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Low-temperature corrosion in fluidised bed combustion of biomass

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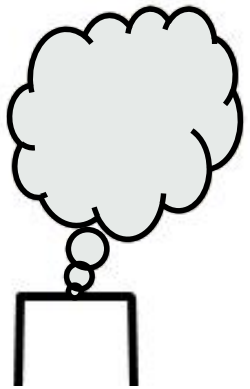
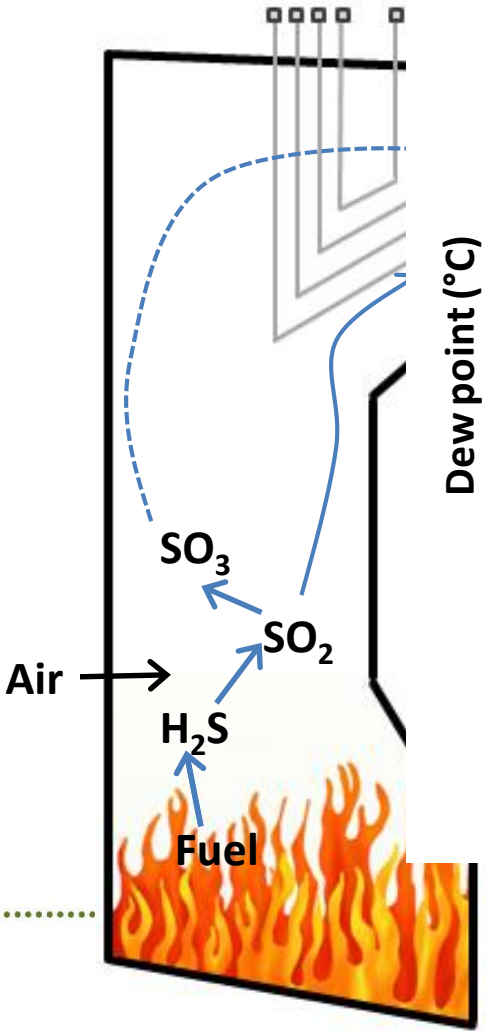
Background

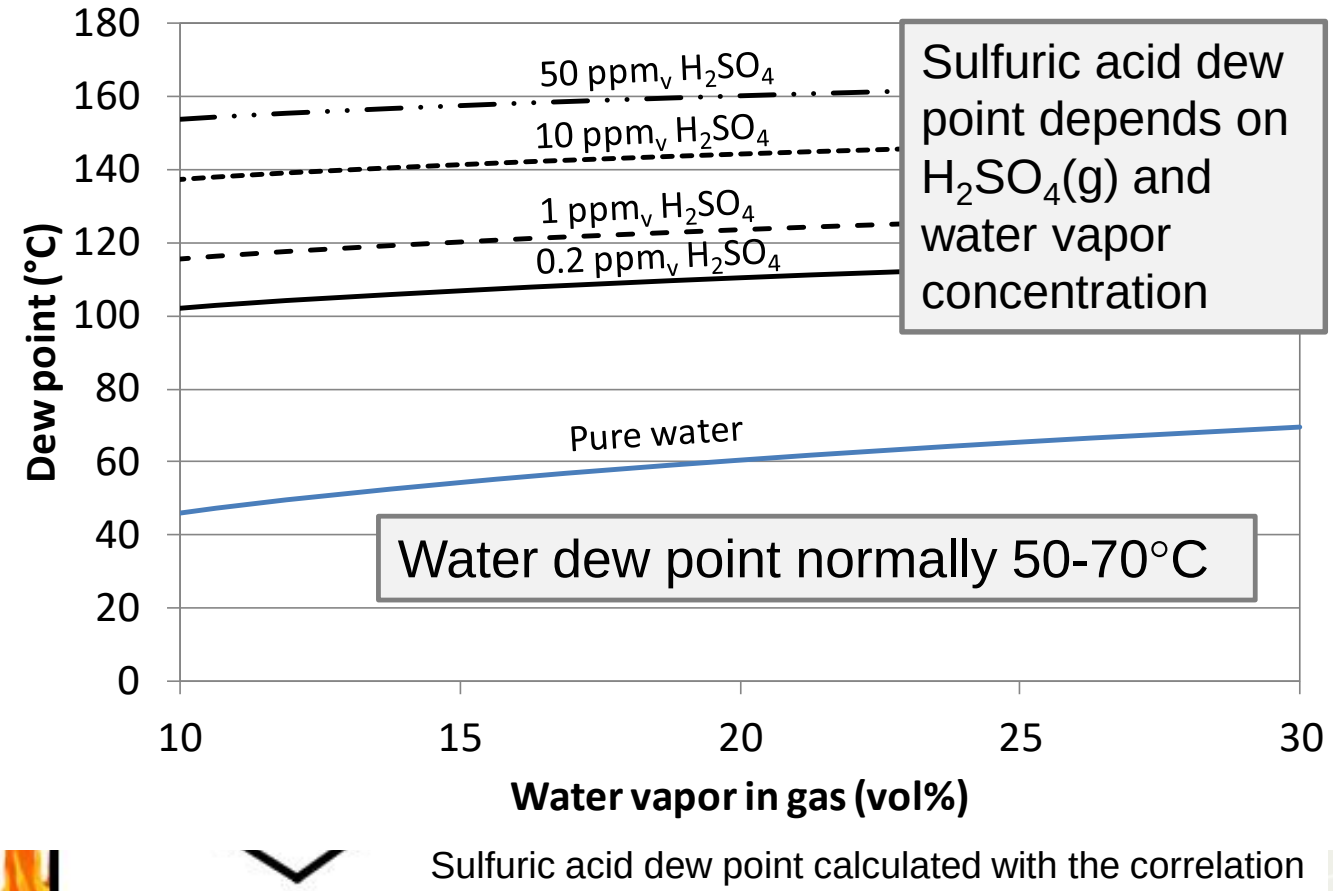
- Industrial interest in extracting more energy from flue gases
- Low-temperature corrosion of pre-heaters and the flue gas channel is a known problem in combustion
- Sulfuric acid has been thought to be the main cause
- Recent studies have shown that hygroscopic deposits causes corrosion in FBC of biomass and waste

Low-temperature corrosion

In fossil fuel combustion the condensation of $H_2SO_4(g)$ causes low-temperature corrosion







Sulfuric acid dew point depends on $H_2SO_4(g)$ and water vapor concentration

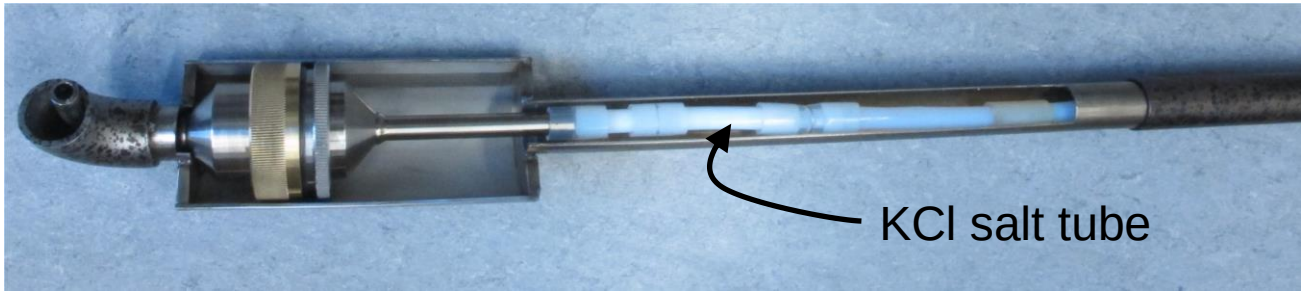
Water dew point normally 50-70°C

Sulfuric acid dew point calculated with the correlation by Verhoff and Banchero, Chem Eng Prog 70.

SO_3 measurements

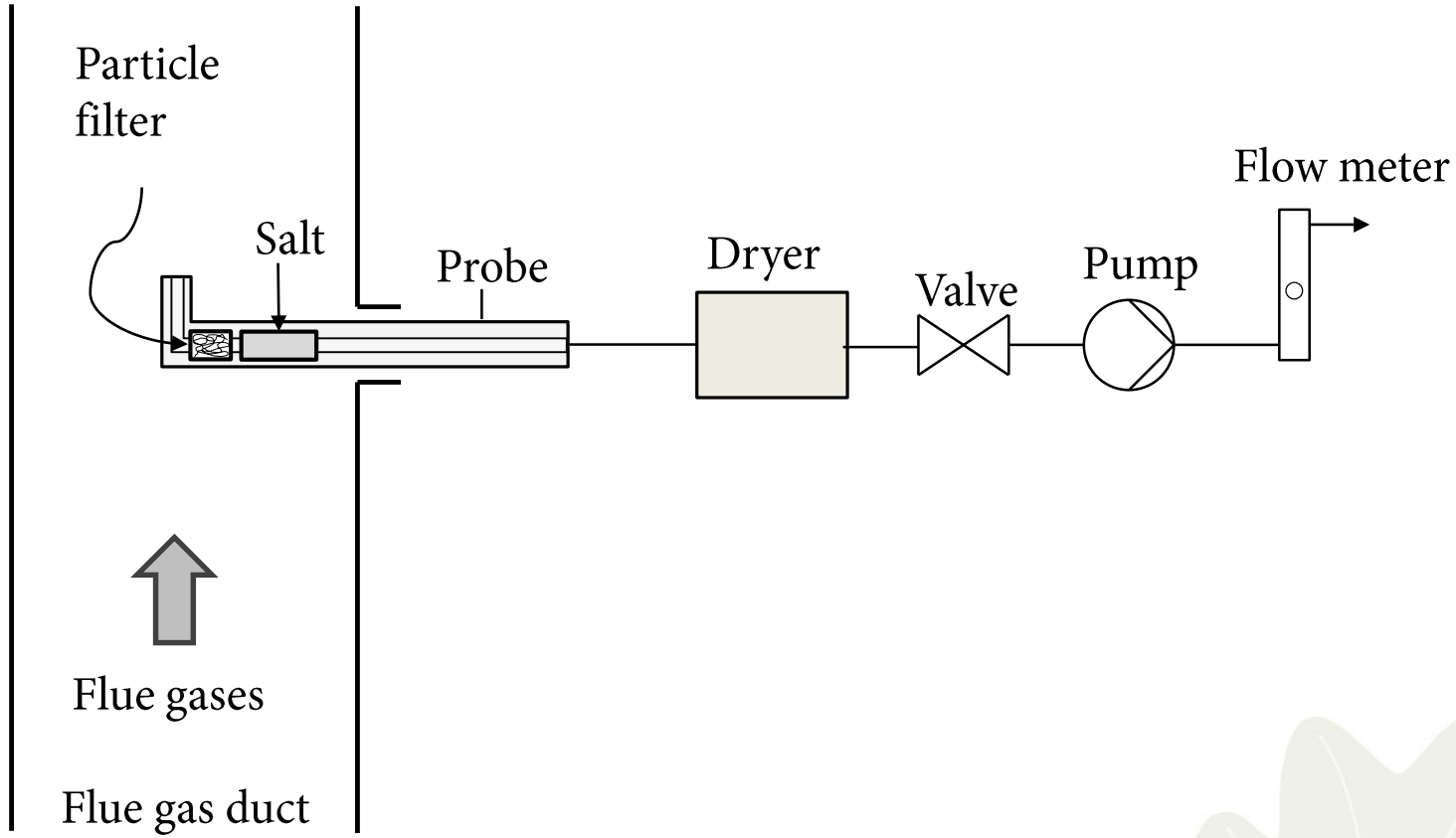
- KCl salt method to measure SO_3/H_2SO_4

$$H_2SO_4(g) + 2KCl(s) \rightarrow K_2SO_4(s) + 2HCl(g)$$



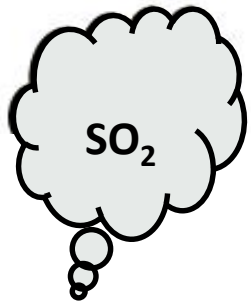
  - Range: 0.01 ppm_v – 20 000 ppm_v
  - Examples: BFB, CFB, Grate combustion, copper smelter, recovery boilers at pulp mills, IC engines, oxy-combustion, gas burners

Salt method to determine SO_3 and H_2SO_4

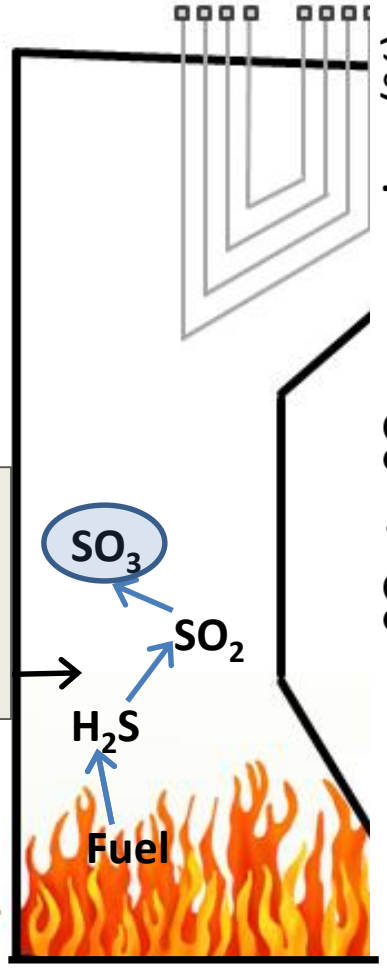


Vainio et al. Fuel 184 (2016)

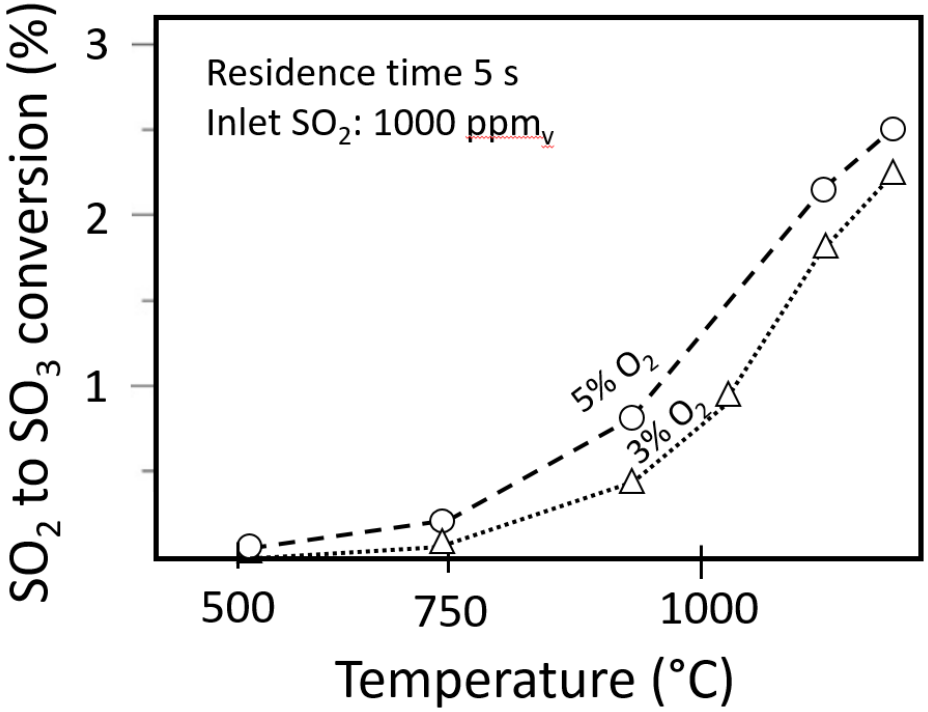
Low-temperature corrosion in BFB combustion of biomass



Low conversion to SO_3 due to low furnace temperature and air-staging



Homogeneous SO_2 to SO_3 conversion

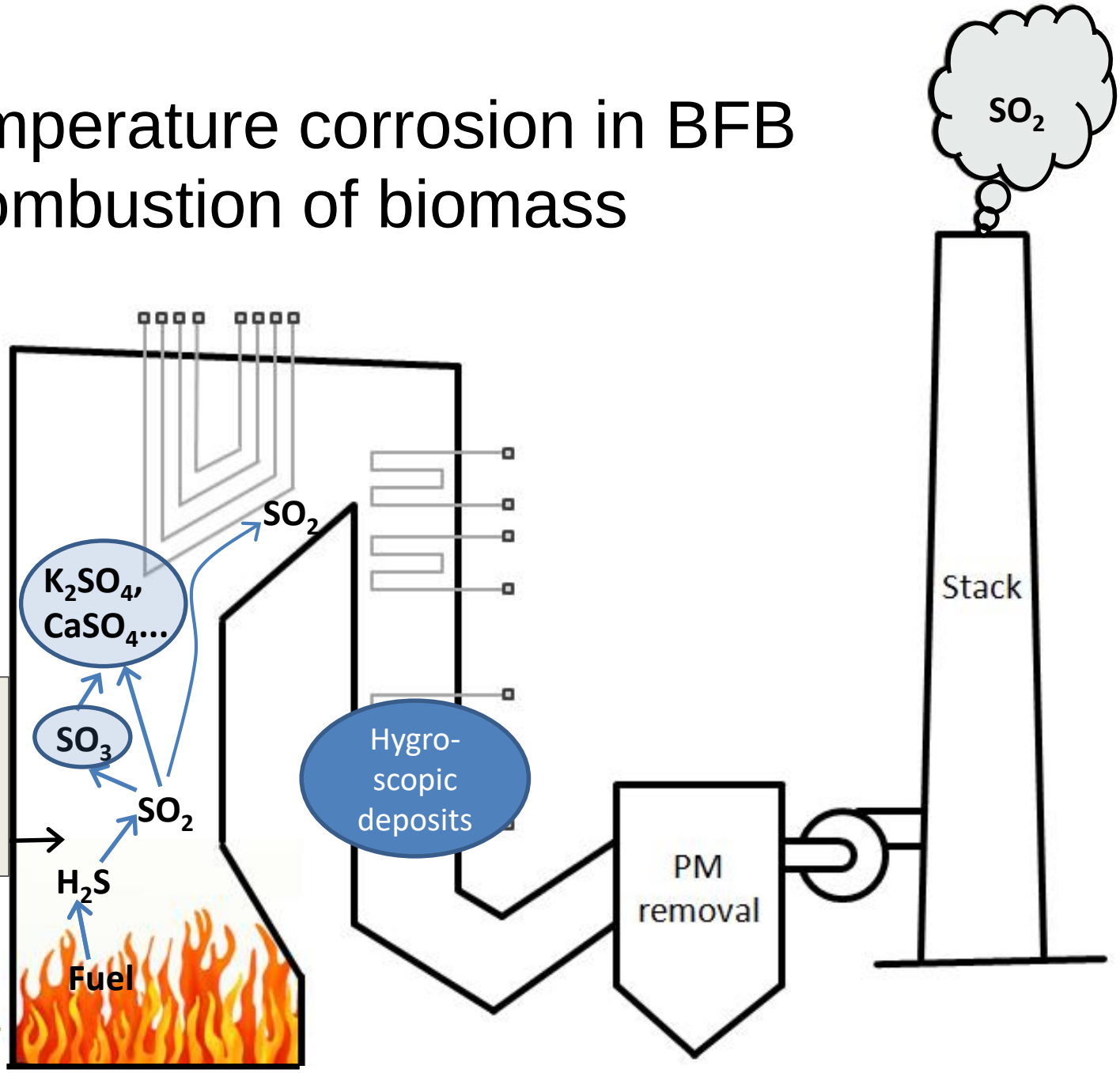


Modified from Fleig et al. Combustion and Flame 160 (2013)

Low-temperature corrosion in BFB combustion of biomass

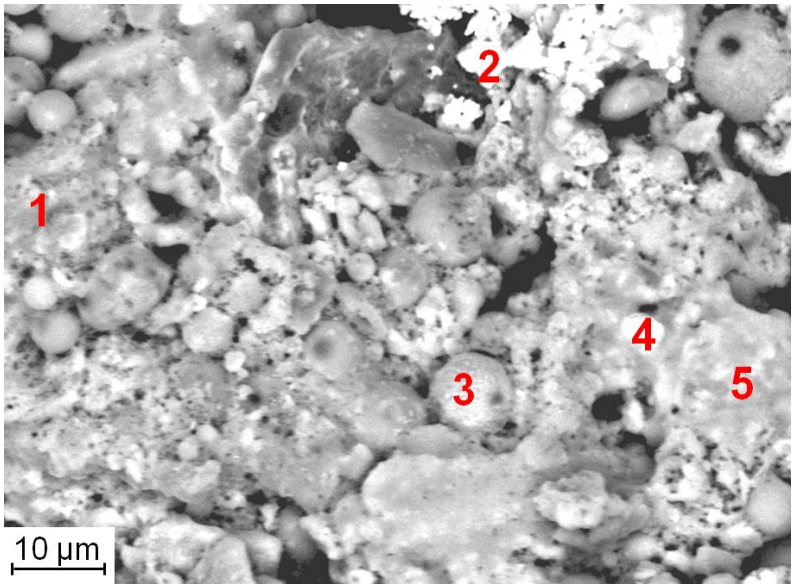
SO_3 very reactive towards alkaline ash

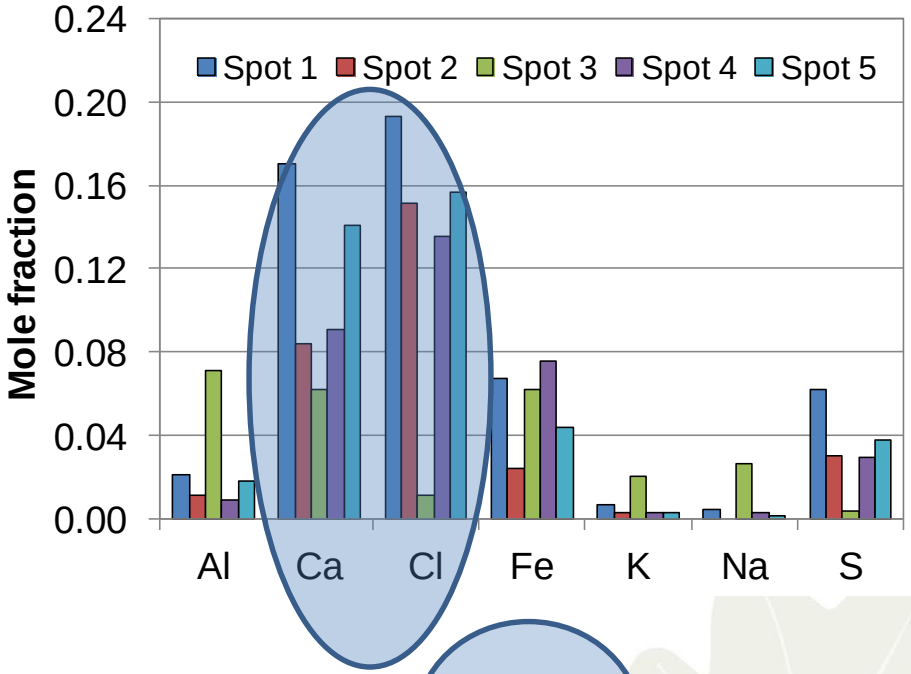
Low conversion to SO_3 due to low furnace temperature and air-staging



BFB combustion of biomass, sludge and demolition wood with limestone addition

Deposit probe at 100°C



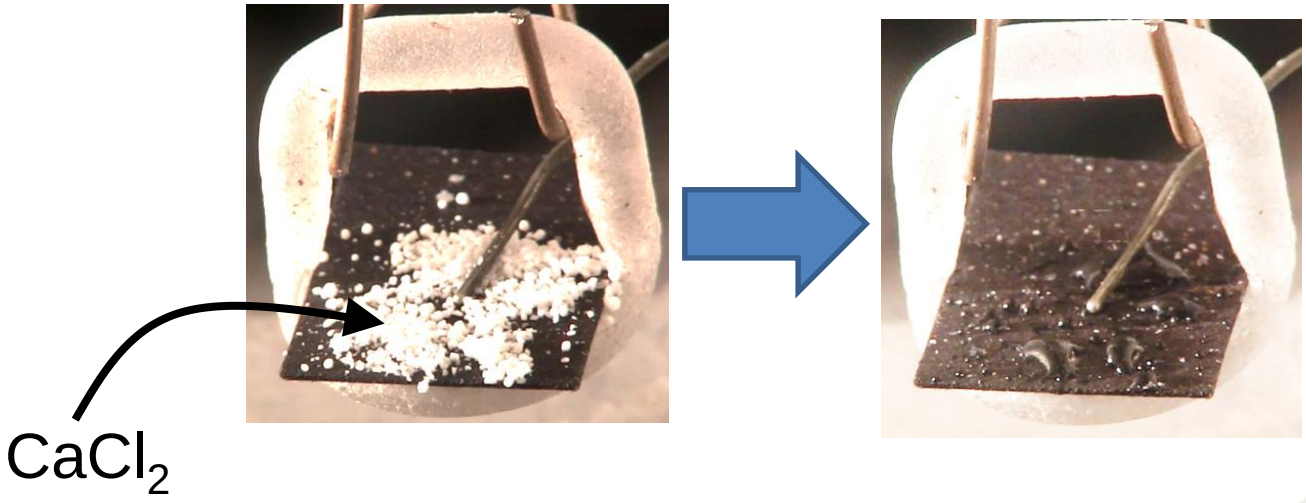


$$CaO(s) + 2HCl(g) \rightarrow CaCl_2(s) + H_2O(g)$$

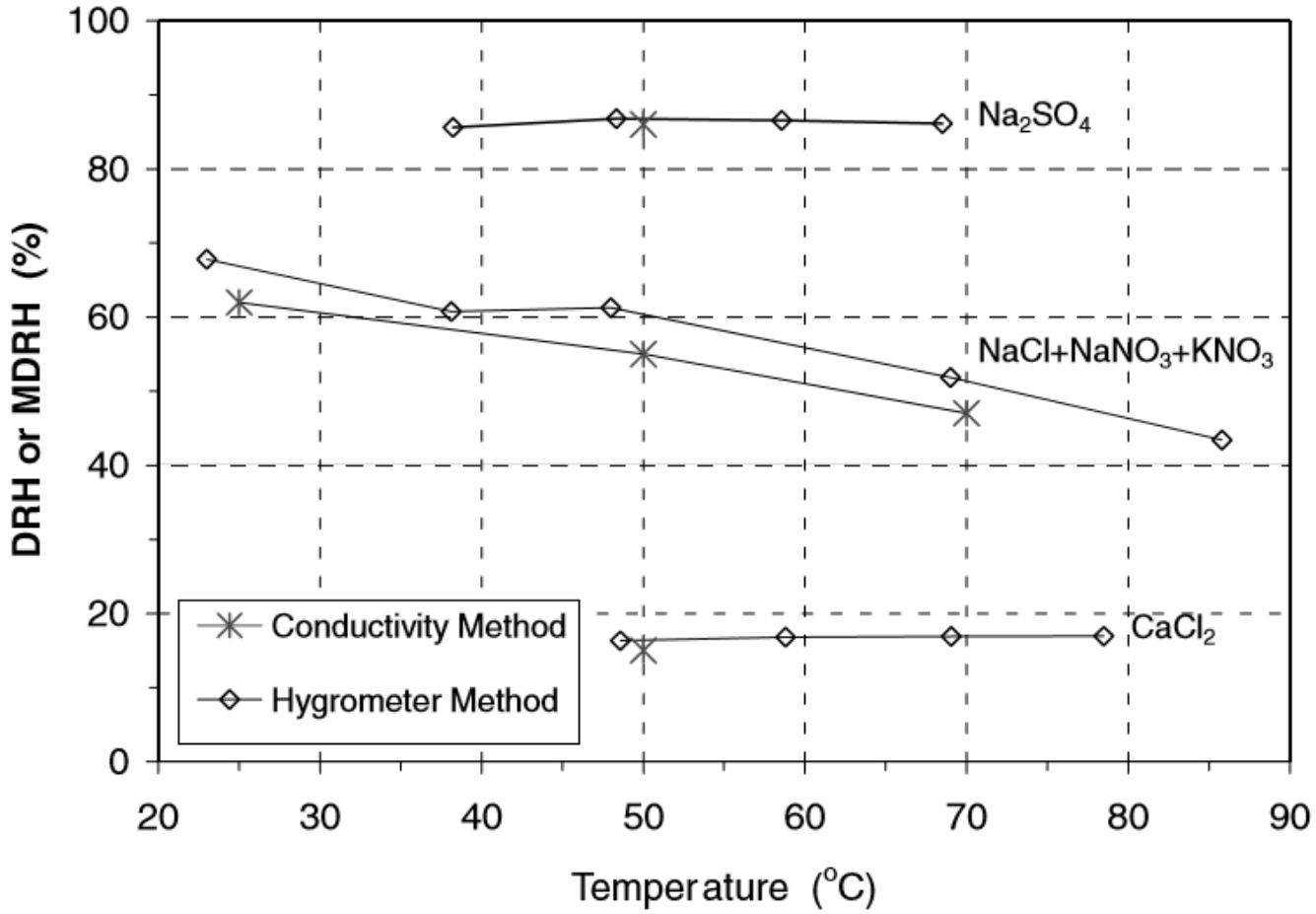
Vainio et al Fuel 184 (2016)

Deliquescence temperature

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

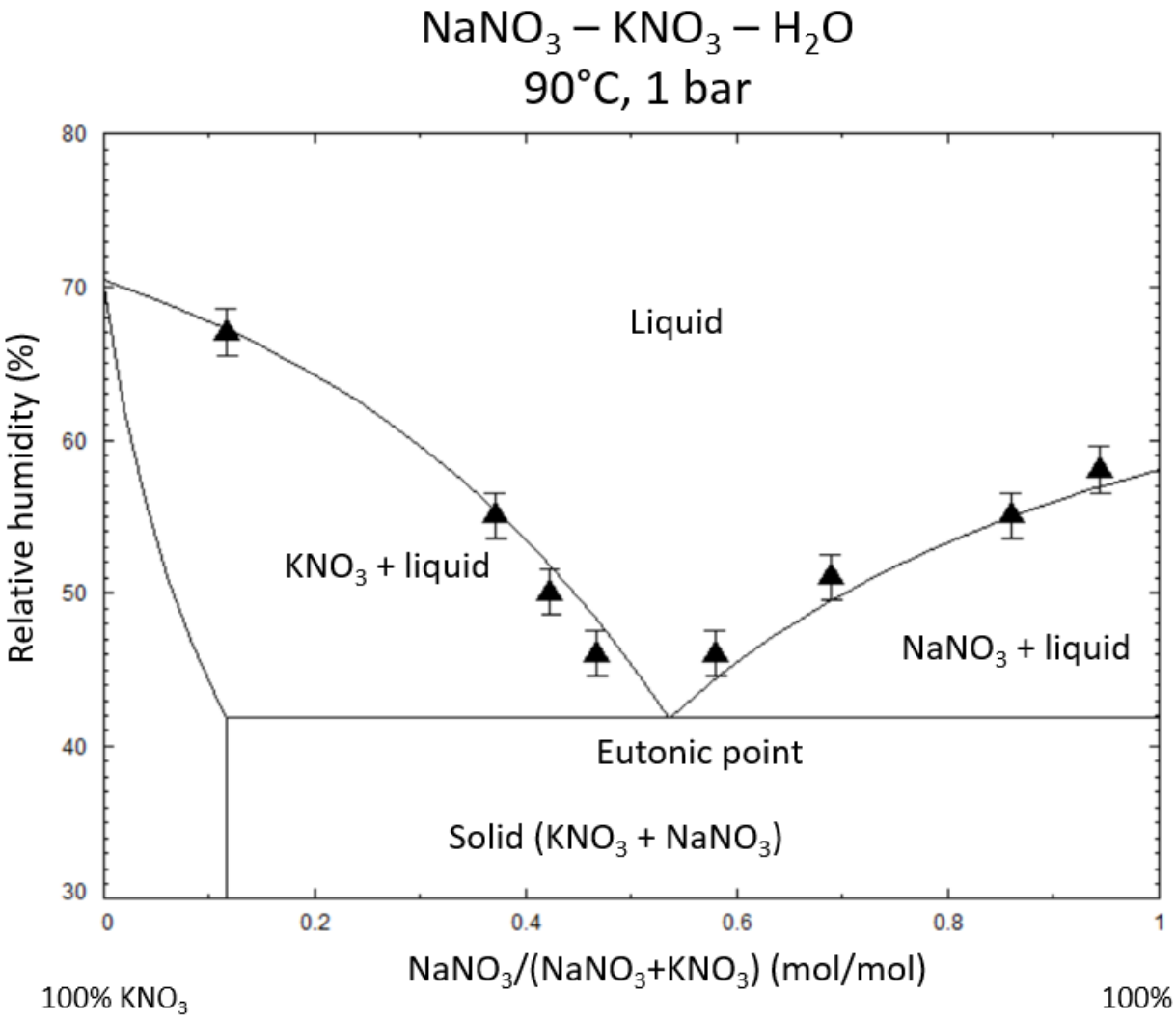


Deliquescence for some salts



Yang et al. Journal of Solution Chemistry, Vol. 35

Thermodynamic calculations - mixtures



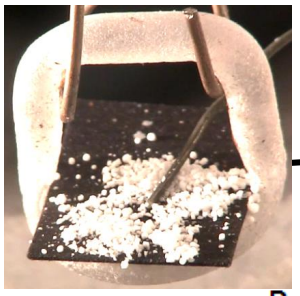
Calcuated with Factsage 6.3
Experimental points from Carroll et al. Geo trans 6(2) (2005)

Study of deliquescence at ÅA

- Deliquescence temperature of $CaCl_2$ and other salts at various water vapor concentrations
- Corrosiveness of deliquescent salts on carbon steel
- Effect of varying water vapor concentration on the deliquescent behavior and corrosion

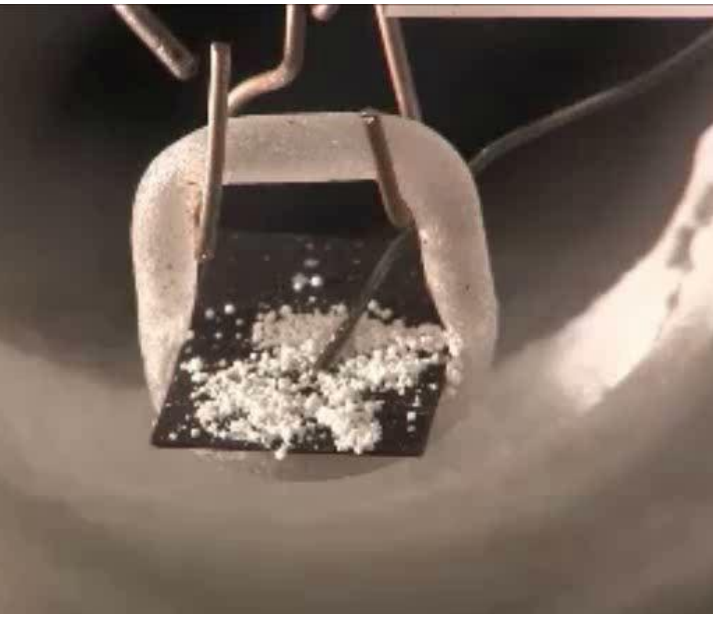
1. Determination of the deliquescence temperature

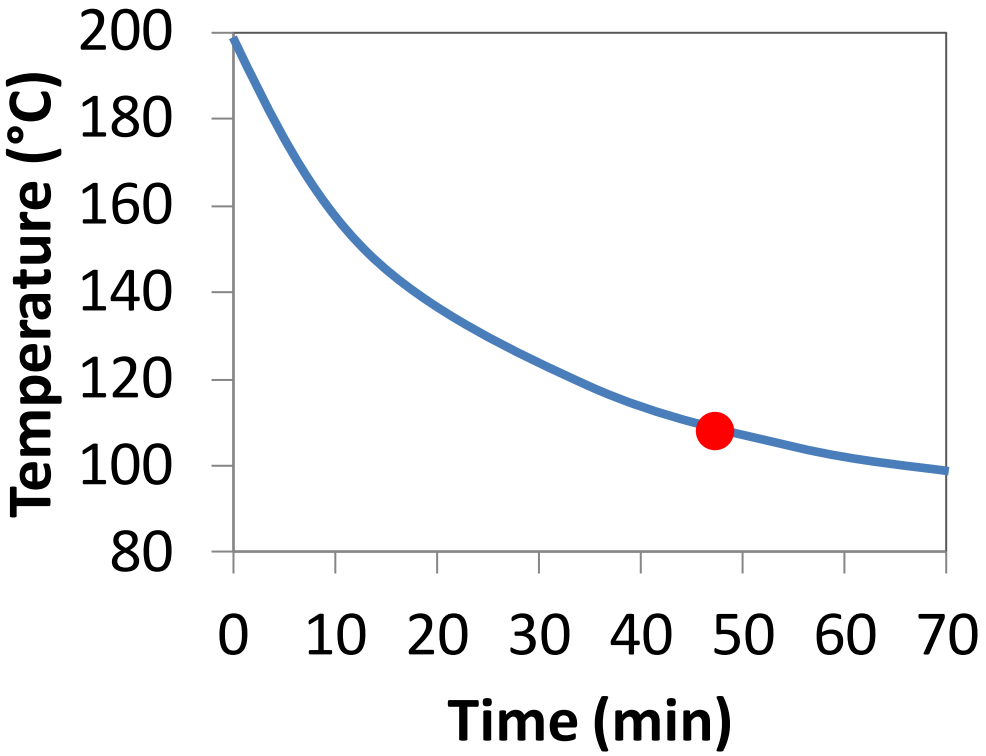
- ~50 mg of $CaCl_2$
- Temperature of furnace slowly decreased from 200°C until deliquescence
- Various H_2O concentrations
- Determination of hysteresis effect



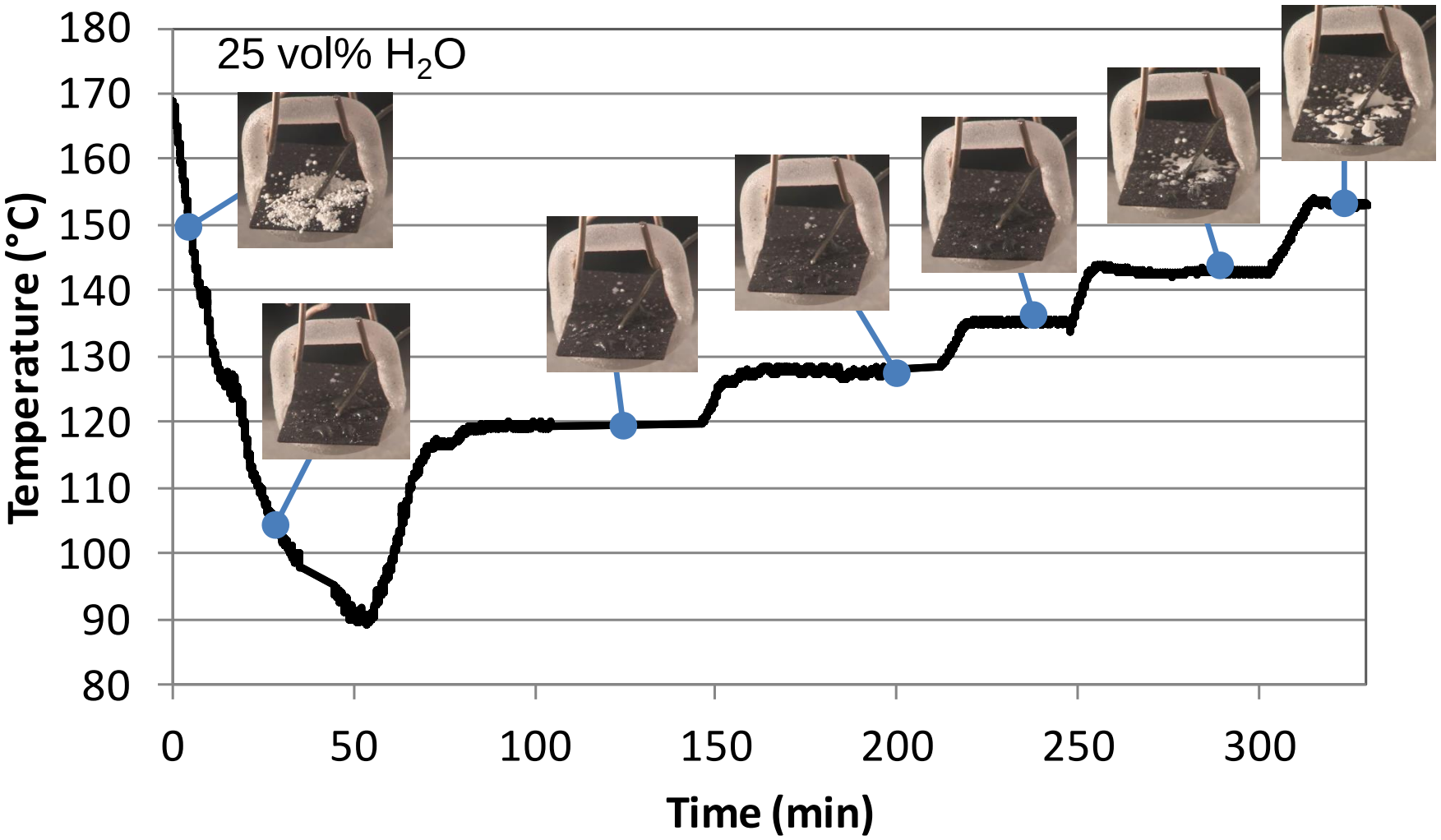
Determination of deliquescence temperature

$CaCl_2$, 25 vol% H_2O

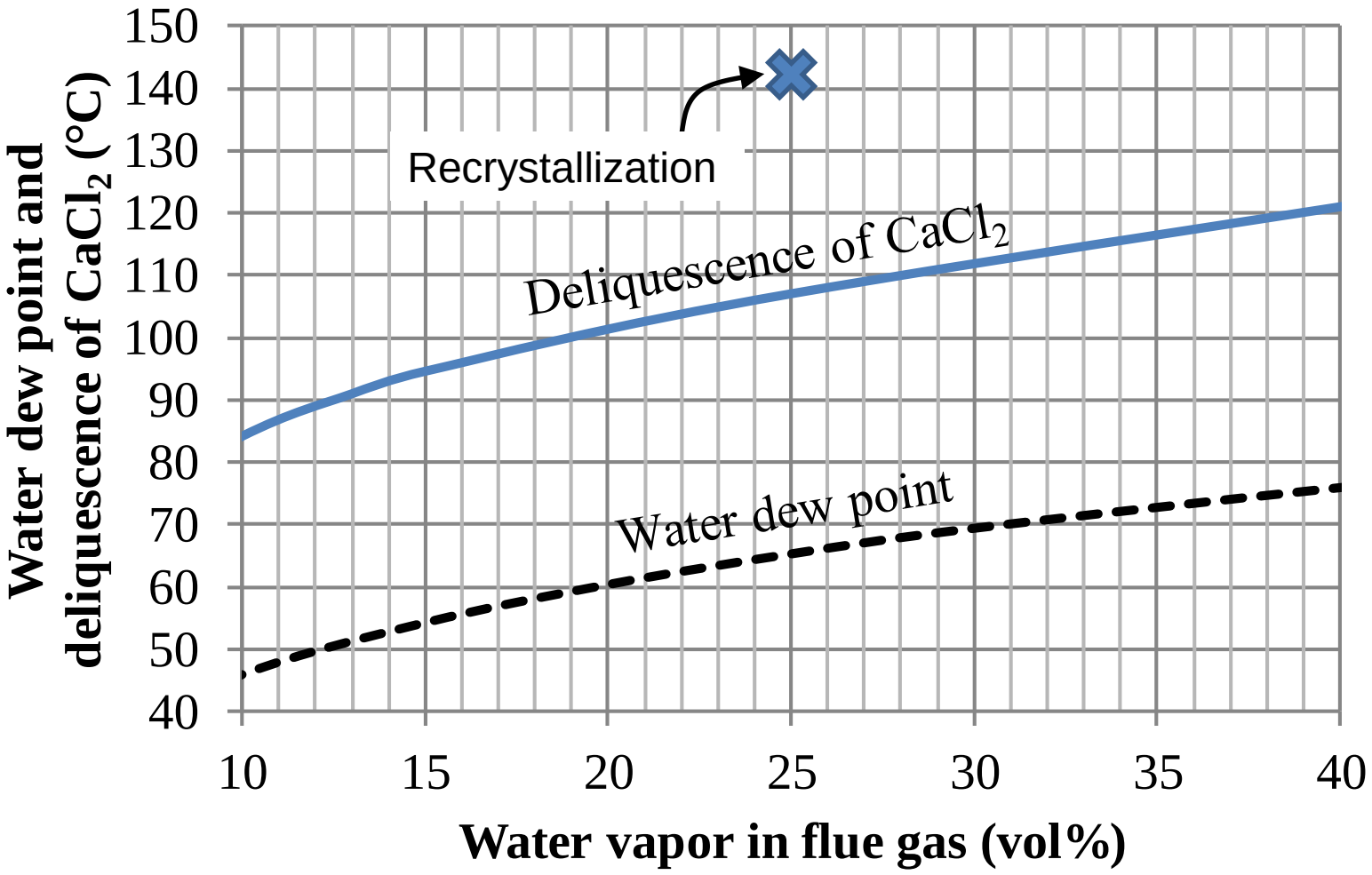




Hysteresis effect of $CaCl_2$

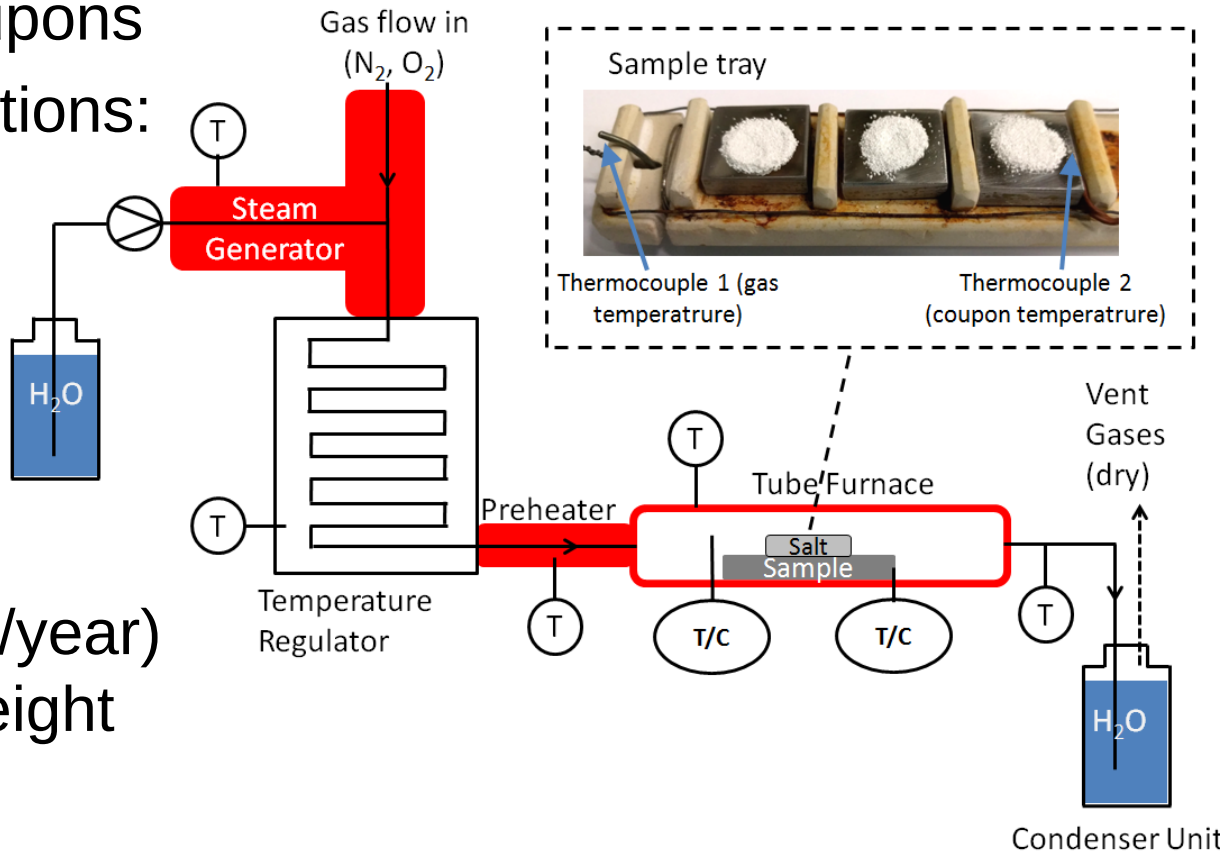


Deliquescence of $CaCl_2$

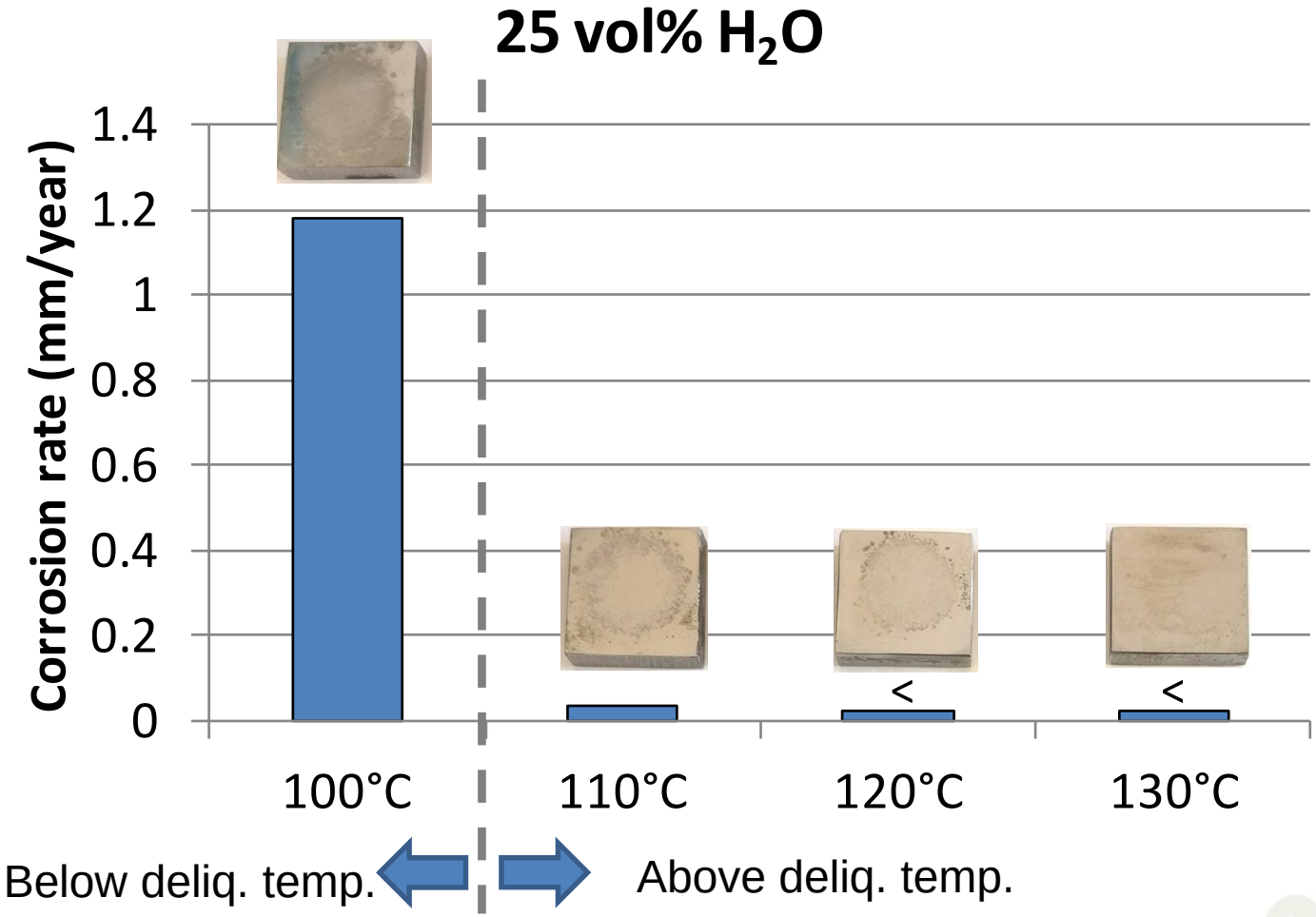


2. Corrosion tests

- 100 mg of $CaCl_2$ placed on carbon steel coupons
- Two H_2O concentrations:
  - 25 vol%
  - 50 vol%
- Temperature
  - 100-160°C
- Exposure time: 4h
- Corrosion rate (mm/year) determined from weight loss

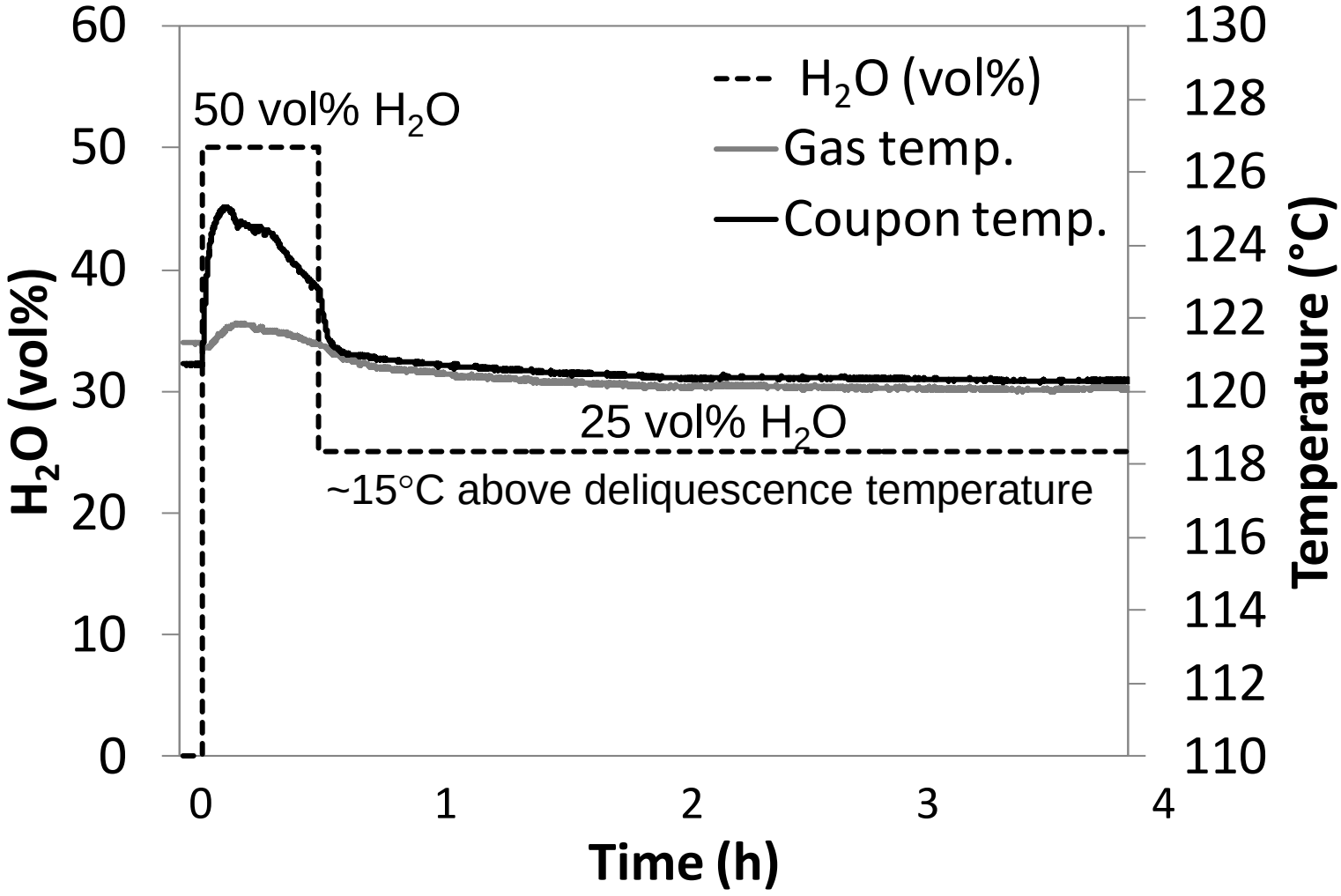


Corrosion rates



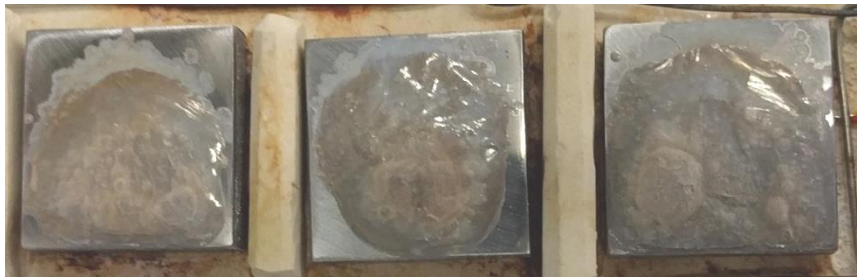
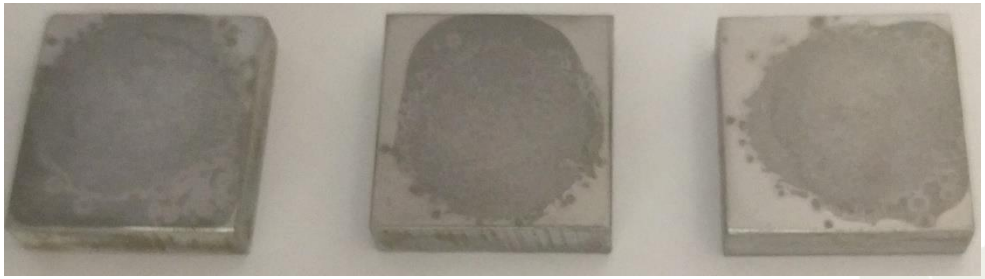
Vainio et al. 2016 Impacts of Fuel Quality on Power Production

Corrosion test with varying H_2O at 120°C



Vainio et al. 2016 Impacts of Fuel Quality on Power Production

Results – hysteresis effect

Before exposure	
After exposure	
Washed samples	

Corrosion rate = 0.5 mm/year

Conclusions

- Hygroscopic deposit in FBC of biomass may cause low-temperature corrosion
- At high water vapor concentrations this may occur at temperatures well above 100°C
- If deliquescence occurs corrosion is usually severe
- Once $CaCl_2$ absorbs water, the water is released at a much higher temperature than the deliquescence temperature
- During down-time of a boiler, hygroscopic deposits may initiate and cause corrosion by absorbing moisture from the air

Acknowledgements

- This work is a part of the project, ‘Low temperature corrosion in combustion – old problem, new approaches’ (Decision No. 289869) is financed by **Academy of Finland** and is gratefully acknowledged

Thank you for your attention!