Low Temperature Corrosion in Recovery Boilers

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Background

- Industrial interest in extracting more energy from flue gases
  - 10 °C drop in flue gas temperature → ~ 0.5 % efficiency improvement of the boiler
- Some historical industrial observations of low temperature corrosion
- H_2SO_4 thought to exist in flue gases of recovery boilers

SKY projects

<u>Understanding Low Temperature Corrosion in Black Liquor Combustion</u>

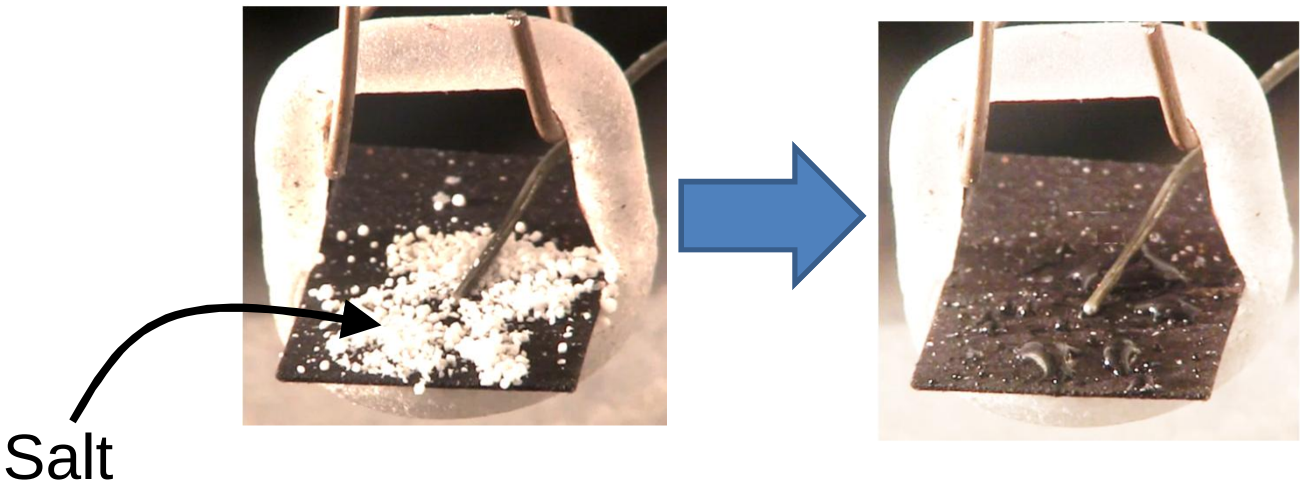
- Measurements in RB boilers (dew point, SO_3/H_2SO_4, corrosion)
- Laboratory study with pure salts (Na_2SO_4, Na_2CO_3, $NaHSO_4$, KCl, NaCl) and some ashes using ST45.8
- *Laboratory study with boiler ashes, short and long term tests with two metals*

Previously

- Recent measurements; H_2SO_4 doesn't exist in RB flue gases
- Hygroscopic compounds may cause corrosion
- In a recovery boiler SO_3 and H_2SO_4 will react with ash forming compounds:
  - $Na_2CO_3(s) + H_2SO_4(g) \rightarrow Na_2SO_4(s) + CO_2(g) + H_2O(g)$
  - $Na_2CO_3(s) + SO_3(g) \rightarrow Na_2SO_4(s) + CO_2(g)$
  - $2NaOH(g) + SO_3(g) \rightarrow Na_2SO_4(s) + H_2O(g)$
- Bisulfate may also be formed:
  - $Na_2SO_4(s) + H_2SO_4(g) \rightarrow 2NaHSO_4(s,l)$

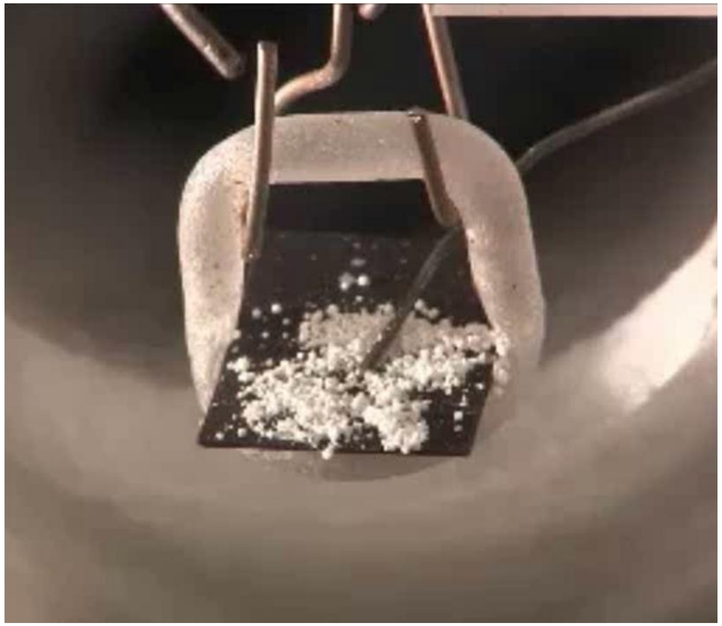
Hygroscopic compounds and deliquescence temperature

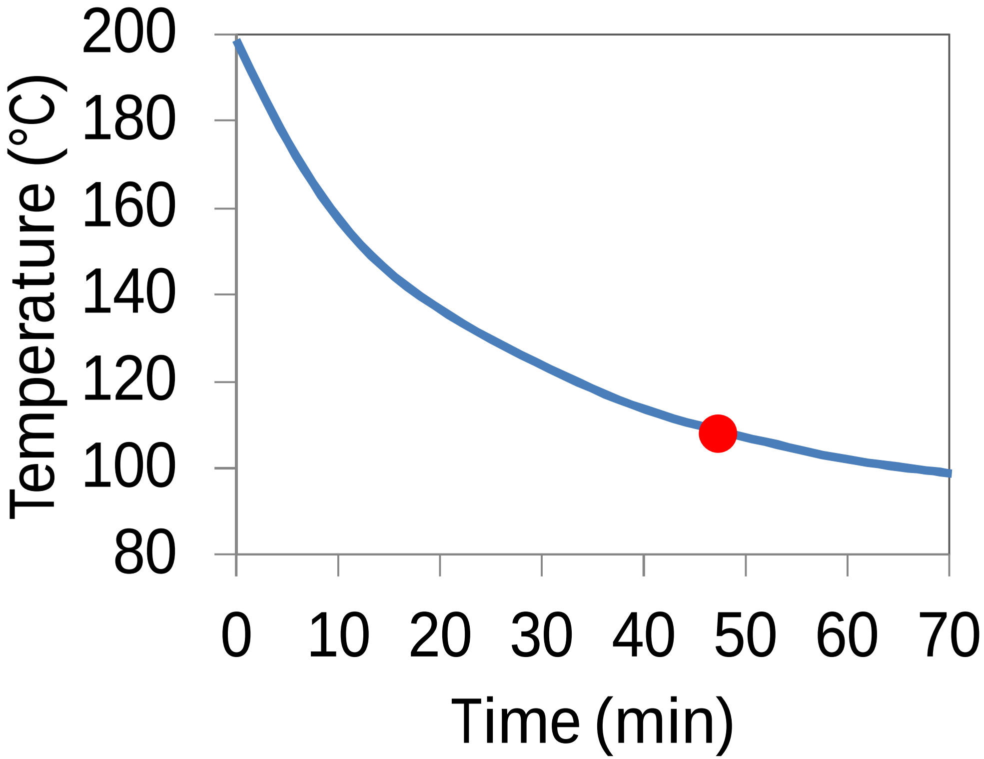
The temperature at which a salt or salt mixture absorbs enough water to fully dissolve at a fixed vol% H_2O



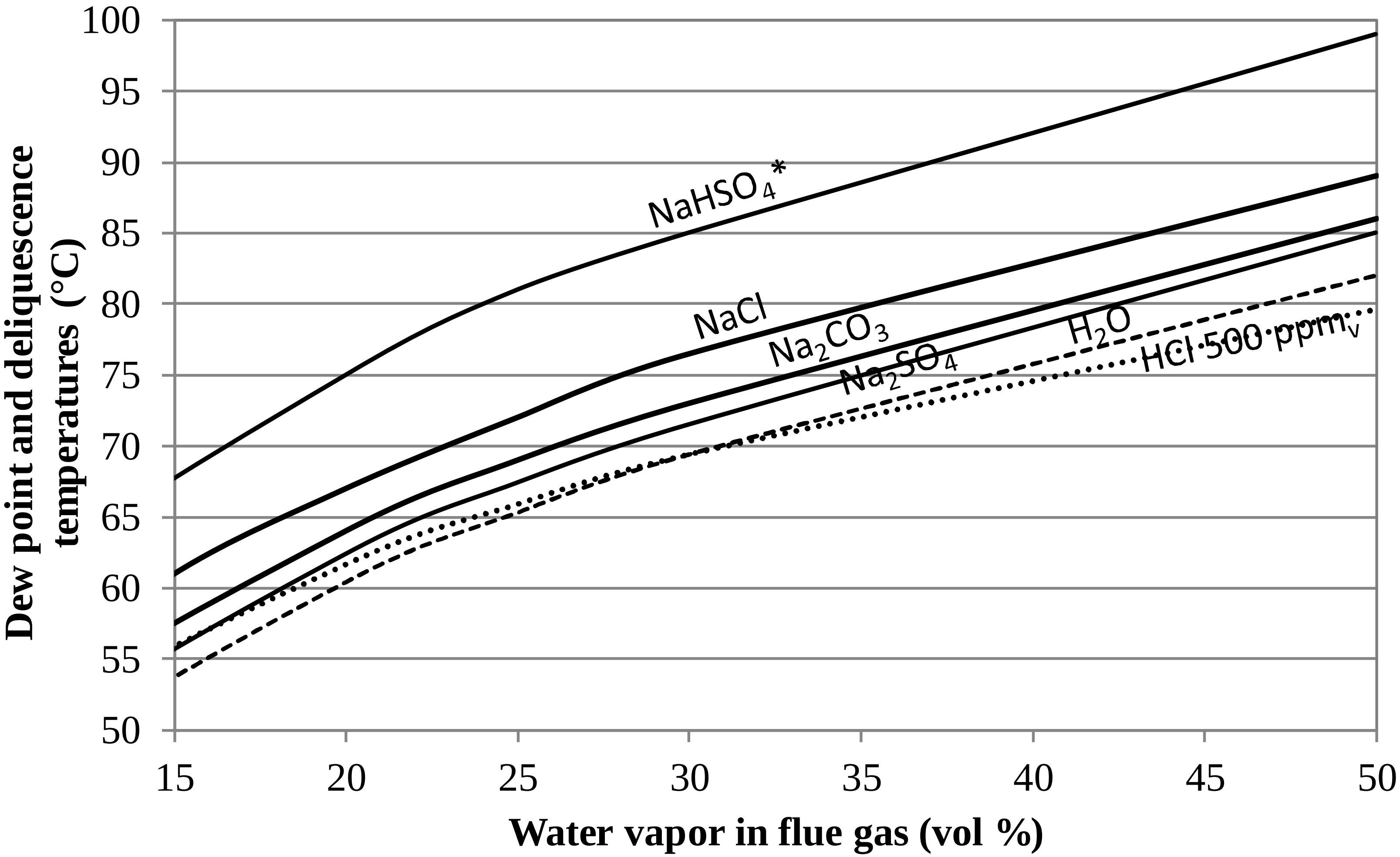
Deliquescence of $CaCl_2$

$CaCl_2$, 25 vol% H_2O





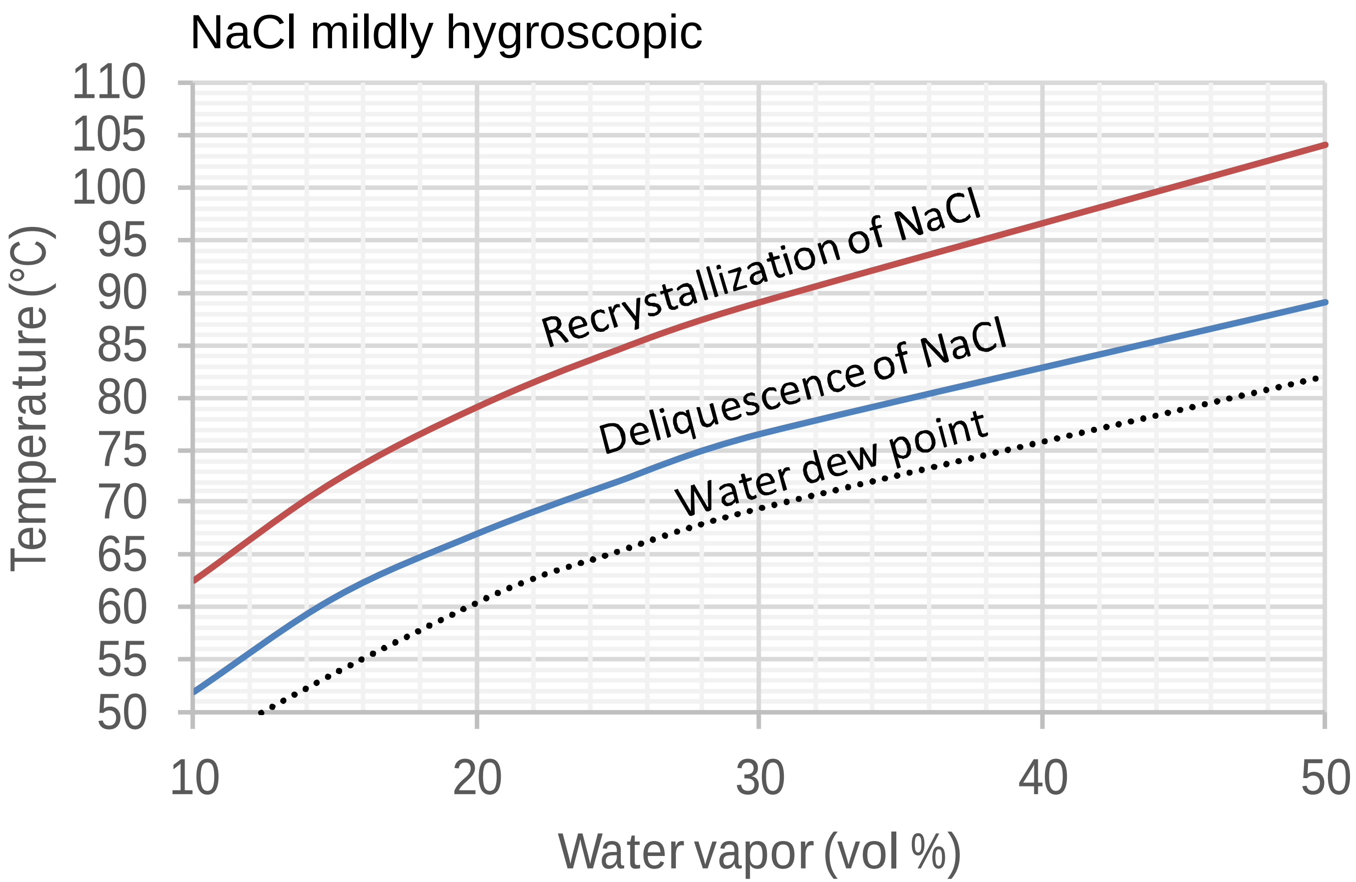
Dew points and deliquescence



*Values for $NaHSO_4$ extrapolated from data at 25°C

Data from: Wolery, T., “Environment on the Surfaces of the Drip Shield and Waste Package Outer Barrier” 2004

Deliquescence and recrystallization

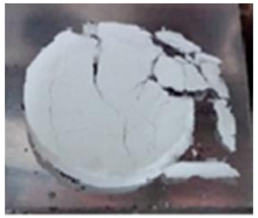
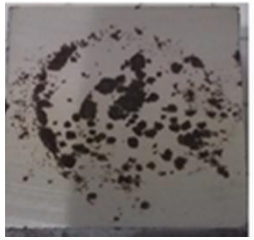
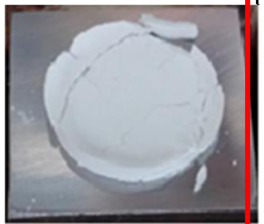
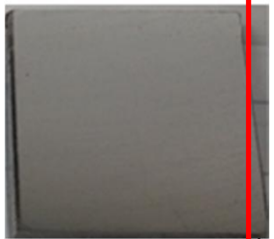
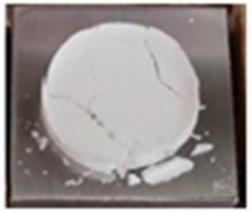


Data from: Tang I.N. J. Geophys. Res., 102 (1997)

Adsorption of water by salts

- Recrystallisation at $T > T_{deliquescence}$
- Different salts absorb water at different T
- Salt mixtures can behave differently than their pure salts
- At least mild corrosion can be expected when water is absorbed

Example: Na_2SO_4

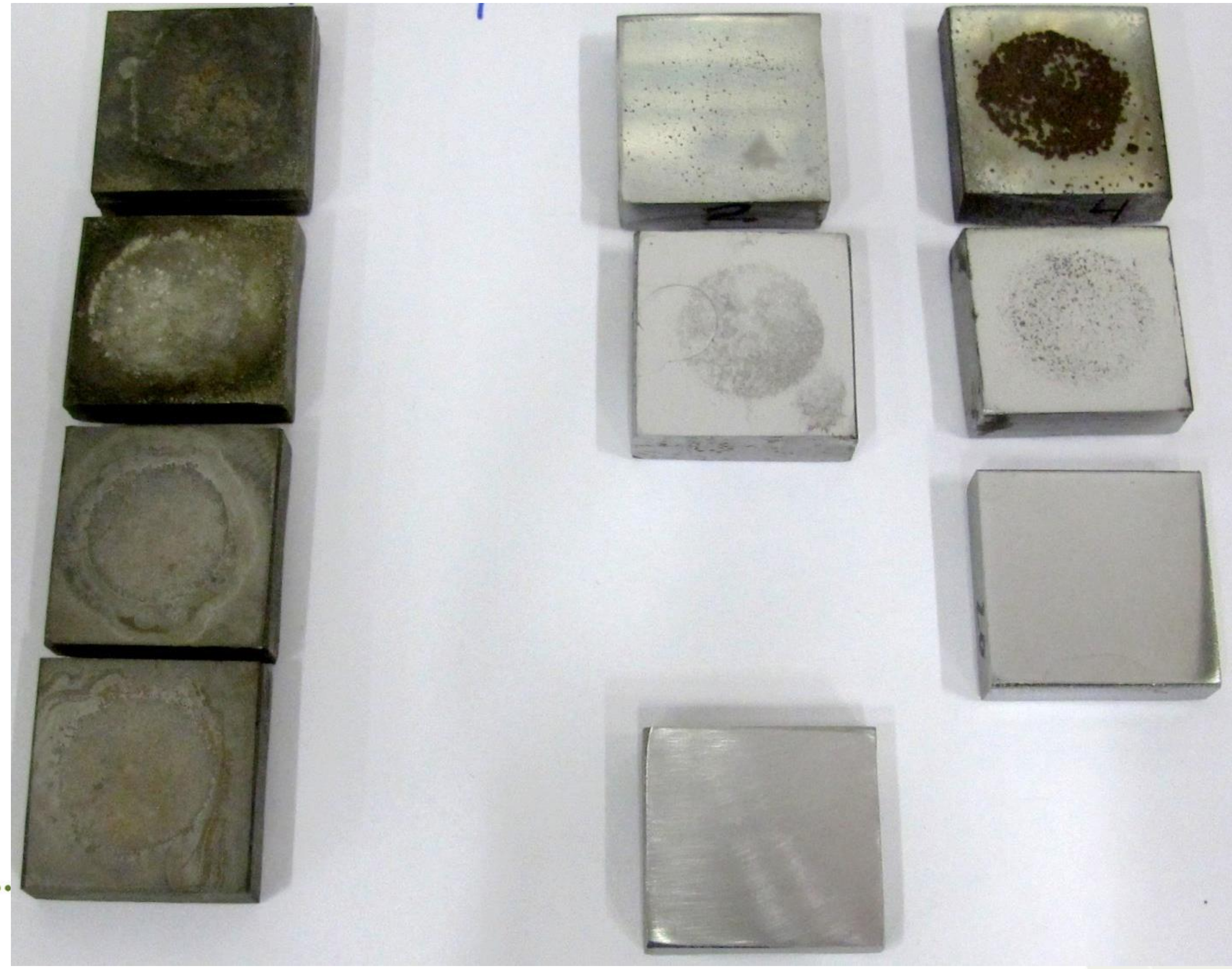
H_2O	70 °C	80 °C	90 °C	100 °C	110 °C	120 °C
27 % Before Wash After Wash	 	 	 	 	 	
60 % Before Wash After Wash				 		 

Comparison of two salts

(60 vol-% H_2O)

$NaHSO_4$ | Na_2SO_4

4 h | 4 h | 24 h



90 °C

100 °C

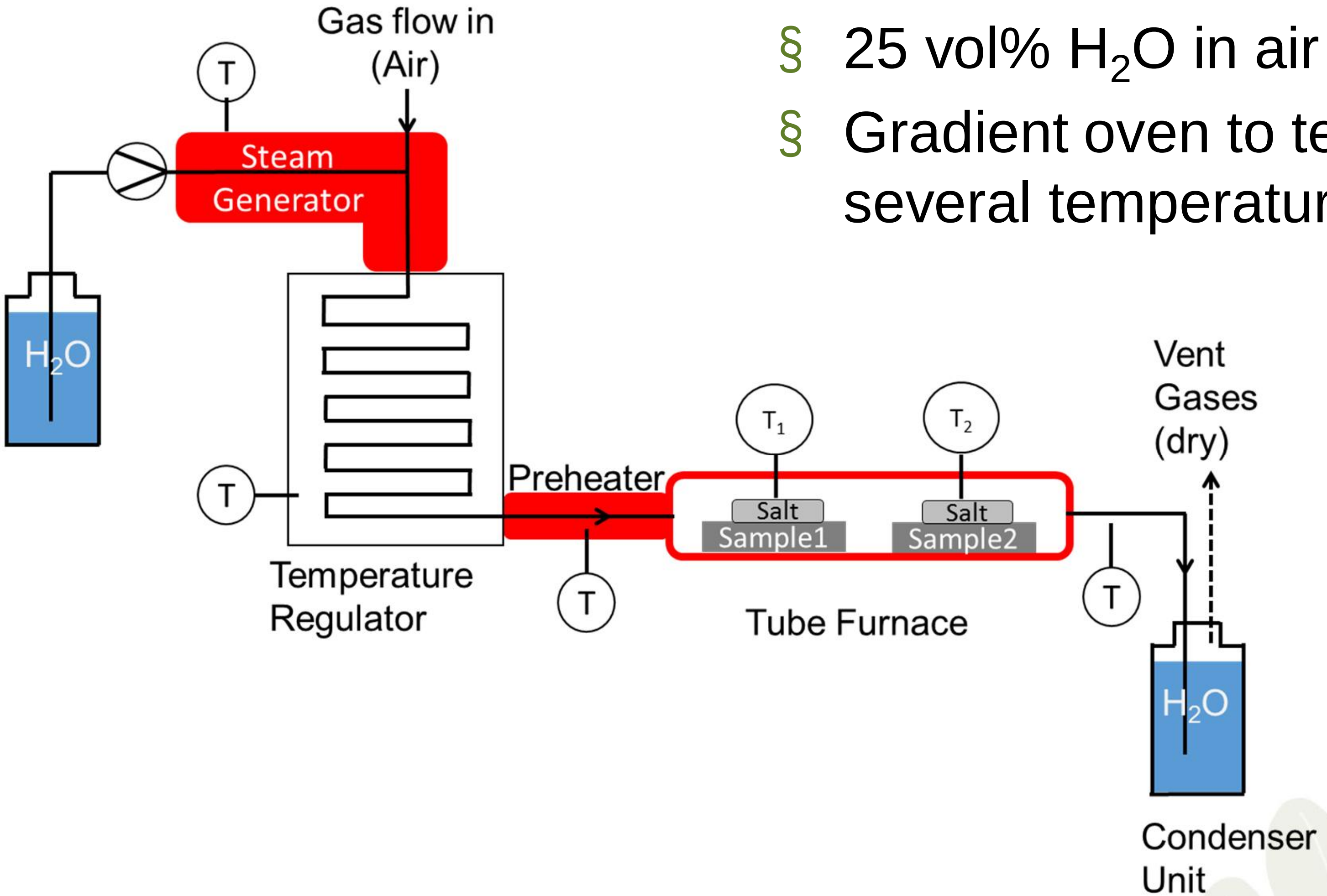
110 °C

120 °C

Objectives

- Understand the role of RB deposits on low temperature corrosion
- Can short, 22 h runs be used to determine when corrosion occurs?
- Choice of metal on corrosion
- Build a setup for long exposures and do tests under controlled conditions for 1000 h

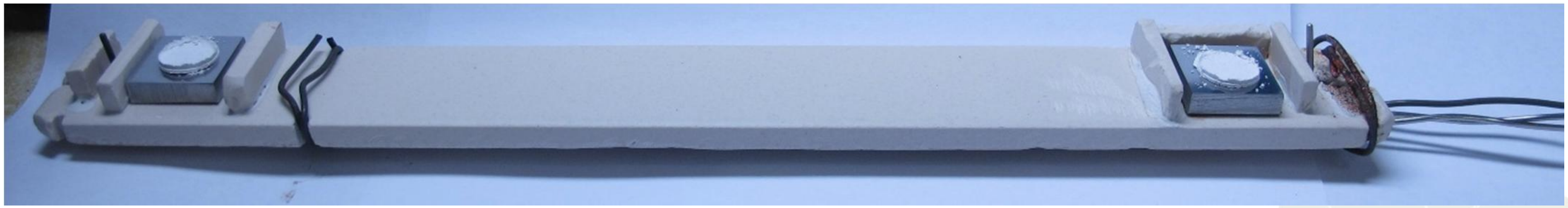
Experimental



- 25 vol% H_2O in air
- Gradient oven to test several temperatures

Experimental

- Samples:
  - 2x2 cm carbon steel coupons
  - St45.8 and 16Mo3
- ~ 0.1 g of ash on the coupon
- Sample holder 22 h runs:



Metal compositions

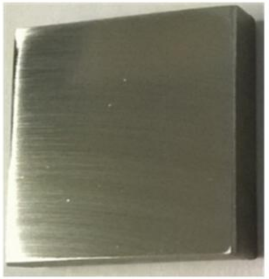
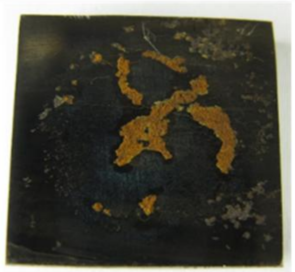
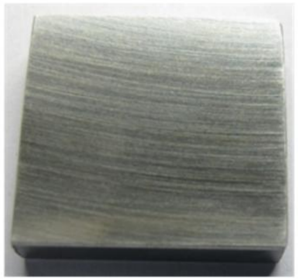
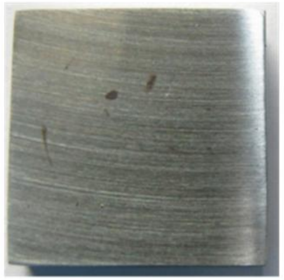
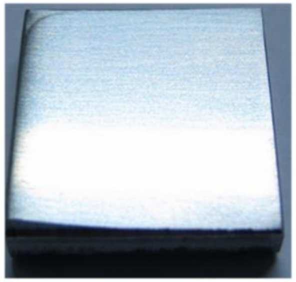
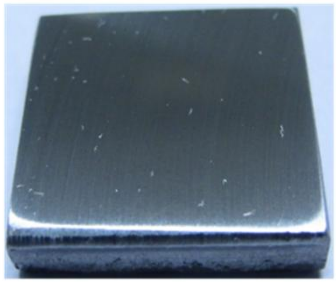
	C wt%	Si wt%	Mn wt%	P wt%	S wt%	Cr wt%	Cu wt%	Mo wt%	Ni wt%
16Mo3	0.12-0.20	≤ 0.35	0.40-0.90	≤ 0.025	≤ 0.010	≤ 0.30	≤ 0.30	0.25-0.35	≤ 0.3
St45.8	≤ 0.21	0.1-0.35	0.4-1.2	0.04	0.04				

SEM-EDX analyses of the ESP ashes

	Na wt%	K wt%	SO_4 wt%	Cl wt%	CO_3 wt%	pH	$S/(Na_2+K_2)$ mol frac
Modern kraft RB	33.2	3.7	44.6	0.7	17.8	11.4	0.60
Kraft RB with low solids BL	32.1	1.8	60.8	0.4	5.0	9.5	0.88
Sulfite boiler	31.5	2.9	59.3	0.0	6.3	6.2	0.85

CO_3 determined by balance in SEM-EDX analyses

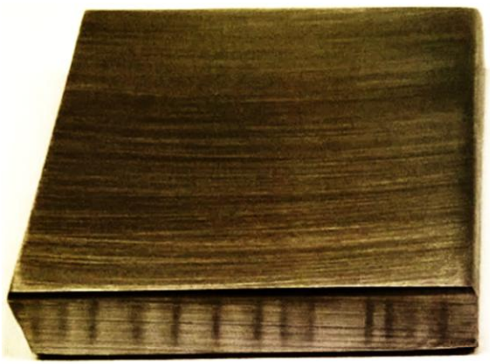
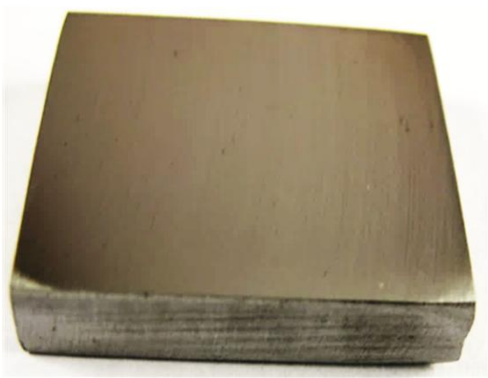
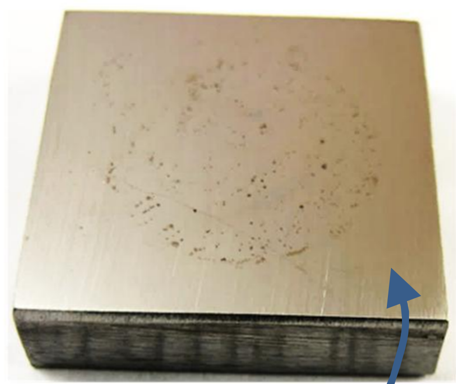
Tests with 16Mo3/5

	90 °C	75 °C	60 °C
Modern kraft RB			
Sulfite boiler			
Kraft RB with low solids BL			

No corrosion seen at 90 °C

Comparison of the materials

Kraft recovery boiler ash (low solids BL)

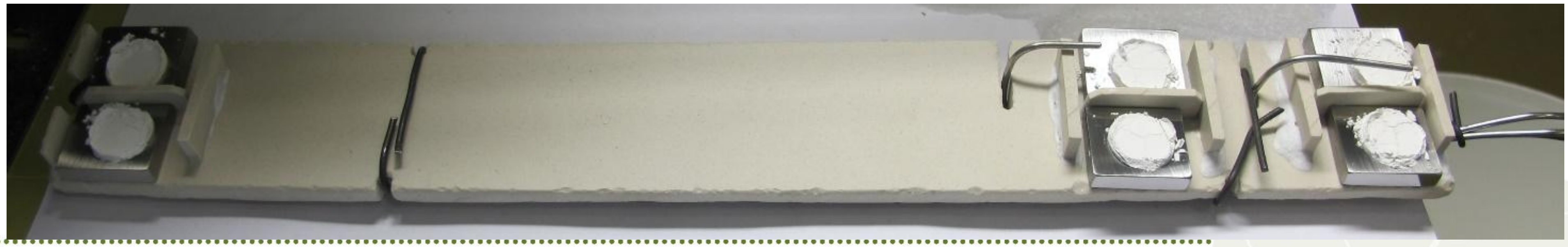
	110 °C	95 °C
16Mo3/5		
ST45.8		

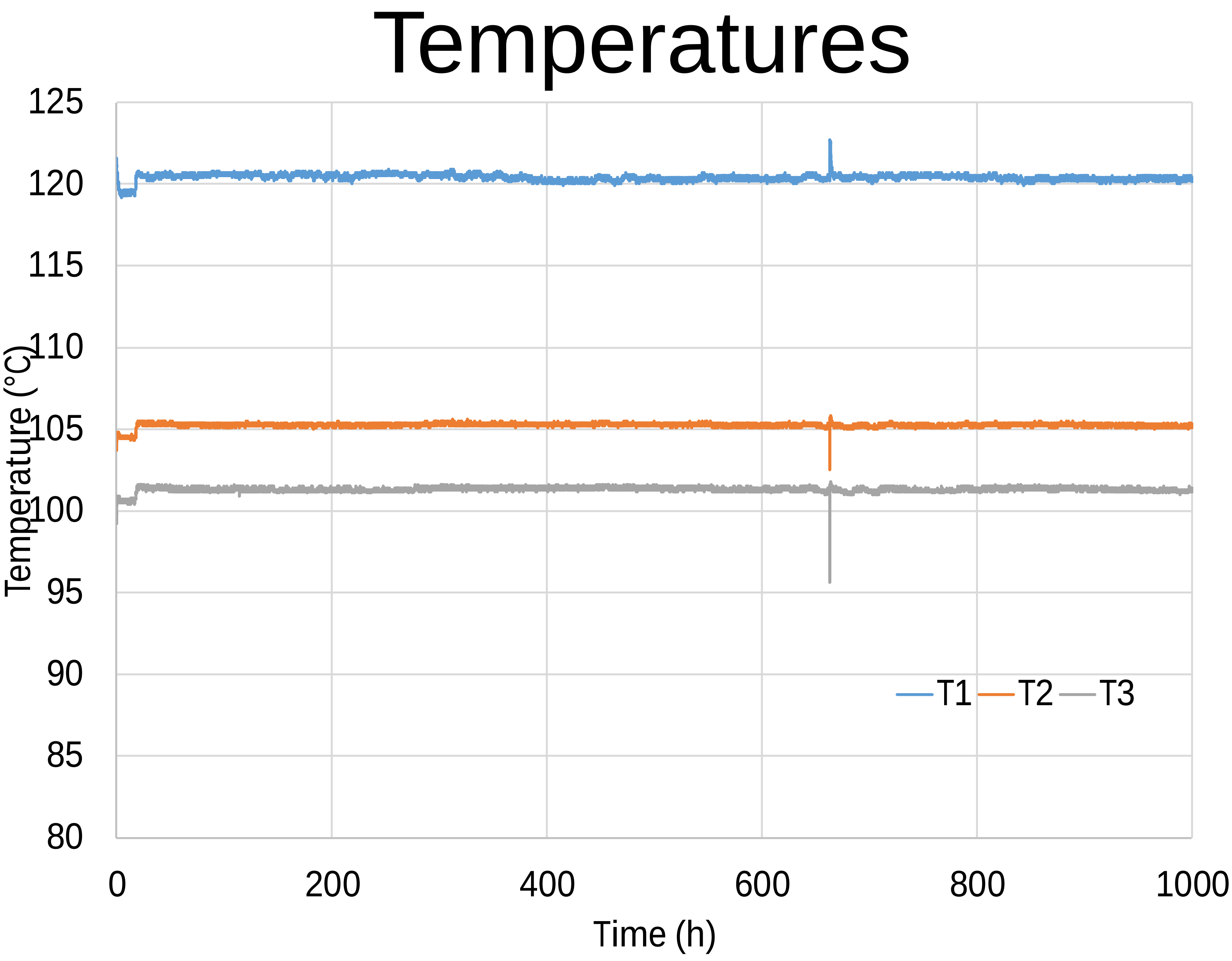
Corrosion

1000 h runs

- Three temperatures and two metals tested simultaneously
- Tests were made to confirm the 22 h results with no corrosion at T > 100 °C
- 25 vol% H_2O in air
- Sample holder for 1000 h:

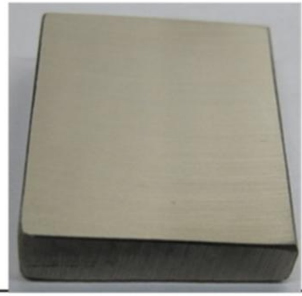
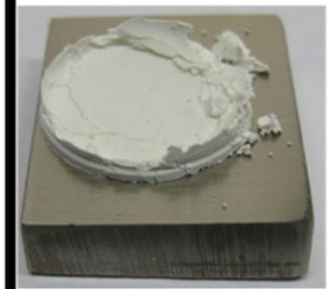
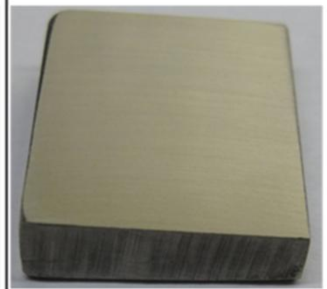
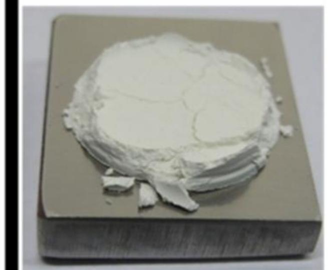
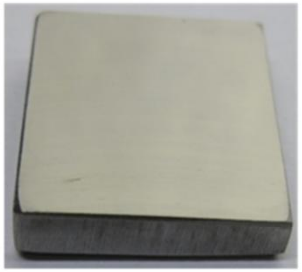
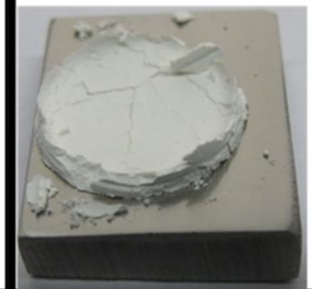
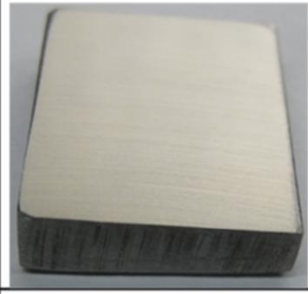
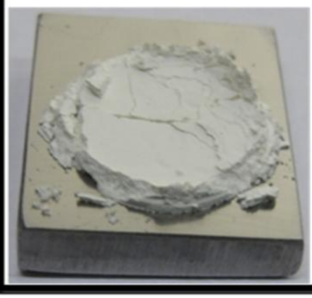
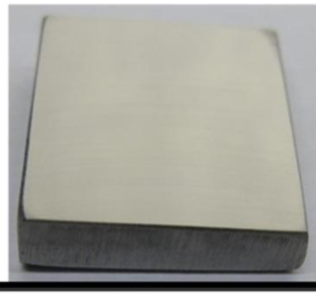
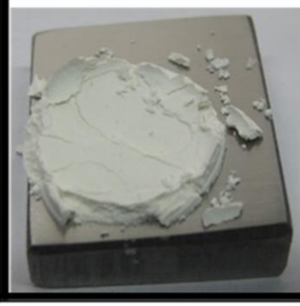
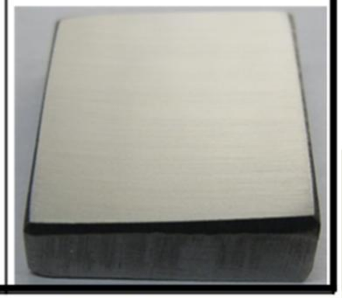
120°C 105°C 101°C





Temperatures
Temperature (°C)
125
120
115
110
105
100
95
90
85
80
0
200
400
600
800
1000
Time (h)
T1
T2
T3

Results - 1000 h run

Temp (°C)	16Mo3/5		ST45.8	
	Unwashed	Washed	Unwashed	Washed
120				
105				
101				

Conclusions

- 16Mo3/5 is less susceptible to corrosion caused hygroscopic salts than ST45.8
- Neither material corroded at temperatures above 100 °C in the 1000 h run
- 22 h tests are valid for screening materials and conditions

Publications

- Vainio, E., DeMartini, N., Laurén, Orang, N., Tran, H., Hupa, M.,: Understanding low-temperature corrosion in recovery boilers – Measurements at four mills, International Chemical Recovery Conference (ICRC), Halifax, NS, Canada, **2017**

- DeMartini, N., Vainio, E., Lauren, T., Hupa, L., Bisulfate Formation and Impact on Low Temperature Corrosion in Kraft Recovery Boilers, International Chemical Recovery Conference (ICRC), Halifax, NS, Canada, **2017**

- DeMartini, N., Vainio, E., Holmblad, H., Hupa, M.: Understanding low temperature corrosion in Kraft Recovery Boilers – Implications for Increased Energy Recovery, TAPPI Peers, September 25–28, **2016,** Jacksonville, FL

- Vainio, E., Laurén, T., DeMartini, N., Brink, A., Hupa, M.,: Understanding Low-Temperature Corrosion in Recovery Boilers: Risk of Sulphuric Acid Dew Point Corrosion? Journal of Science & Technology for Forest Products and Processes, 4(6), pp 14-22, **2015.**

- Vainio E., Laurén T., DeMartini N., Brink A., Hupa M.: Sulfuric Acid Induced Low Temperature Corrosion in Recovery Boilers?, International Chemical Recovery Conference, 9-12 June, **2014,** Tampere Finland, Vol 2, pp 189-203.

Acknowledgements

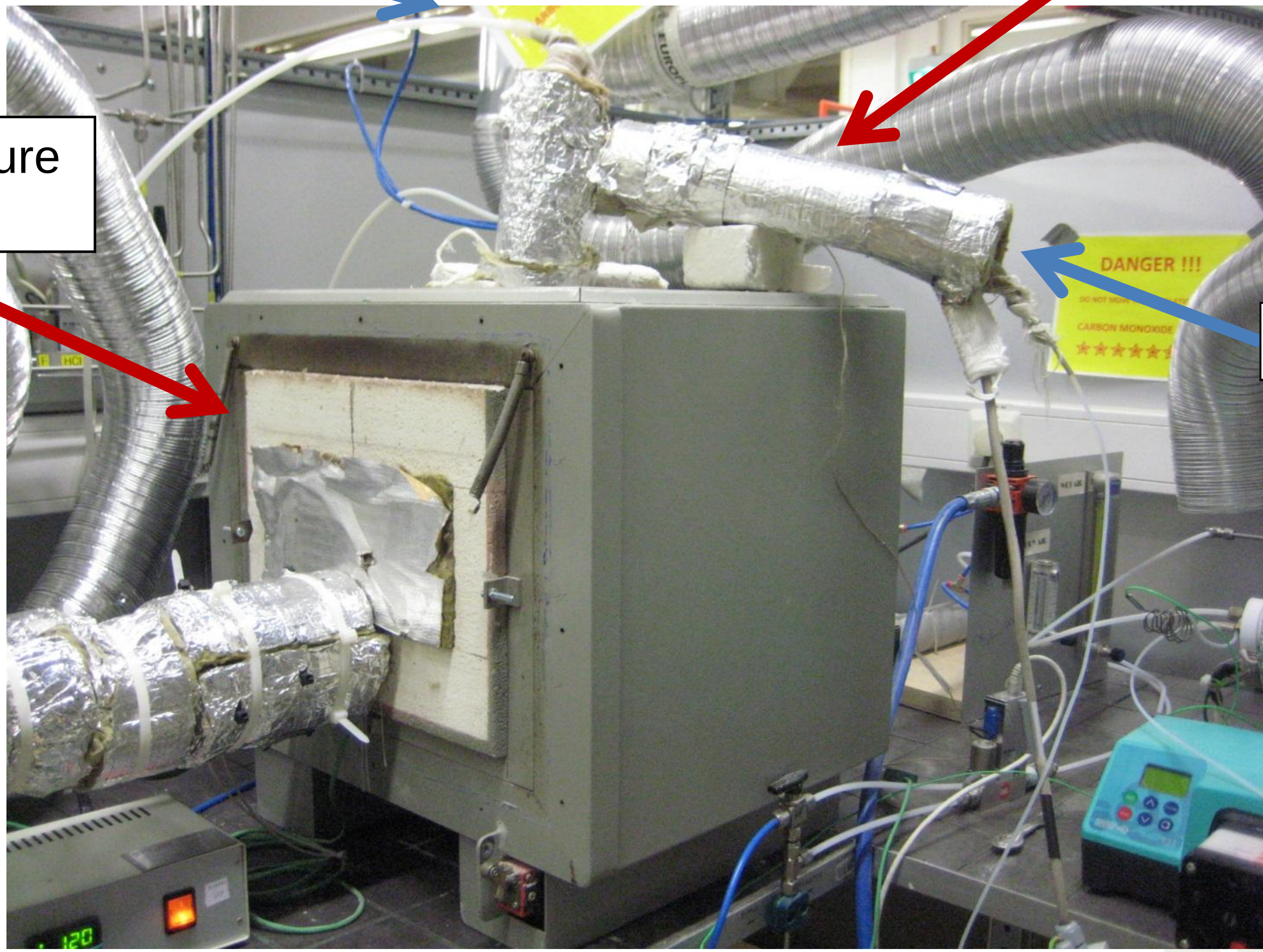
- Our thanks to SKY and member companies for continued support of projects at ÅAU

Experimental setup

Gases in

Steam Generator

Gas temperature regulator



Water in

Experimental setup