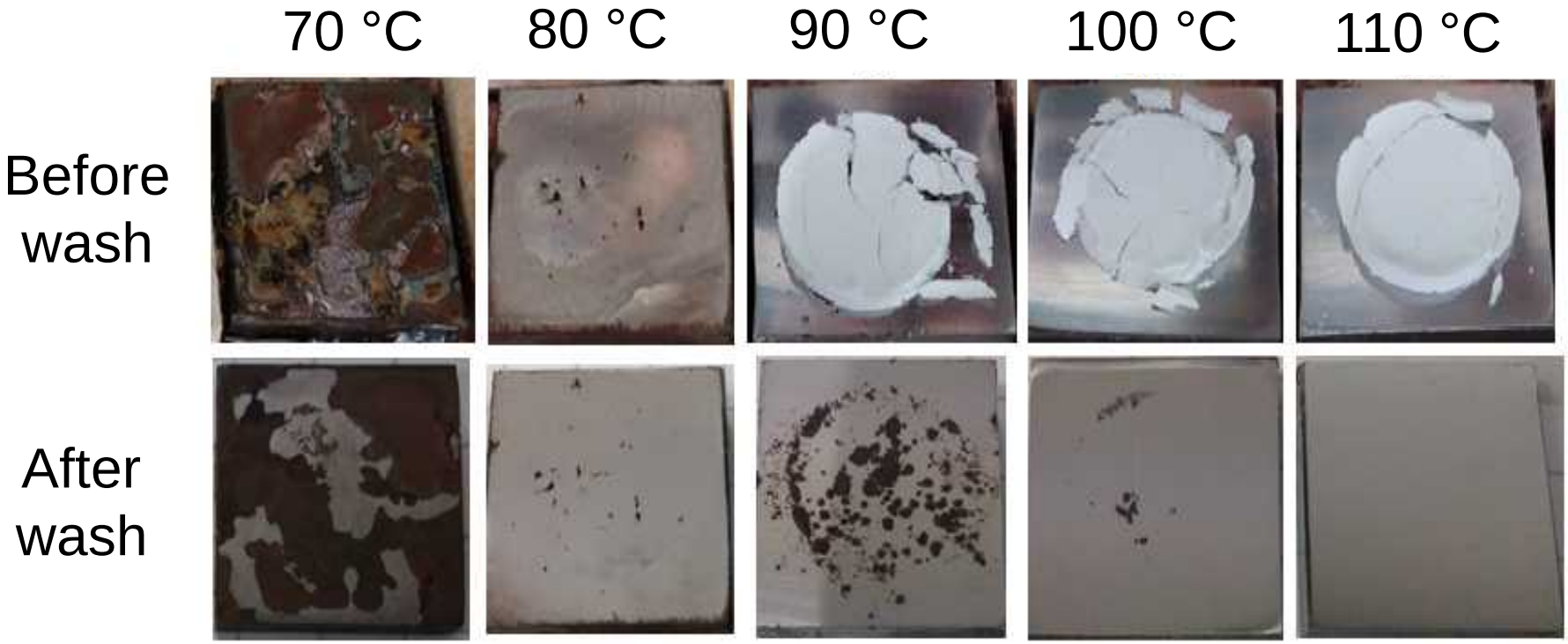
Salt: 90% Na_2SO_4 & 10% Na_2CO_3
Temperature: 80 °C
H_2O: 27 vol-%
Exposure: 24h

Precipitator Ash 1

Salt: Precipitator Ash 1

H_2O: 27 vol-%

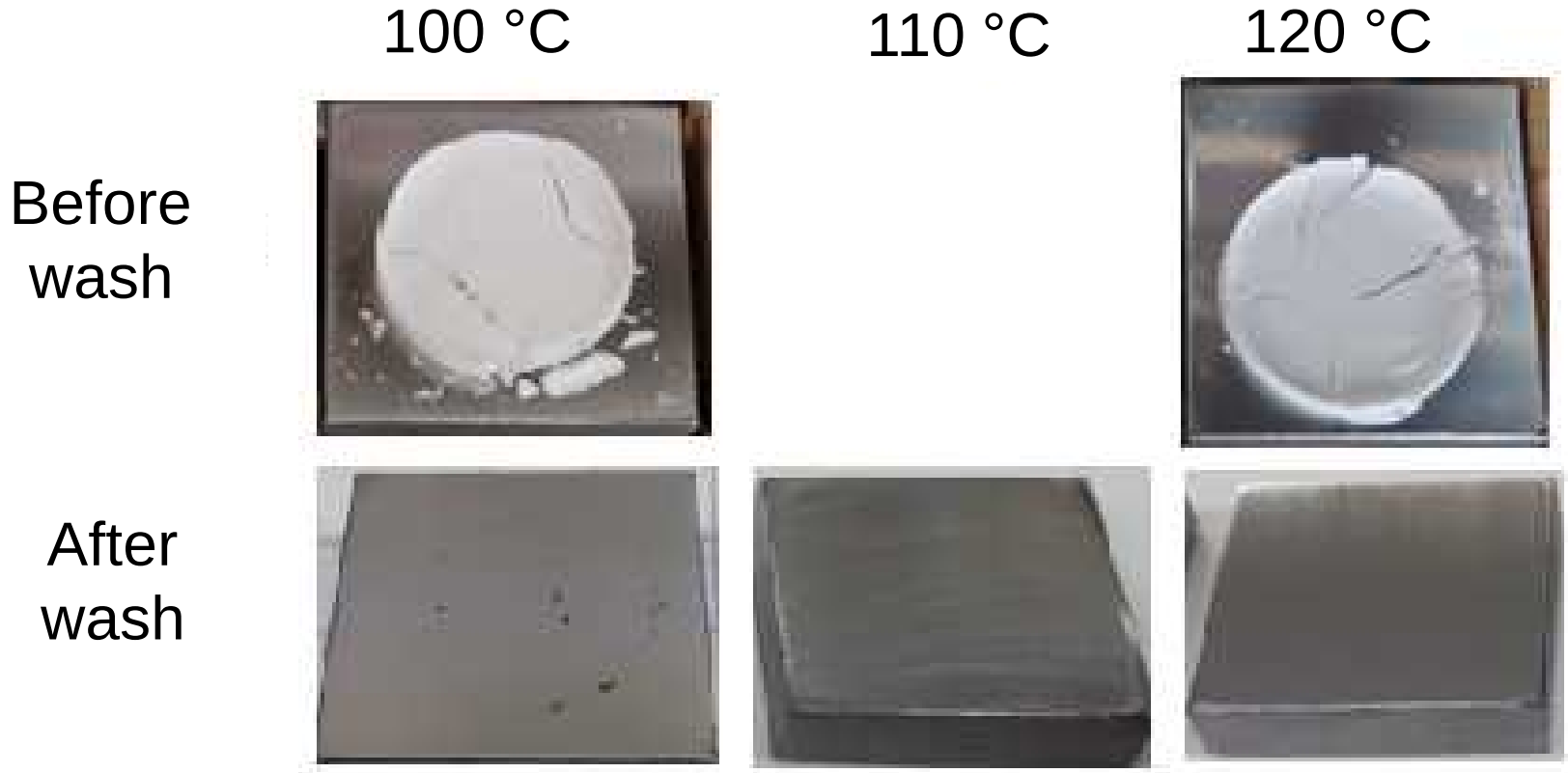
Exposure: 24h



Salt: Precipitator Ash 1

H_2O: 60 vol-%

Exposure: 4h



Salt: Precipitator Ash 1
Temperature: 110 °C
H_2O: 80 vol-%
Exposure: 24h

Precipitator Ash 2

Salt: Precipitator Ash 2
Temperature: 100 °C
H_2O: 27 vol-%
Exposure: 4h

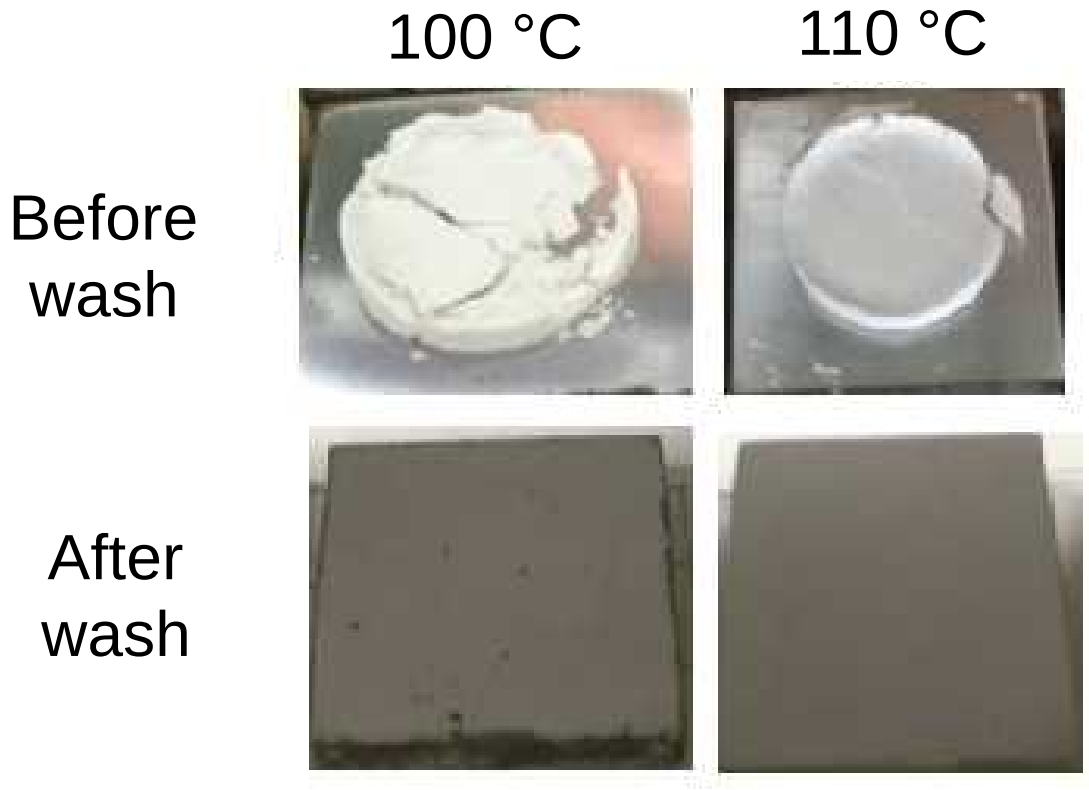
Before wash

After wash

Salt: Precipitator Ash 2

H_2O: 60 vol-%

Exposure: 4h



Conclusions

	27% H_2O	60% H_2O	80% H_2O
Na_2SO_4	90 °C	110 °C	
Na_2CO_3			-[a]
PA1	110 °C	110 °C	120 °C[b] (?)
PA2	100 °C	110 °C	

[a]No corrosion seen even though salt absorbed enough water to be totally dissolved

[b]Very light corrosion seen at 110 °C, so expect no corrosion at 120 °C

Conclusions

- Absorbtion of H_2O by hygroscopic salts appears to be the mechanism for low temperature corrosion

- Academy of Finland support for Emil Vainio to understand this phenomena of water adsorption by salts in biomass fueled boilers

Conclusions

- **These results indicated 110 °C (both gas and steel) is a safe temperature from a corrosion perspective**
- More deposits should be tested
- Some corrosion studies in a gradient needed
- Tests with moments of higher H_2O to similuate local fluctuations seen with sootblowing

Acknowledgements

- Our thanks to SKY and member companies for continued support of projects at ÅAU

- We’d like to acknowledge Niklas Vähä-Savo now with Vapo Oy for his work in phase 1