Corrosion
as a result of dew points and deliqueszent salts in the boiler and in the flue gas treatment

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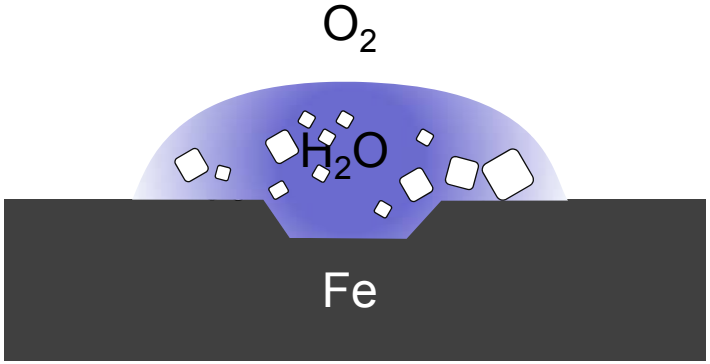
Agenda:
- Deliquescence
- Phenomena
- Mechanisms
- Monitoring

...using the examples of ammonium- and calciumchloride
...for dew point (sulphuric acid) click on www.chemin.de

Deliquescent Salts

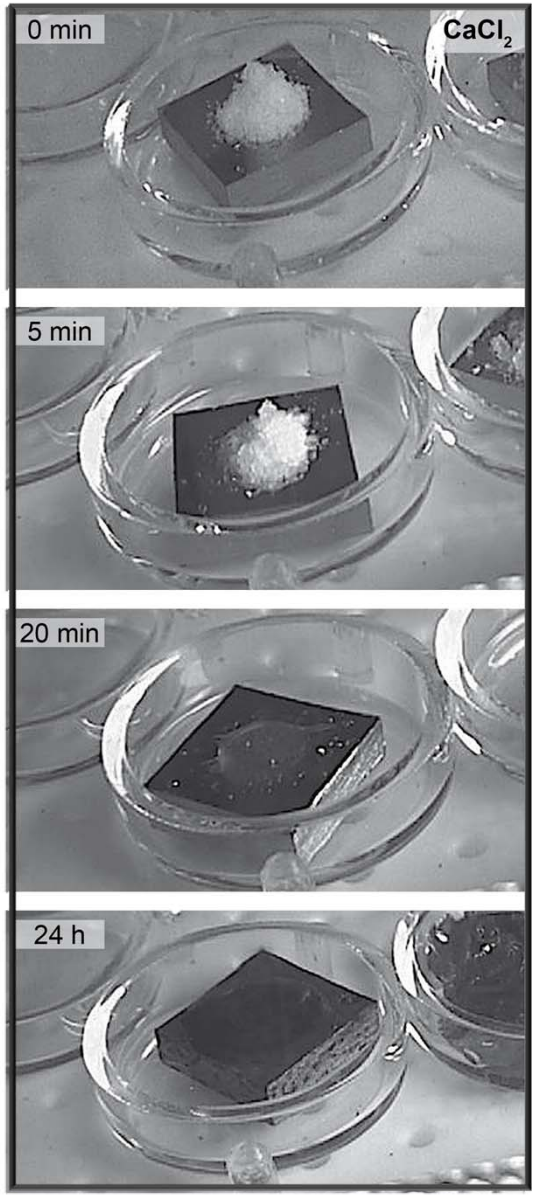
Deliquescent salts are strongly hygroscopic, they deliquesce and form an aqueous electrolyte (saturated, acidic solution).

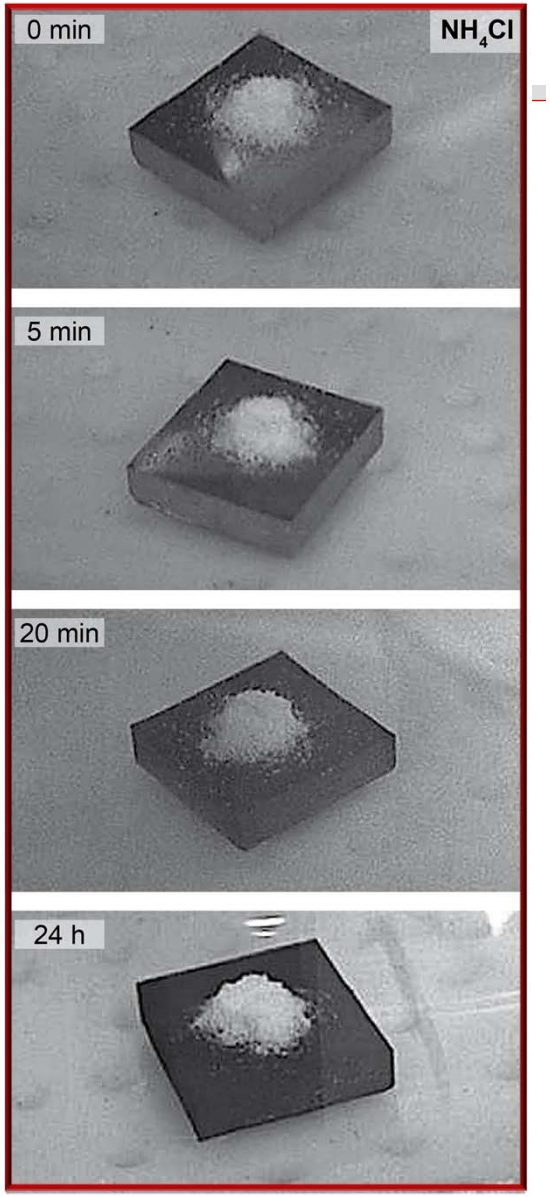


Examples:

- Calciumchloride $CaCl_2$
- Ammoniumchloride NH_4Cl

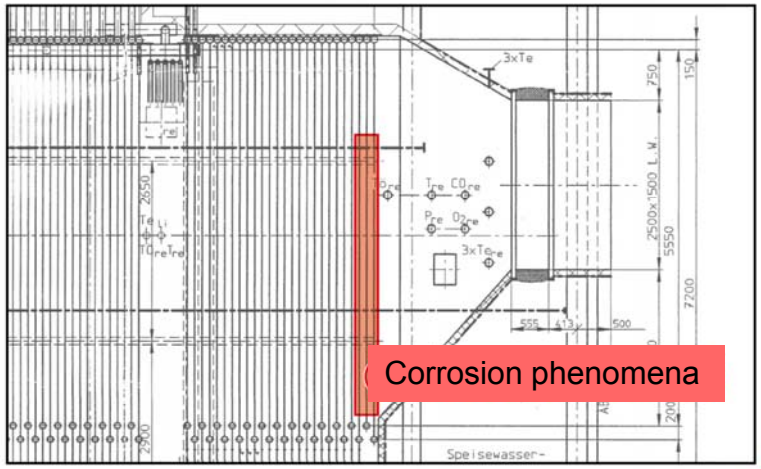
Tests on corrosivity at defined O2- and moisture-content and material temperature

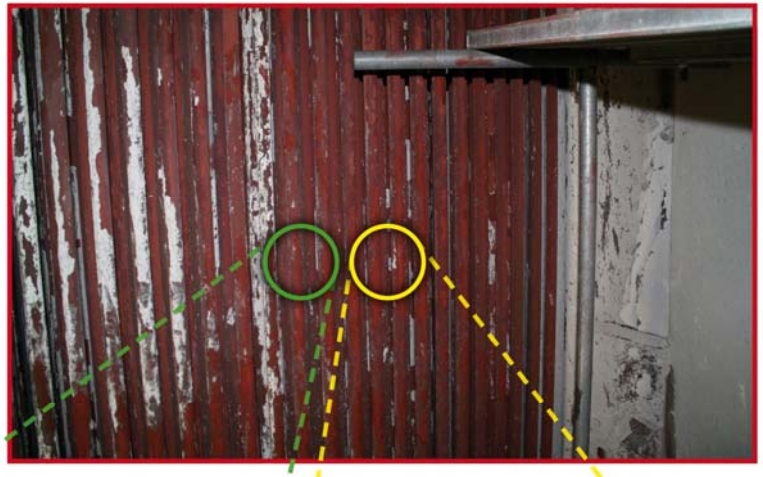


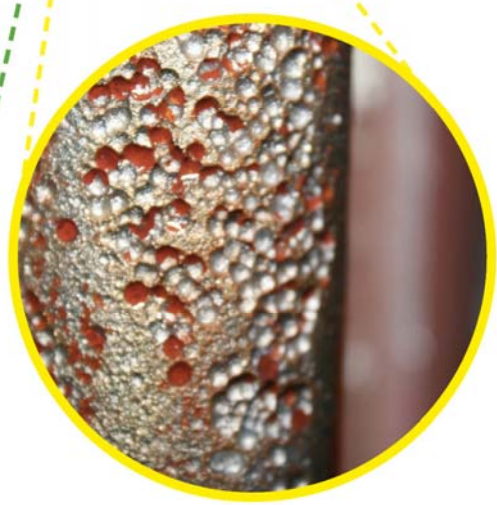


Phenomena1/2: Corrosion on ECO- and sidewall tubes

Fuel: Waste
Firing: Grate
Denox: SNCR





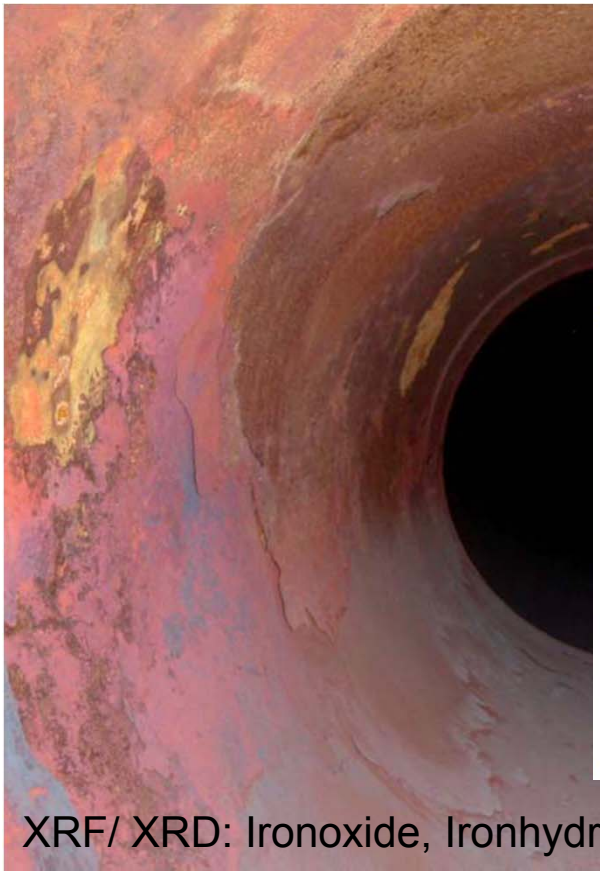


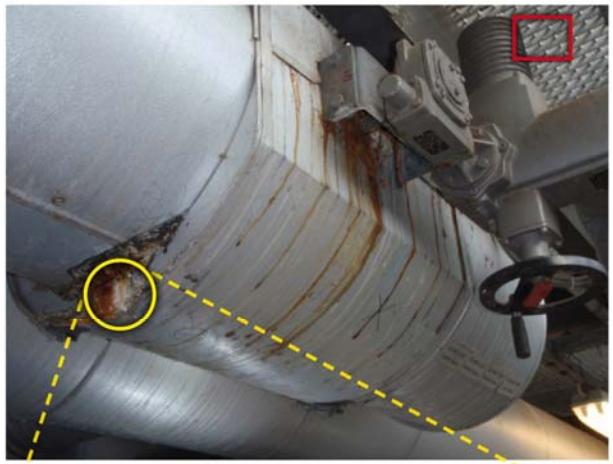
XRD: Ironoxide, Ammoniumironchloride

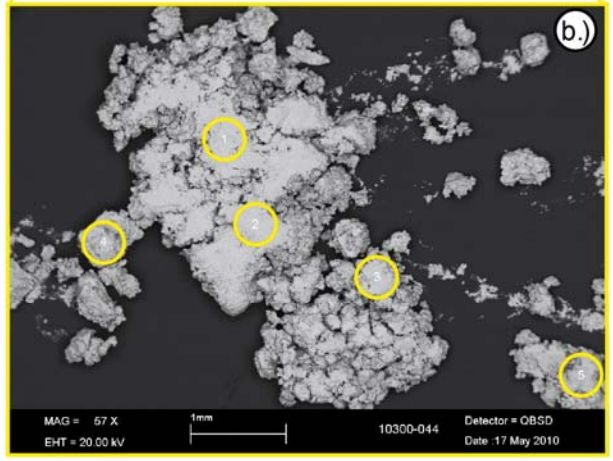
Wet chemical analysis: Ammonium

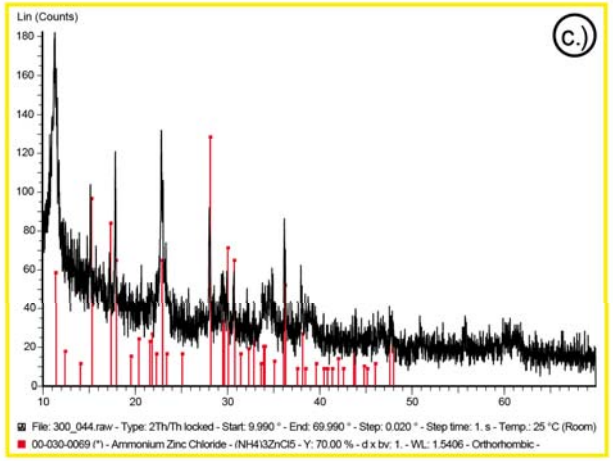
Phenomena 2/2: Corrosion in rezi-duct behind bag filter

Fuel: Waste wood (AI-AII)
Firing: Grate
Denox: no









XRF/ XRD: Ironoxide, Ironhydroxide, Chlorine 1-2 wt.-%

Operating experience with deliquescence corrosion

Fuel:
- Waste
- Refuse derived fuels RDF
- Biomass (renewables,waste wood)
- Co-incineration (?)

Components:
- Economizer
- Walls (sheet and tube steel)
- Flue gas cleaning
- Reci-ducts behind bag filter

Corrosion by deliquescent salts

Firing:
- Grate
- Bubbling fluidized bed
- Circulating fluidized bed
- With/ without SNCR-system
- Reducing NOx-emissions

Materials:
- Steel P235GH

Mechanisms: Desublimation, then deliquescence

Gas

Liquid

Solid

Condensation

e.g. dew point corrosion by sulphuric acid

Desublimation

Step 1: Desublimation of e.g. ammoniumchloride

either NH_4Cl (g) → NH_4Cl (s)

or NH_3 (g) + HCl (g) → NH_4Cl (s) oder (g) → (s)

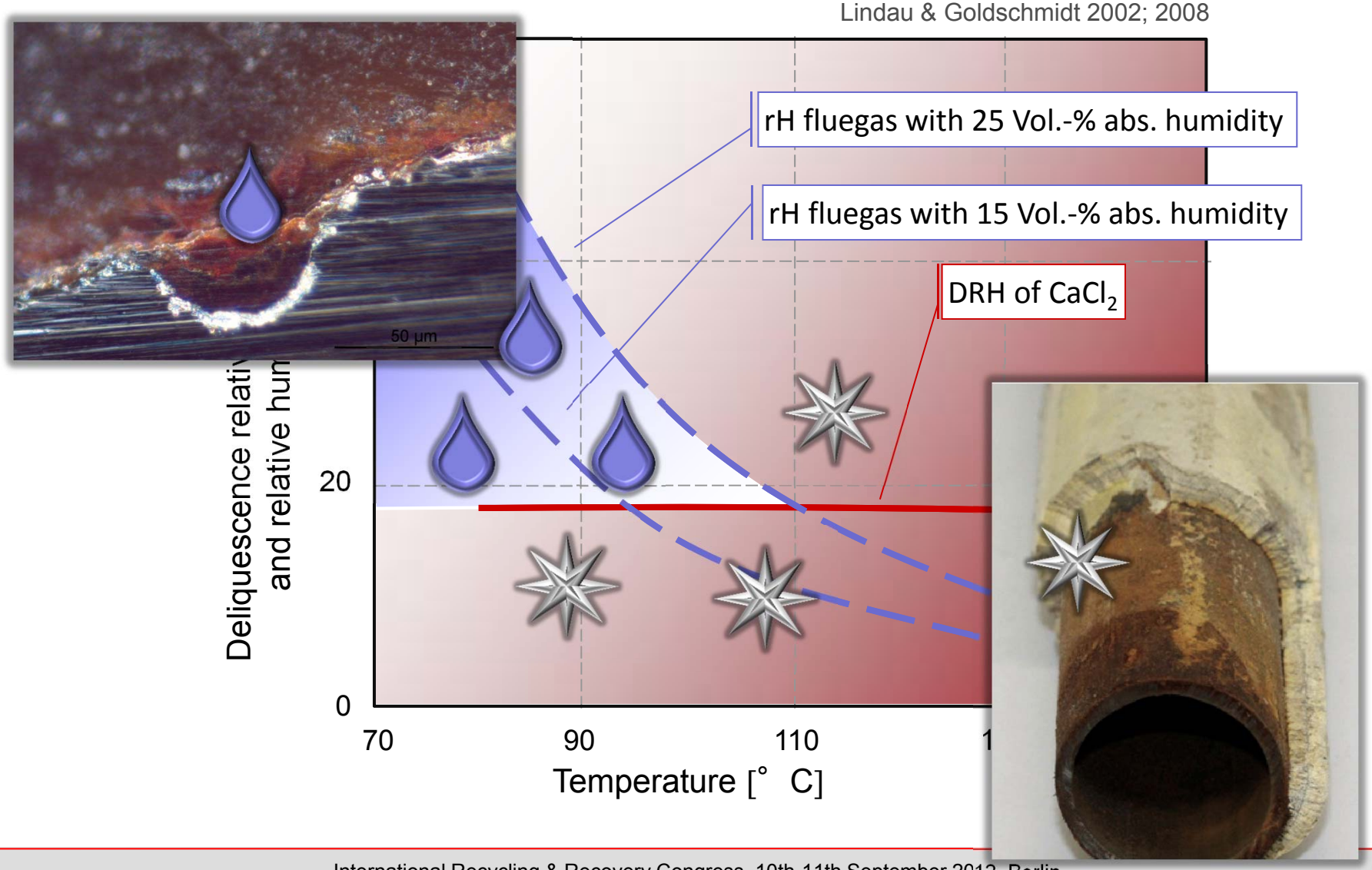
...and when enough relative humidity is avilable
(DRH, Deliquescence Relative Humidity)...

Step 2: Deliquescence

NH_4Cl (s) + H_2O (g) → aqueous elektrolyte

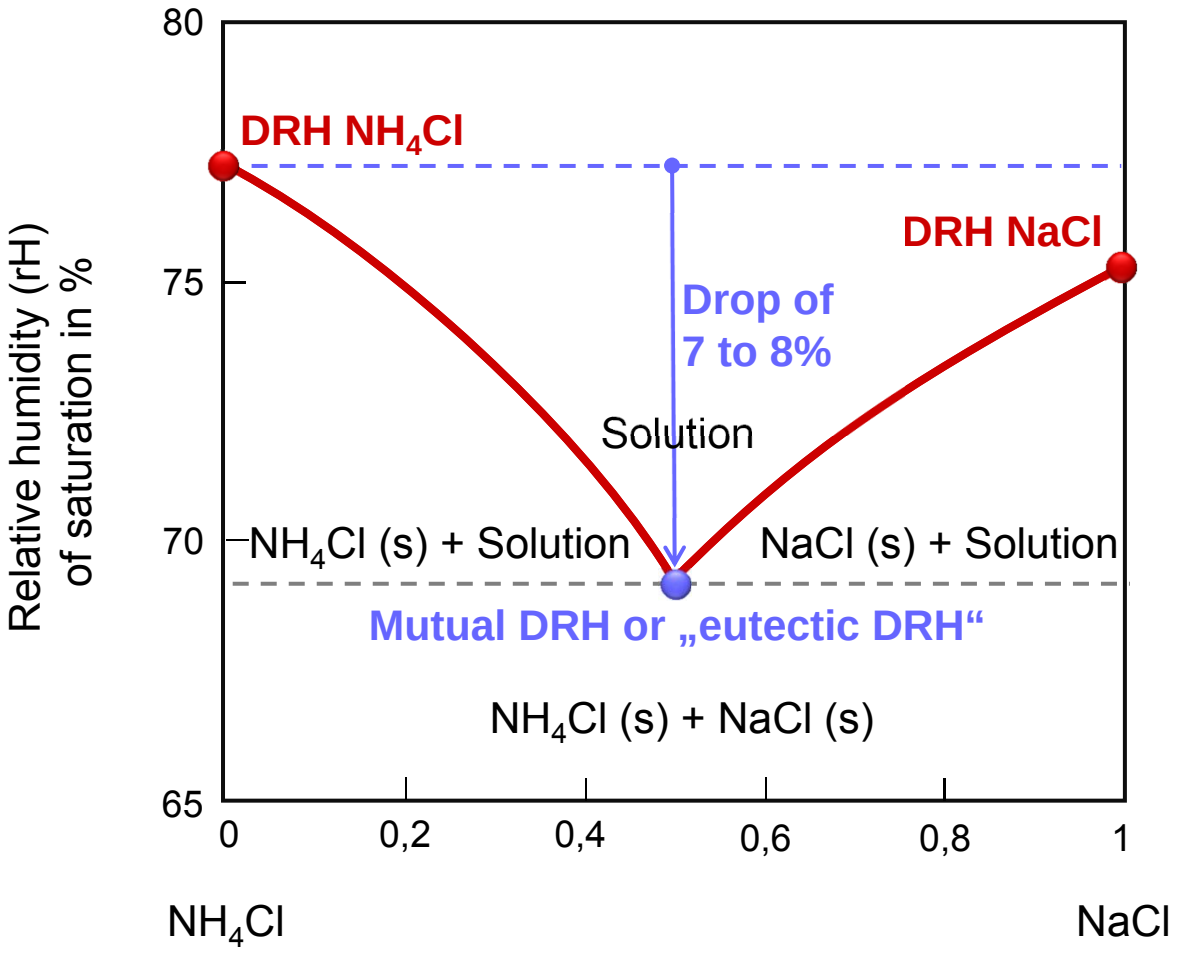
Mechanisms 1/3: Deliquescence relative humidity DRH

Lindau & Goldschmidt 2002; 2008



Mechanisms 2/3: Eutectic deliquescence humidity (mutual DRH)

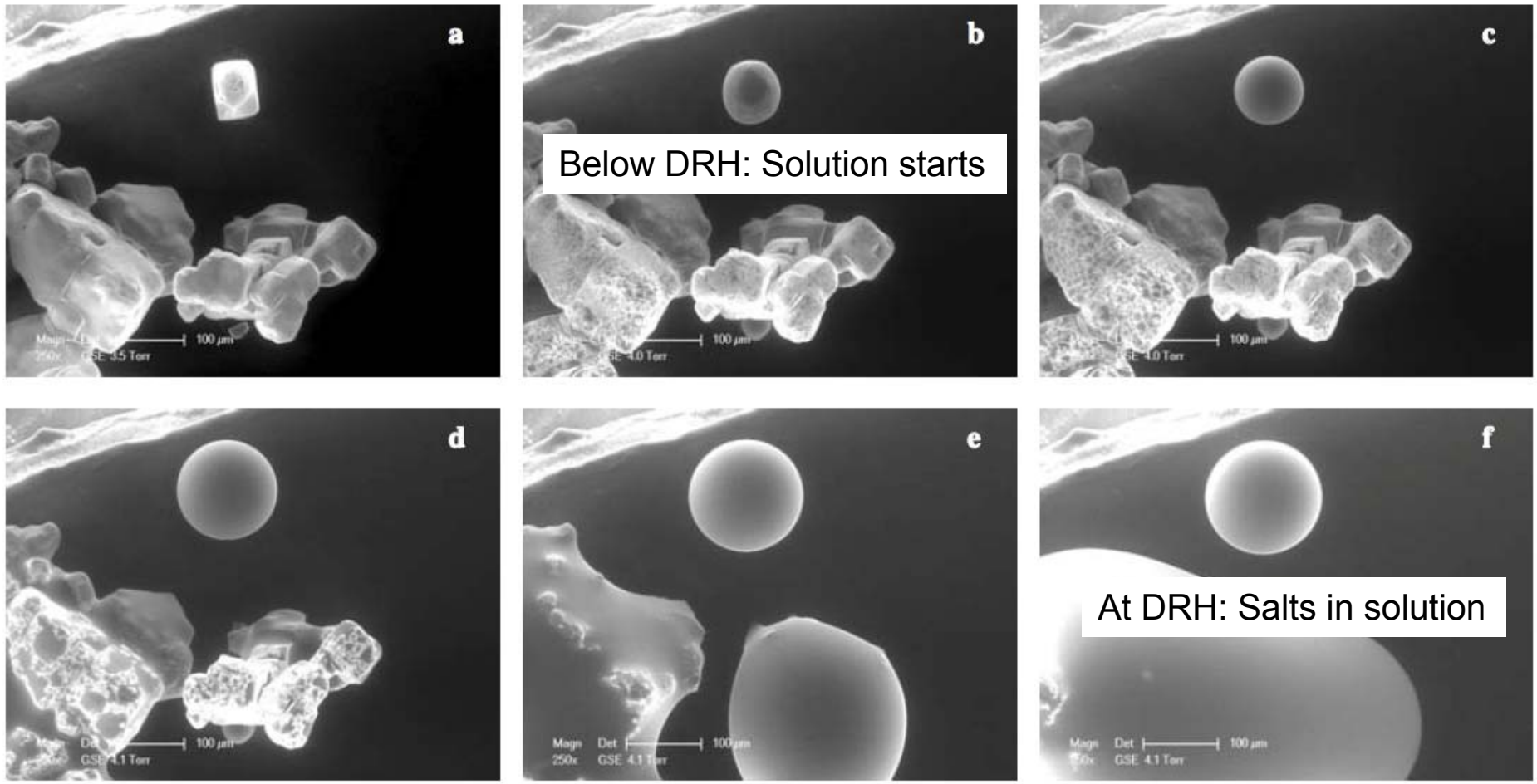
Kelly, Wexler, Chan & Chan 2007



Mechanisms 3/3: Particle size & distribution, capillary-condensation

Deliquescence of NaCl studied below DRH with ESEM (environmental-SEM):

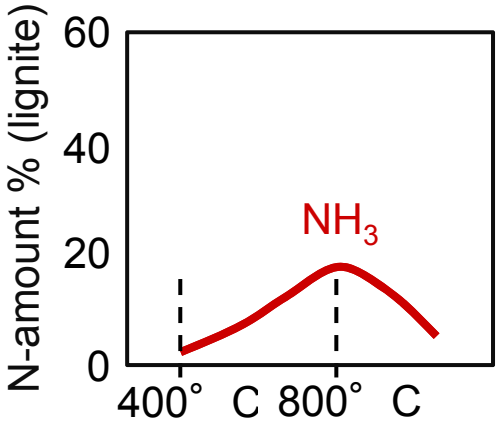
Langlet et al. 2007



Ammonia for ammoniumchloride formation 1/2: Generated in the fire

...to form ammoniumchloride (NH_4Cl) ammonia (NH_3) is needed; HCl is omnipresent.

NH_3 from lignite



Fuel testing

Tan & Li 2001

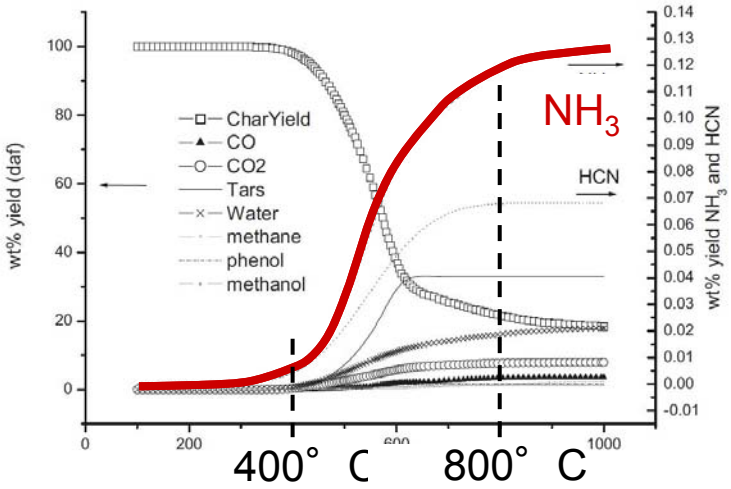
NH_3 from bituminous and lignite

„NH_3 is directly formed during firing, not a secondary product“

Lab testing

Yuan, Zhou & Wang 2012

NH_3 released from wood

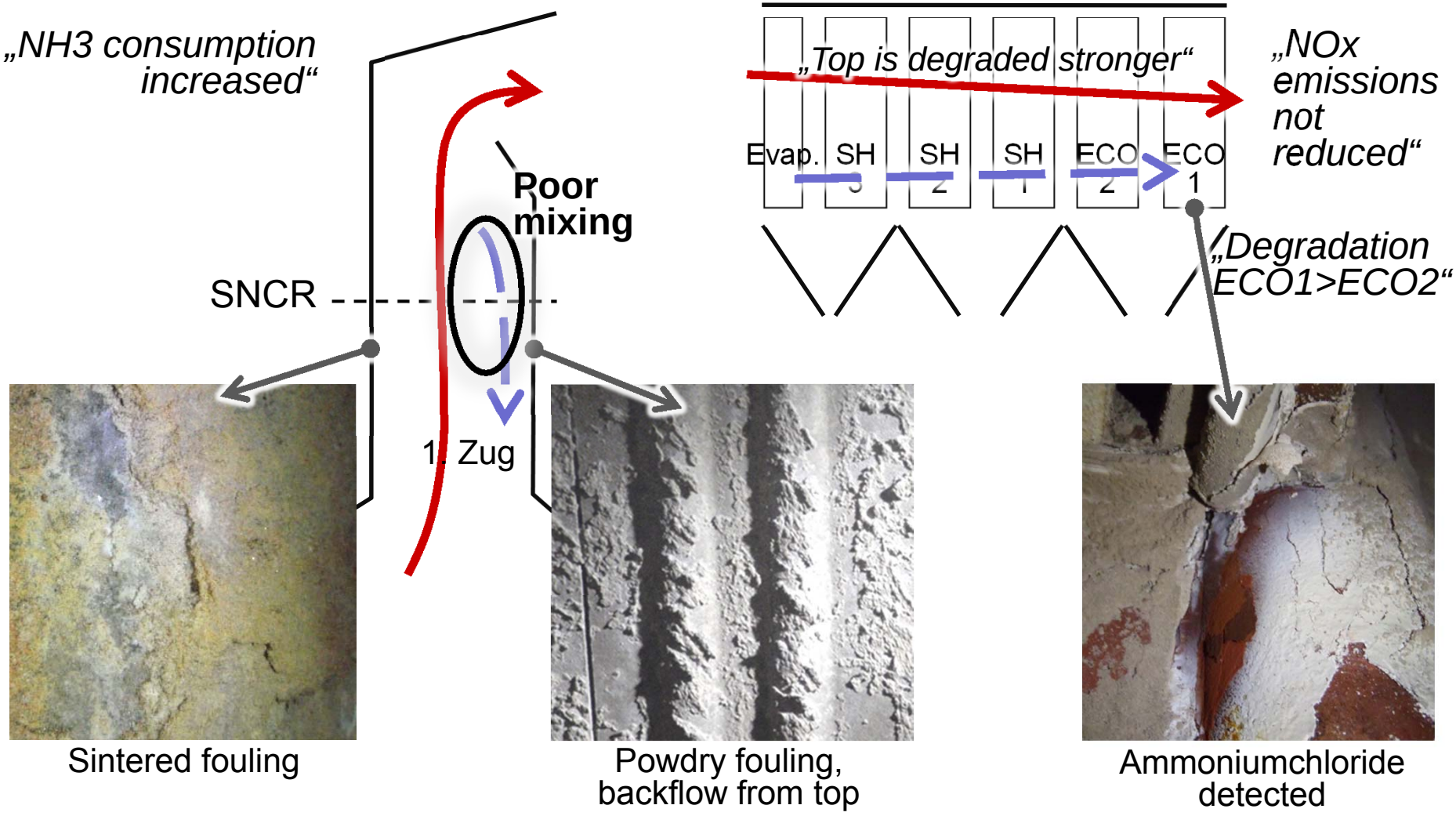


Calculation

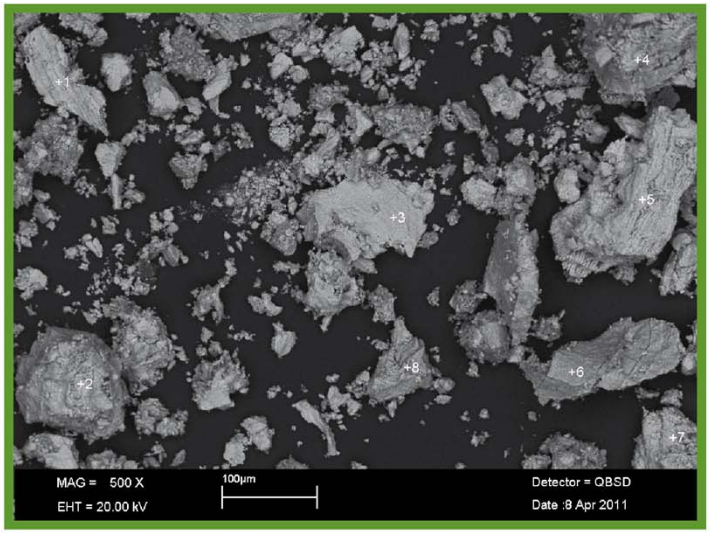
Williams, Jones & Pourkashanian 2012

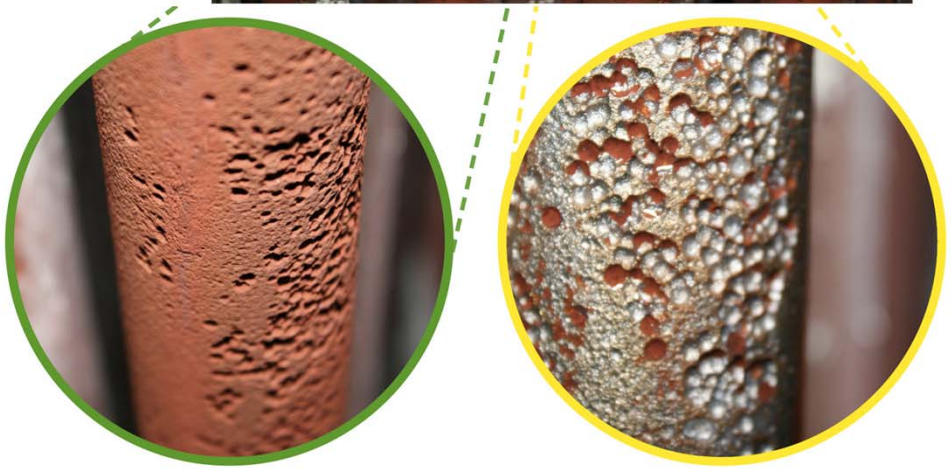
...NH_3 oxidizes mostly >800° C, but not fully;
...NH_3 can form periodically (peaks depending on fuel and firing)

Ammonia for ammoniumchloride formation 2/2: Slip from SNCR



Monitoring 1/3: Sampling during boiler stop

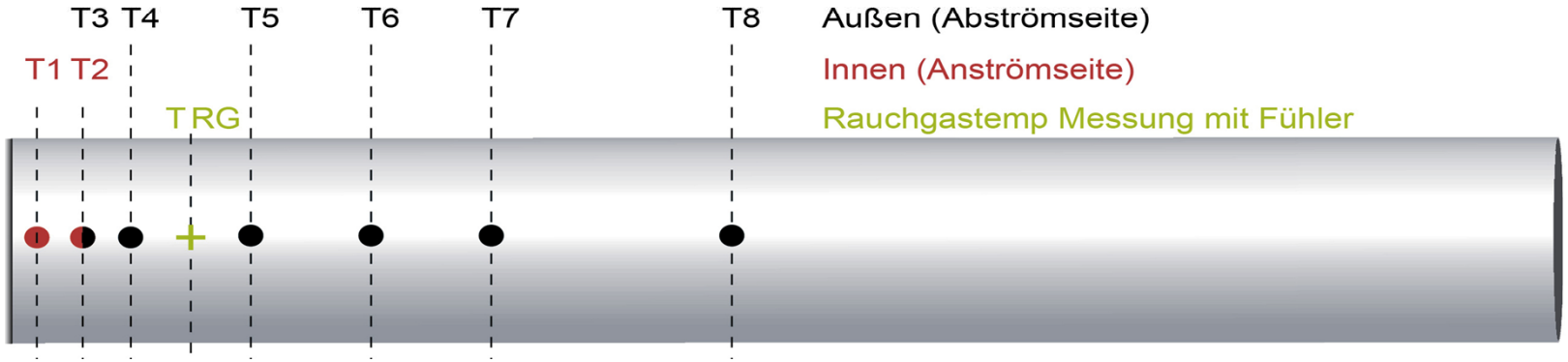


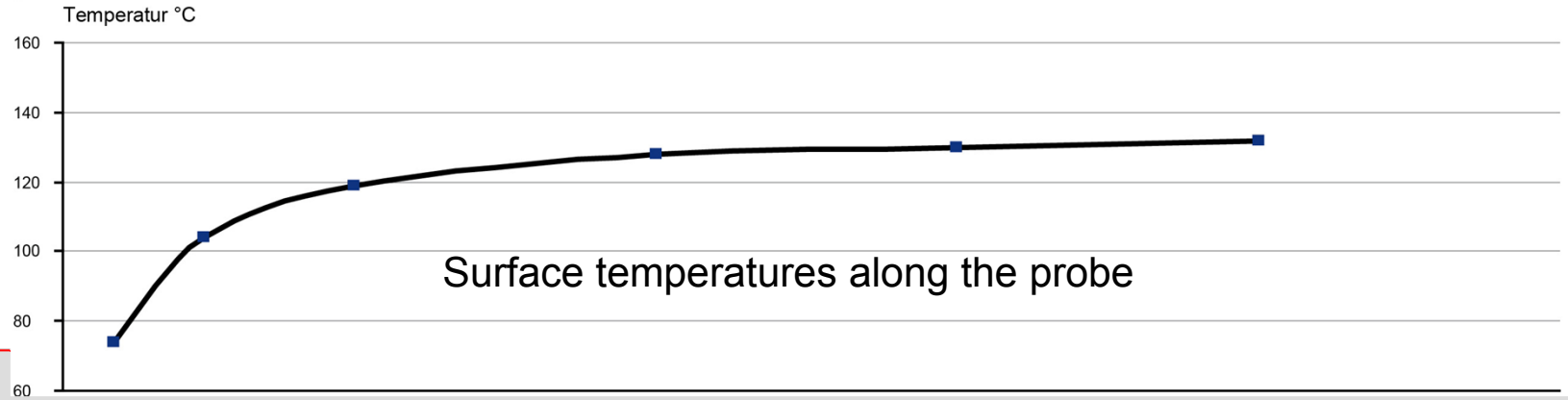


Wet chemical analysis

Probennr.		1	2
F	mg/l	5	1,4
Cl	mg/l	770	920
Br	mg/l	60	87
S	mg/l	146	102
Na	mg/l	61,8	4,8
K	mg/l	54,2	4,3
Ca	mg/l	176	8,9
Fe	mg/l	231	440
Nitrit	mg/l	---	---
Nitrat	mg/l	---	---
NH4	mg/l	145	187

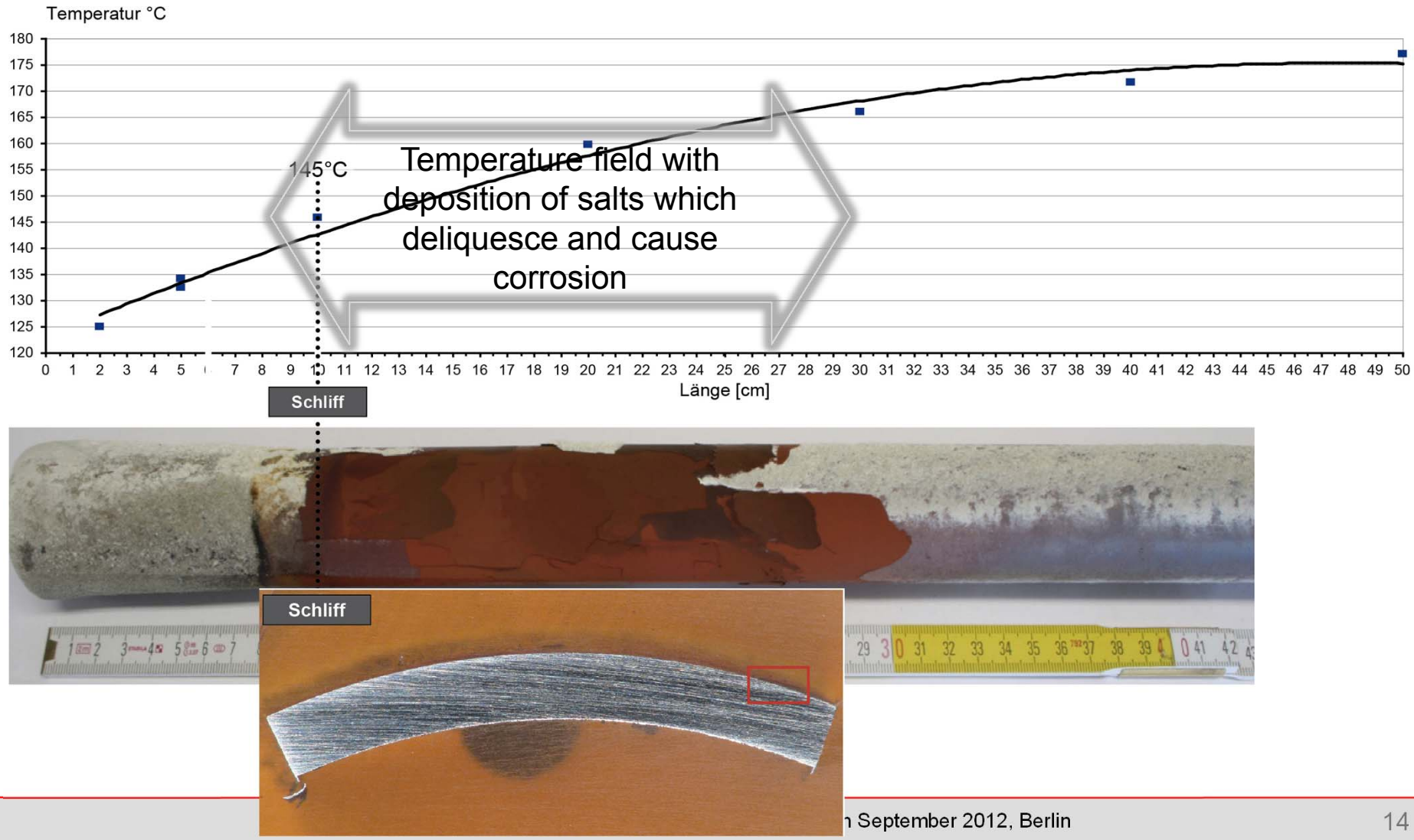
Monitoring 2/3: Deposition probe during boiler operation





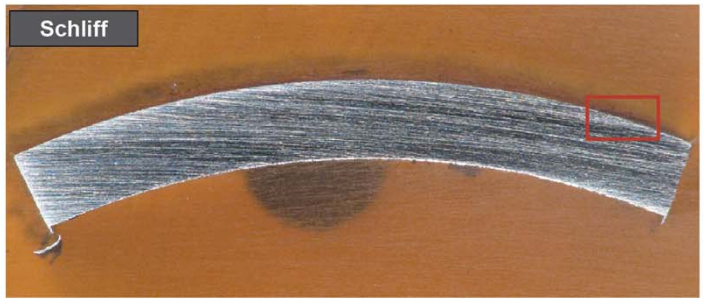
Deposition probe during boiler operation

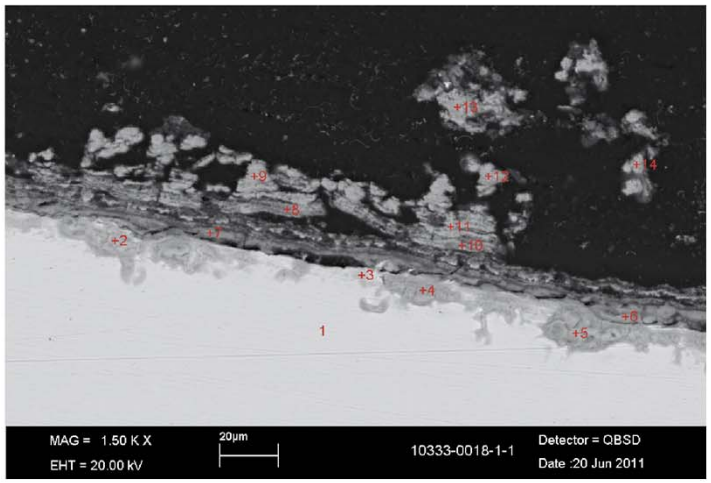
Surface temperatures along the probe



CheMin

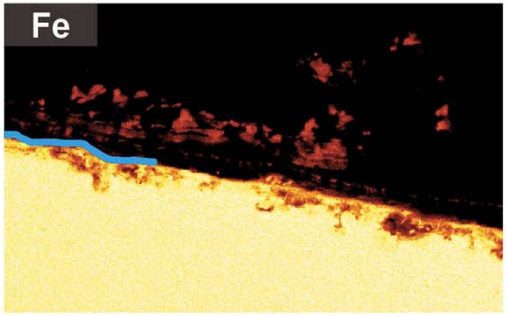
Deposition probe during boiler operation

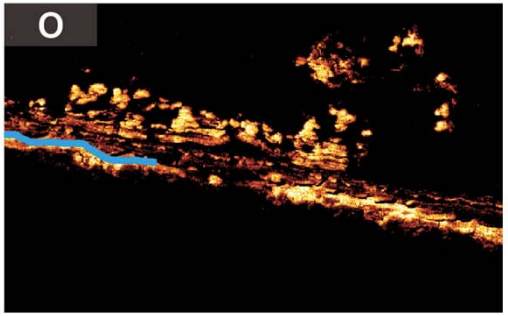


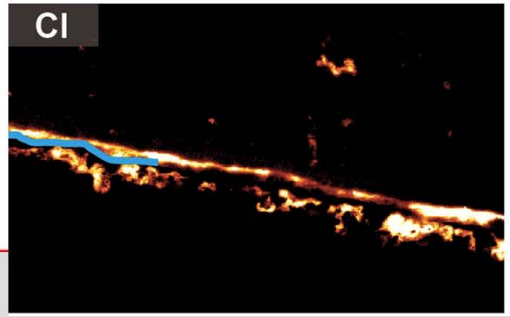


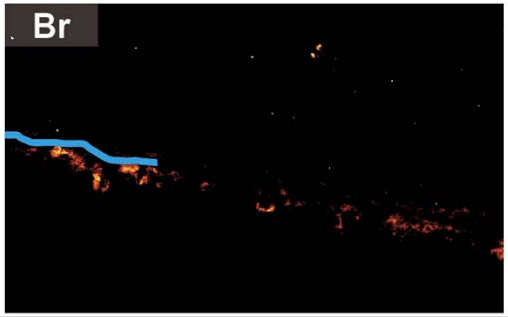
Schliff	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Stickstoff	-	-	-	-	-	+	+	-	-	-	-	+	+	-
Sauerstoff	---	28,1	20	32,7	24	29,9	19,2	29,8	33,1	28,7	33,5	32,4	33,9	34
Natrium	---	---	---	---	---	---	---	---	---	---	---	---	0,5	0,2
Aluminium	0,3	---	---	---	---	---	---	---	---	---	---	---	---	---
Silizium	0,3	0,2	0,3	0,2	0,2	0,3	0,2	---	---	4,8	---	---	0,2	0,2
Schwefel	---	---	---	---	---	---	---	2,6	0,8	2	1,4	1,4	3,4	1,6
Chlor	---	9,4	5,7	5,5	25,2	13,4	36,7	5,2	1,5	3,5	1,7	5,6	1,5	1,1
Kalium	---	---	---	---	---	---	---	---	---	---	---	---	0,6	---
Mangan	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Eisen	99,3	58,7	72,8	60,4	48	55,8	41,8	62,1	64,1	60,4	63,2	59,2	59,1	62,5
Brom	---	3,6	1,2	1,2	2,4	0,5	1,8	---	0,3	0,5	---	1,1	0,9	0,4
Summe	100	100	100	100	100	100	100	100	100	100	100	100	100	100

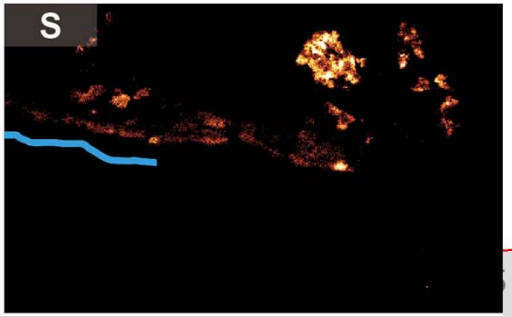
---: nicht nachgewiesen, +: qualitativ nachgewiesen











Monitoring 3/3: Lab testing

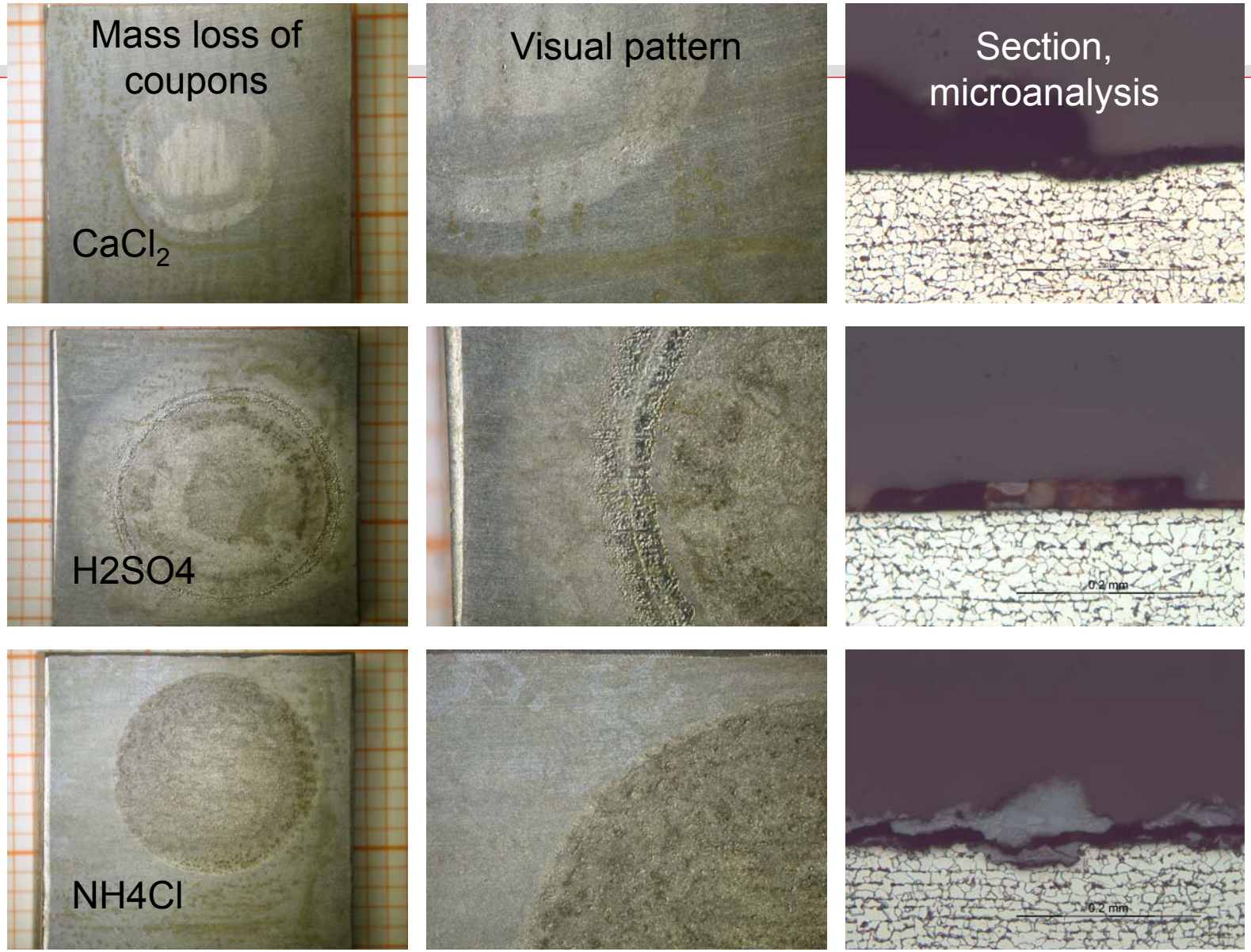
Testing of:

- Relative corrosivity of different salts or liquids
- Corrosivity of real deposits/ filter dust at defined conditions
- Material testing under defined salts or under real deposits/ filter dust
- Results within weeks

Condition	Tested	Limits
Moisture absolut [Vol.-%]	ca. 0-30	up to 70
Surface temperature [° C]	80-110	up to 150
Atmosphere [° C]	90-120	up to 160-180
Oxygene content [Vol.-%]	ca. 6-21	<6

Lab Testing

Relative corrosivity of different salts and acids under defined conditions tested in a few days



Thank you for your attention

Deliquescent apparition - width: 15 mm