Investigations into corrosion in SV Purmerend BWC system

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May 2016
ECN-L--16-047

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26 May 2016,
SV Purmerend

Project objectives

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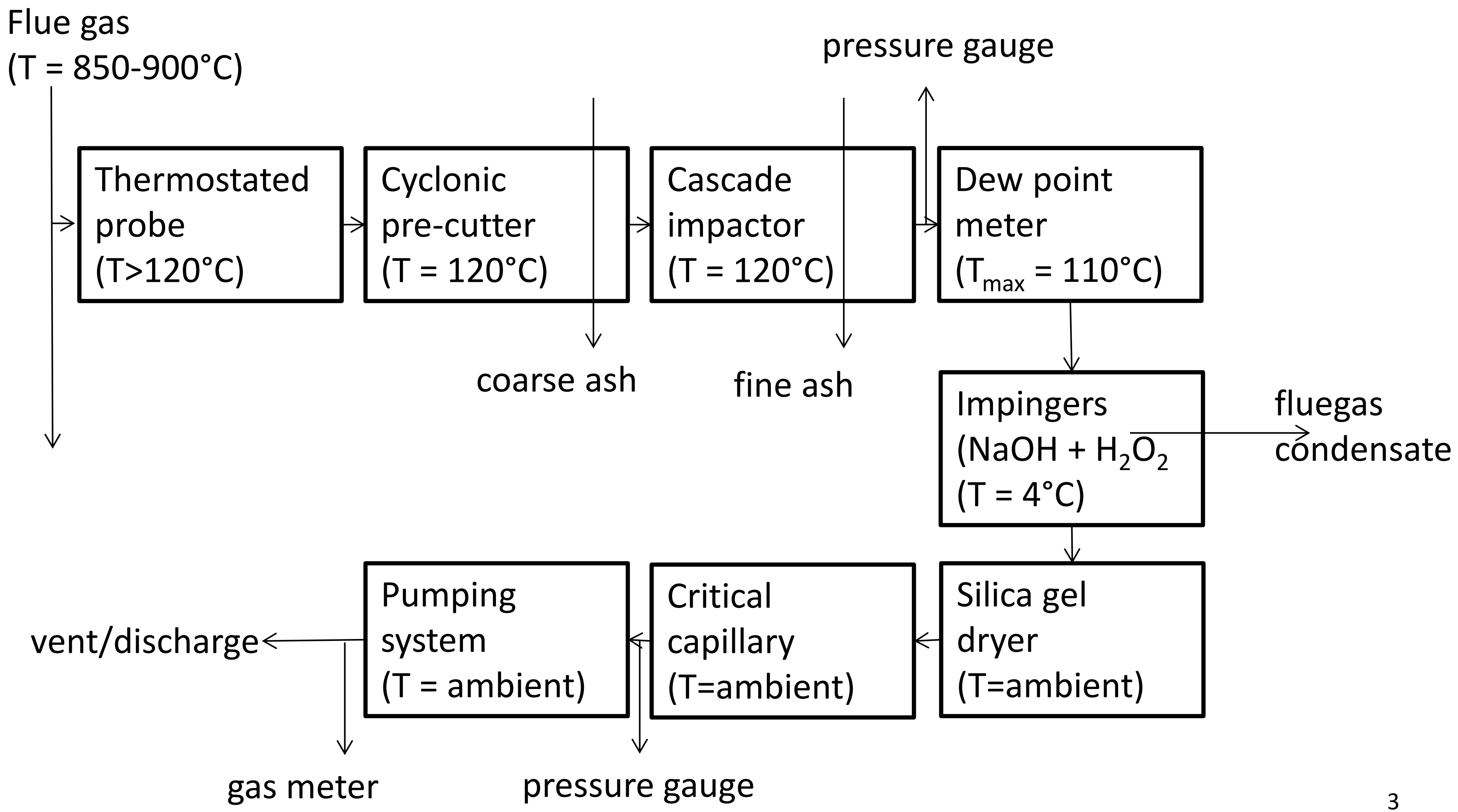
- to deliver a set of on-line (real time) measured dew points of the real flue gas in (one of) the Stadsverwarming Purmerend boiler unit(s)
- to give insights into the fine solids load and nature in the flue gas
- to give insight into humidifier influence on the dew point value
- SNCR/deNOx influence on the dew point value

PM sampling equipment

line up



Flue gas
(T = 850-900°C)

pressure gauge

Thermostated probe (T>120°C)

Cyclonic pre-cutter (T = 120°C)

Cascade impactor (T = 120°C)

Dew point meter (T_{max} = 110°C)

coarse ash

fine ash

Impingers (NaOH + H_2O_2 (T = 4°C)

fluegas condensate

Pumping system (T = ambient)

Critical capillary (T=ambient)

Silica gel dryer (T=ambient)

vent/discharge

gas meter

pressure gauge

PM sampling equipment

Cascade impactor

University of Washington PILAT V impactor:

- 12 stages (pre-cutter/PDP, 10 jet stages)
- minimum cut-off: <0.2 µm
- all stainless steel
- deposition substrates/filters:
  - non-greased stainless steel
  - backup filter: none to prevent water/acids

PM sampling

analyses

Analyses:

- Dew points recorded on-line
- Correction for pressure applied "manually"
- pre-cutter and deposition substrates with particles in the range of 50-0.2 um on 10/11 stages, were weighed back. This gave the total dust mass value (mg) and size-resolved distribution curve.
- divided by the gas volume sucked during the measurement this number was translated into dust load (mg/mn3).
- two dust specimens analysed by means of SEM/EDX to verify their composition and morphology.
- three historical flue gas condensates analysed by Ion Chromatography for chlorides and sulphates and Inductively-Coupled Plasma/Atomic Emission Spectroscopy for main and trace elements analyses.

sampling

general observations

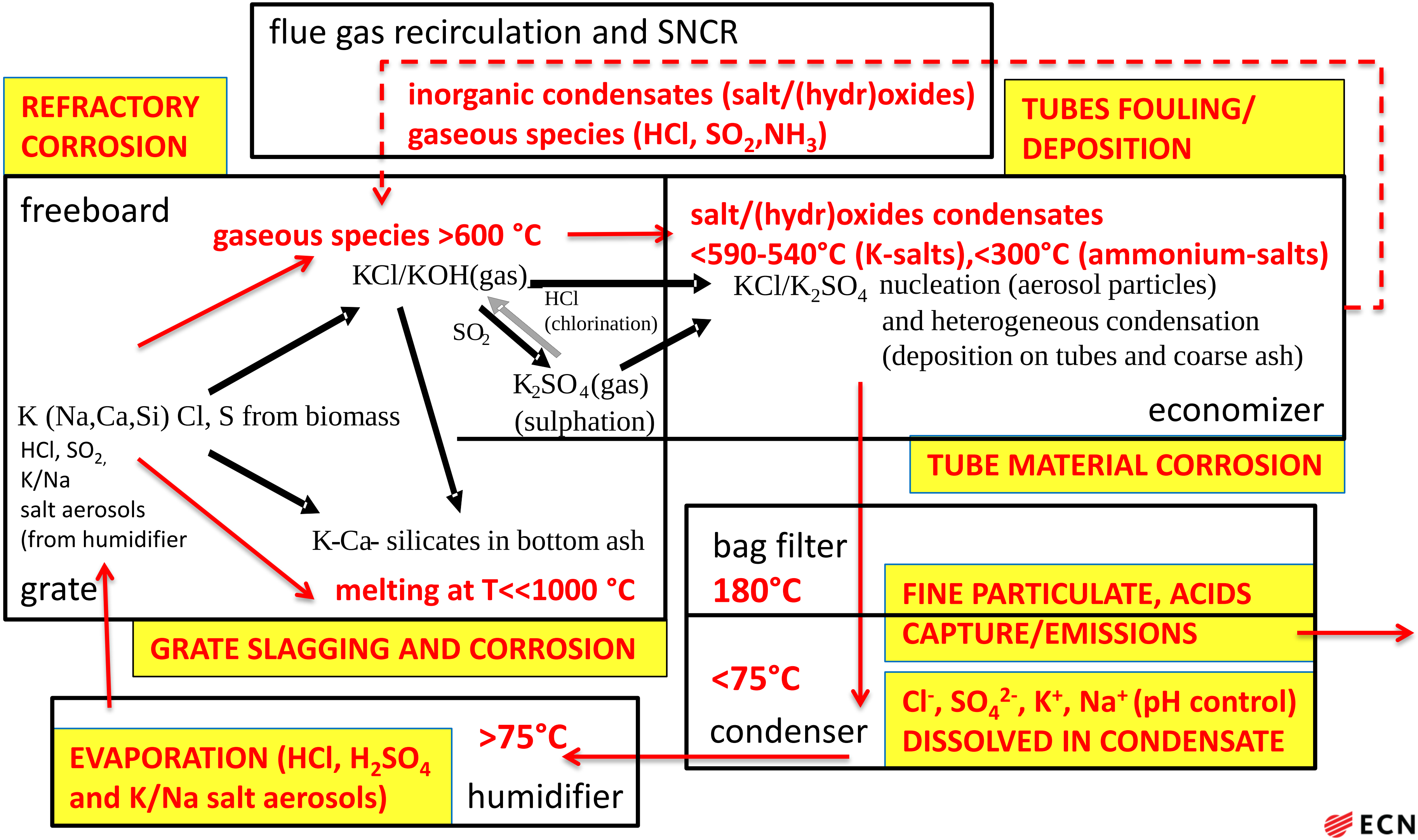
The following was observed:

- There was white film deposit build up on the probe's body at the instant it was introduced into the system
- Little if any coarse deposits on the probe
- No condensation in the trace heated part of the sampling system
- No visible deposits in the transfer duct of the probe
- Deposits in the cascade impactor on the form of typical "stacks" and no films
- No deposition of any kind in the dew point meter
- Upon cooling, transparent condensate forming in the transfer line (ambient) between dew point meter and the impingers
- Slow and minor deposit formation in the critical capillary
- Slow yet steady pressure drop/vacuum build up in the system (as measured at during the measurement

Results and discussion

Biomass problem elements chemistry:

(earth) alkalis, Cl and S fate in SVP system



flue gas recirculation and SNCR

inorganic condensates (salt/(hydr)oxides)
gaseous species (HCl, SO_2,NH_3)

REFRACTORY CORROSION

TUBES FOULING/ DEPOSITION

freeboard

gaseous species >600 °C

KCl/KOH(gas)

HCl (chlorination)

SO_2

K_2SO_4(gas) (sulphation)

K (Na,Ca,Si) Cl, S from biomass

HCl, SO_2,
K/Na
salt aerosols
(from humidifier

K-Ca- silicates in bottom ash

melting at T<<1000 °C

grate

GRATE SLAGGING AND CORROSION

salt/(hydr)oxides condensates
<590-540°C (K-salts),<300°C (ammonium-salts)

KCl/K_2SO_4 nucleation (aerosol particles)
and heterogeneous condensation
(deposition on tubes and coarse ash)

economizer

TUBE MATERIAL CORROSION

bag filter
180°C

FINE PARTICULATE, ACIDS CAPTURE/EMISSIONS

<75°C

condenser

Cl^-, SO_4^{2-}, K^+, Na^+ (pH control) DISSOLVED IN CONDENSATE

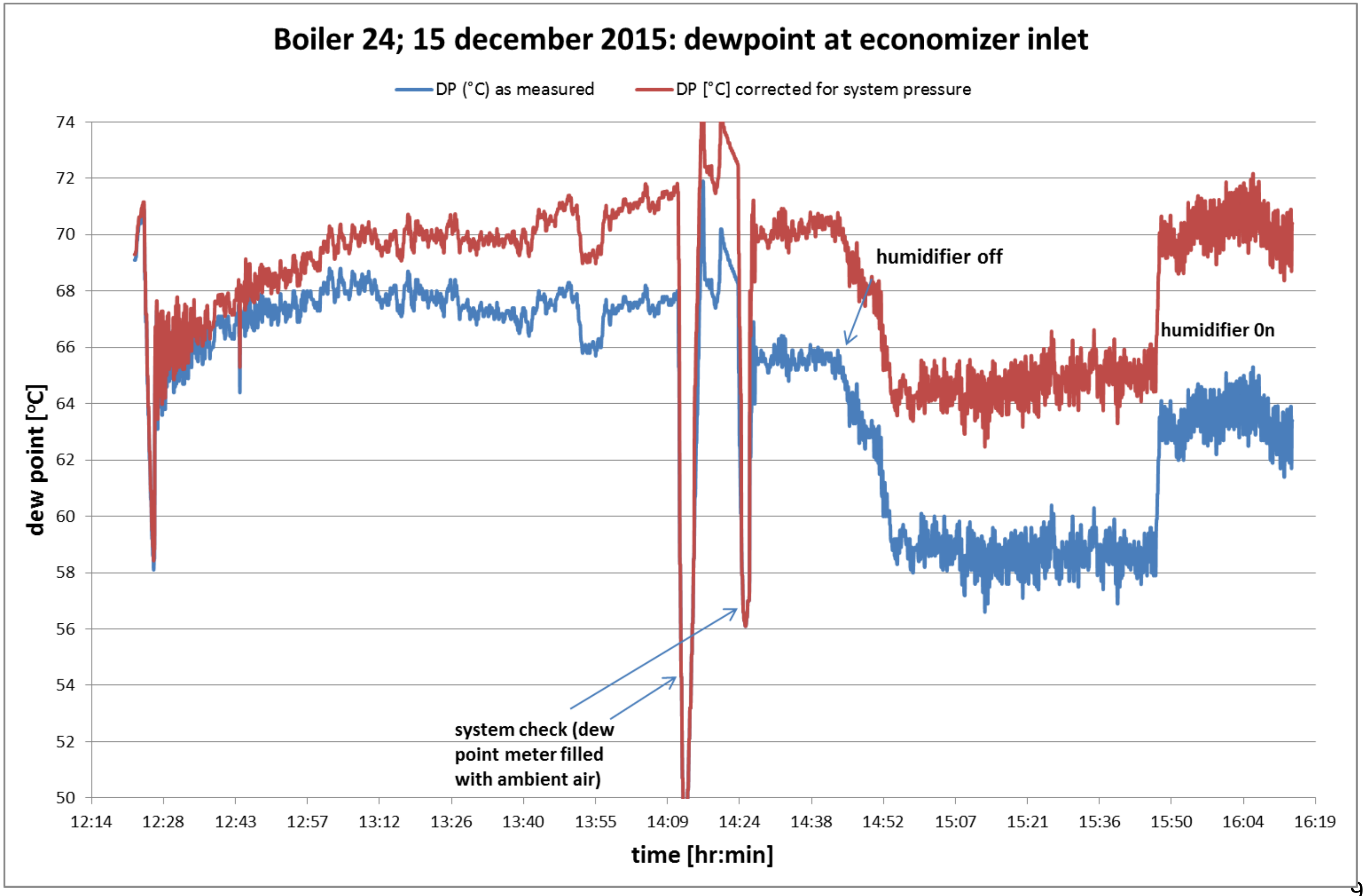
EVAPORATION (HCl, H_2SO_4 and K/Na salt aerosols)

>75°C

humidifier

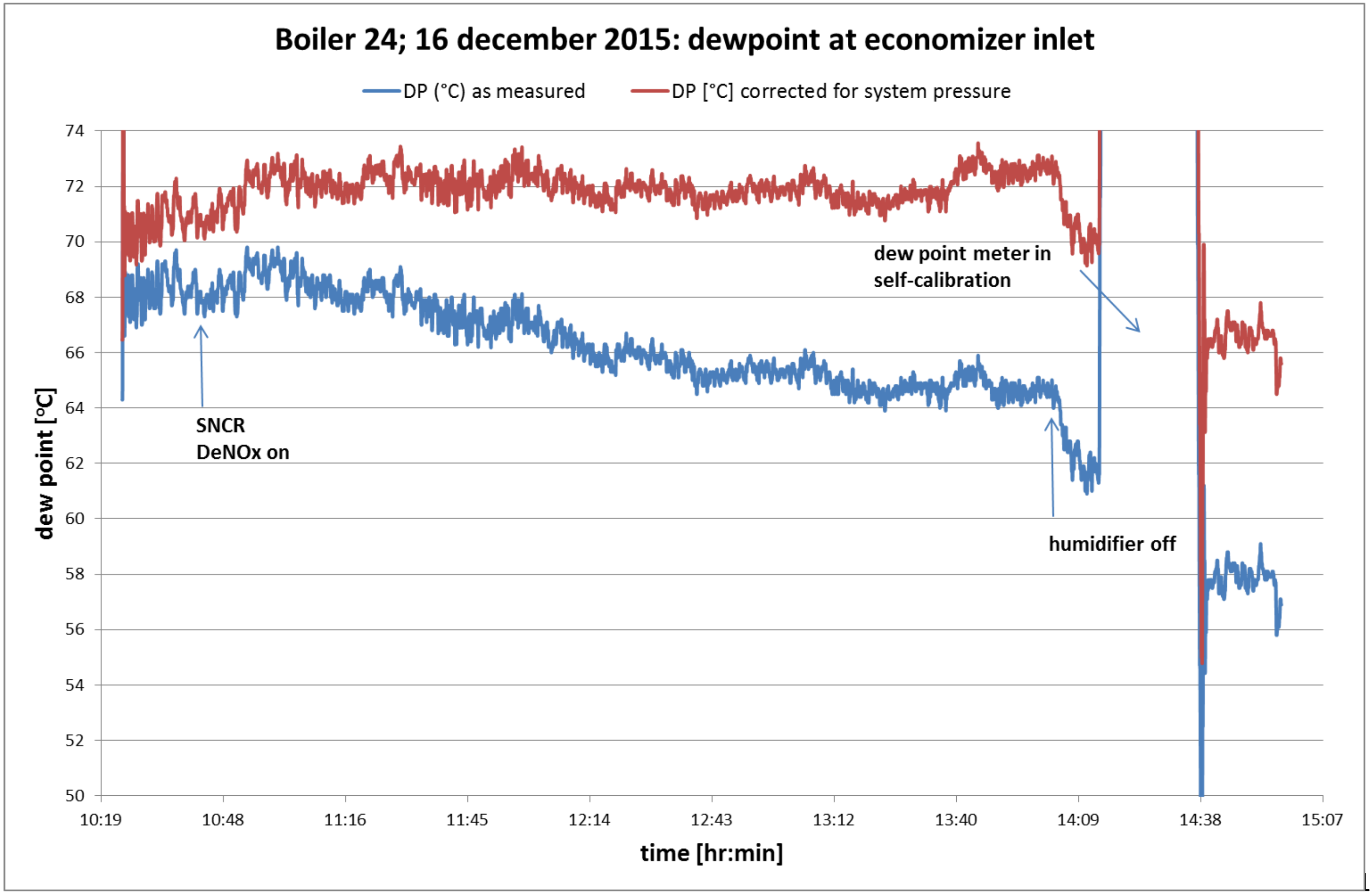
Results

dew point (1)



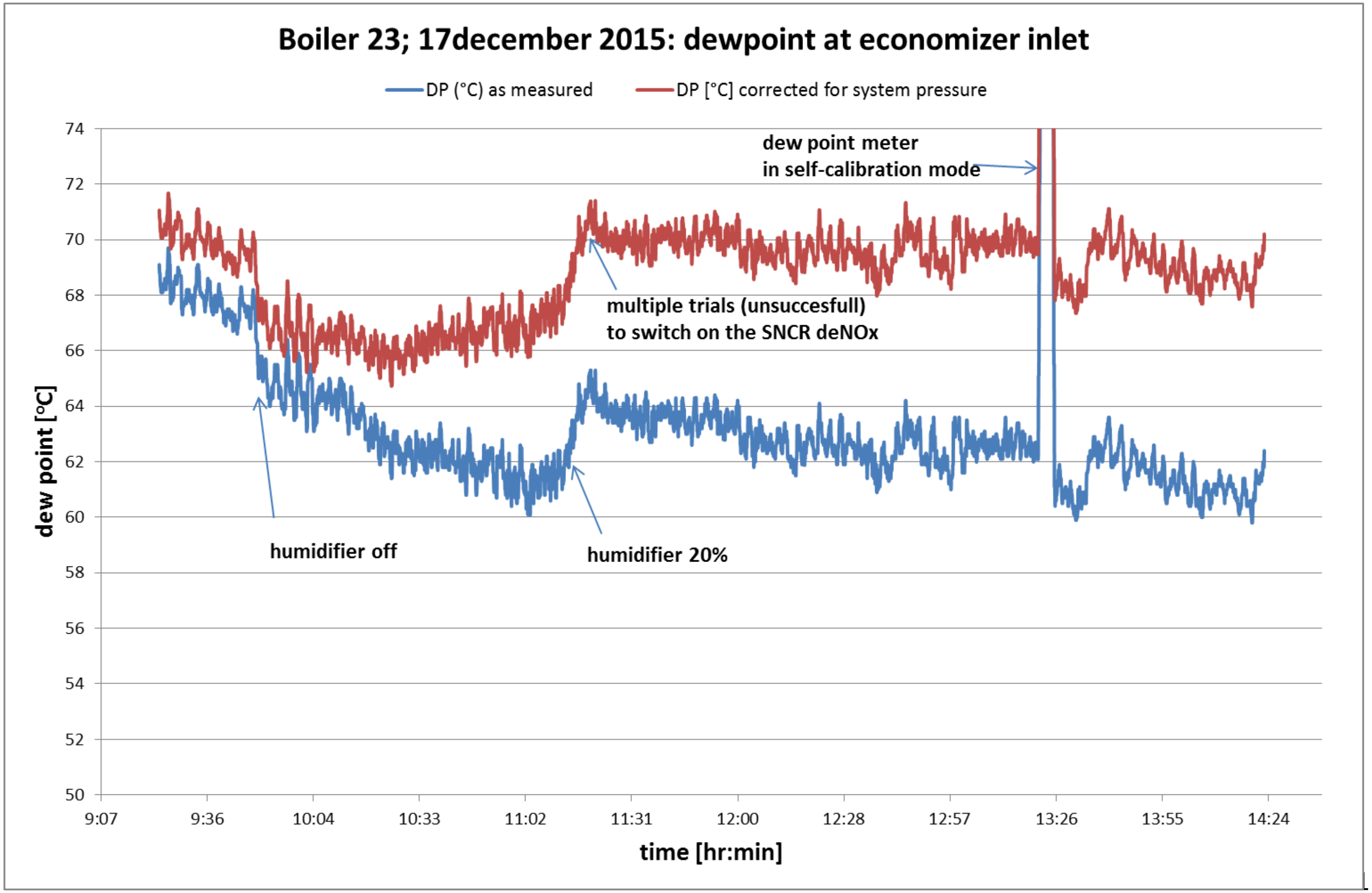
Results

dew point (2)



Results

dew point (3)



Results

dew point: discussion

- Under a constant operating regime:
  - the dew point is varying in a relatively narrow range, but appears to be decreasing in the measurement time.
  - co-incising with the slight pressure drop build-up in the overall sampling system, resulting in slightly negative pressure (a measured minimum of -310 mbar(a)) at the cell inlet.
  - Correcting the on-line recorded value for the actual system pressure, results in the flattening of the recorded signal.
  - At the maximum humidifier duty, the value of the dew point is in the range of approx. 70-71 °C without the SNCR system (vis Dec 15 at Boiler 24) and 72-73 °C with the SNCR system on.
- Switching on/off the humidifier and varying the duty leads to quick changes in the dew-point value.
  - switching the system on or increasing its duty results in a fast (few minutes) increase in the dew point value.
  - switching it off results in a slower (15-25 min.) but noticeable decrease of the measured value.

Results

dew point: discussion

- Without the humidifier:
  - the dew point measured (and corrected for pressure) is in the range of 65-67 °C for both Boiler 24 and Boiler 23.
- Running the humidifier at partial duty (20%, boiler 23 on Dec 17):
  - increases the dew point to around 68-69 °C.

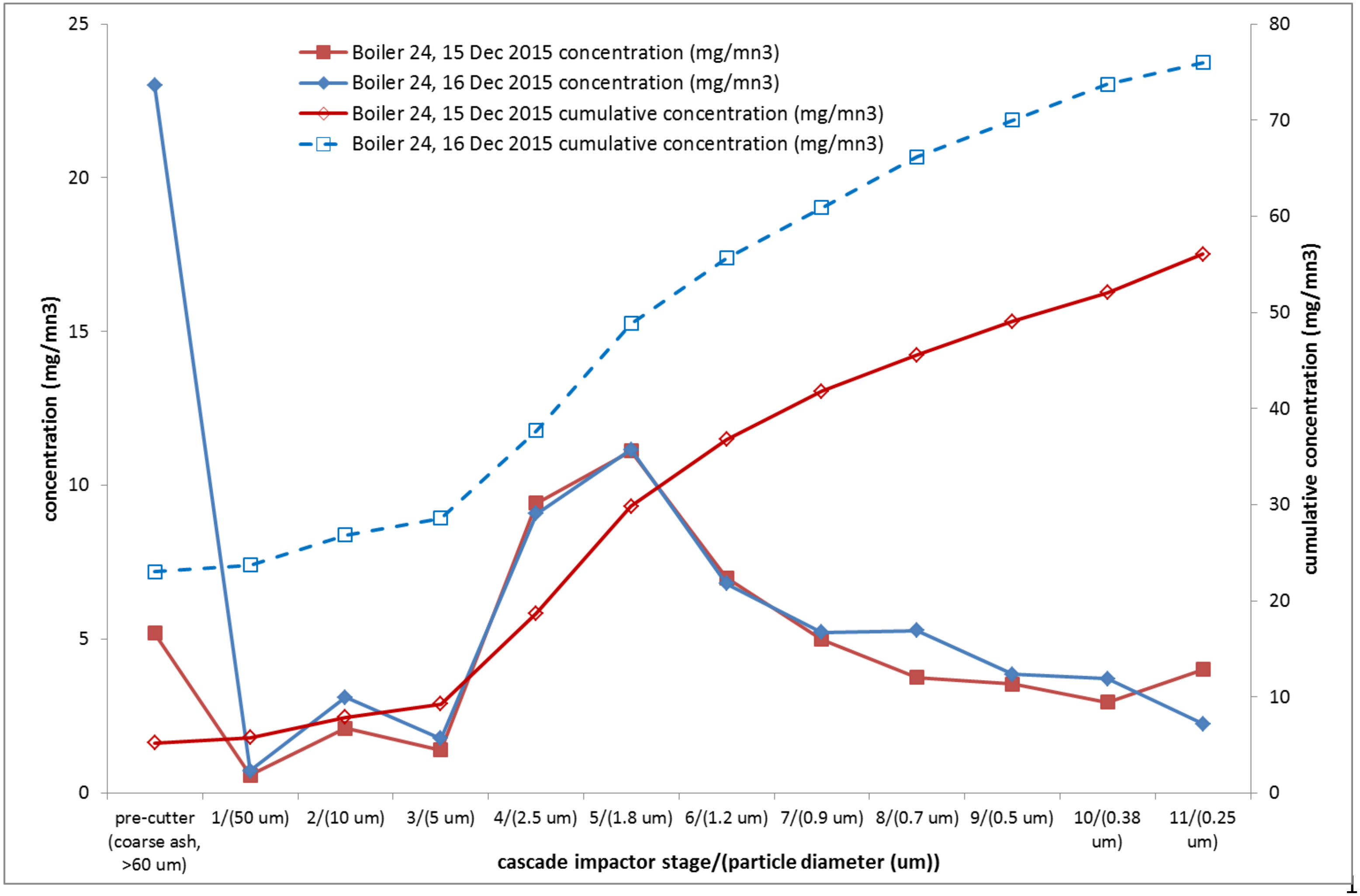
Results

condensate analyses (historical samples)

- Some precipitation after cooling down, dissolved when the samples were heated in the analytical process.
- All samples highly increased in SO_4^{2-} and Cl^-, ranging for Cl: 100 (in B24) – 200 (B23); and for SO_4: 194 (B11) – 1092 (B23) mg/kg.
- S, as measured by ICP/AES are well in line with the sulphates levels - sulphur is present in dissolved form.
- Dominant cation is Na (182-568 mg/kg), correlating with the overall anion load. Possibly due to the pH control system.
- Samples also contain iron (Fe), not correlating with the anion load (36 mg/kg in B24, 10 mg/kg in B11 and 0.7 mg/kg in B23).
- Chromium (Cr) ranges from under the detection limit (0.013) to 0.66 mg/kg and coincide with the increased levels of Fe
- Well-detectable Si, K, Ca, B and Mg, in the range of 0.1-3 mg/kg.
- Zinc concentration is also increased,
- Other elements, including the regulated toxic metals are, only present at low concentrations, at or below the detection limit.

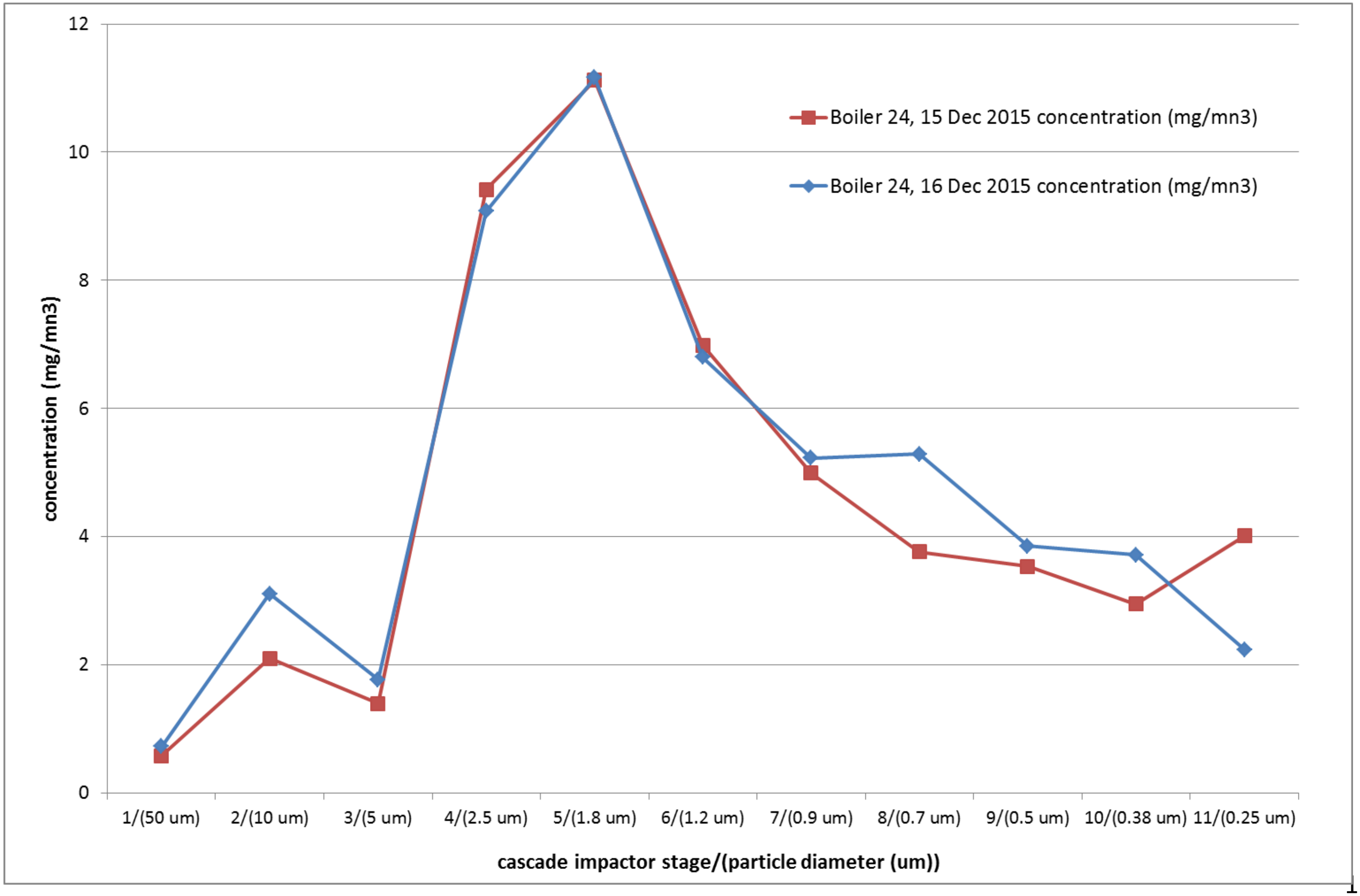
Results

dust load (1): overall, including coarse dust



Results

dust load (2): cascade impactor stages (fine dust)



Results

dust load : discussion

- Minor amount of coarse dust (> 60 µm, dry, granular and non-sticky, off-white) ca. 5 mg/m_n^3 on Dec 15th and ca. 20 mg/m_n^3 amount obtained on the 16th
- All of the deposits from the cascade impactor were bright white.
- Substrate load from approx. 0.8 mg/m_n^3 (d.l.) to 12 mg/m_n^3.
- Total fine dust load obtained consisted at 50.8 mg/m_n^3 to 52.9 mg/m_n^3 for Dec 15th and Dec 16th respectively.
- This total fine dust load is quite high for wood-fired grate-type systems, but within the range for clippings, park-maintenance and thinning wood.
- > 80 % w/w smaller than 2.5 µm, with a maximum peak at around 1.5-2 µm aerodynamic diameter, values typical for condensation induced volatile salts particles.

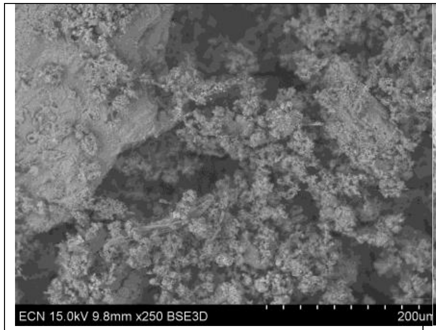
Results

dust load : discussion

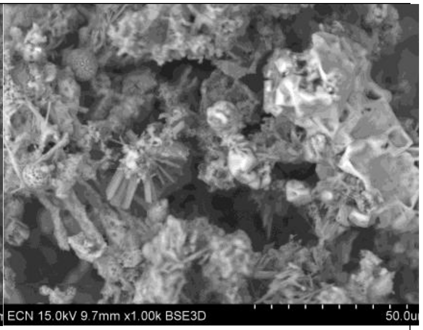
- Even at the finest stage (~0.25 µm), still levels of 2-4 mg/m_n^3.
- Deposits also forming in the orifice of the critical capillary, suggests measurable concentrations of particles < 200 nm.
- All of the particulate obtained in the cascade impactor is very fine and can lead to thermophoresis induced deposition and corrosion on the heat exchanging surfaces in the combustion system.
- Capturing such particles in a dry filtering system (either electrostatic or a bag filter) might prove challenging.
- Nonetheless the de-dusting train at SV Purmerend, with a combined bag filter and a condenser/scrubber system, offers likely enough residence time to form a condensate film on these fine particles and hence capture them efficiently.

Results

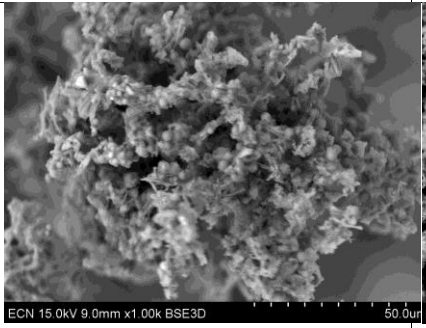
dust morphology (1): overall, including coarse dust



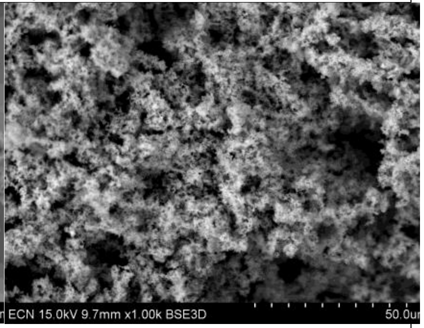
Pre-cutter



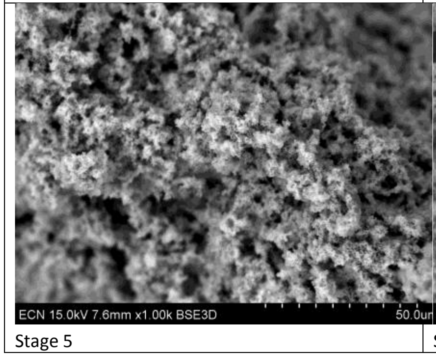
Stage 2



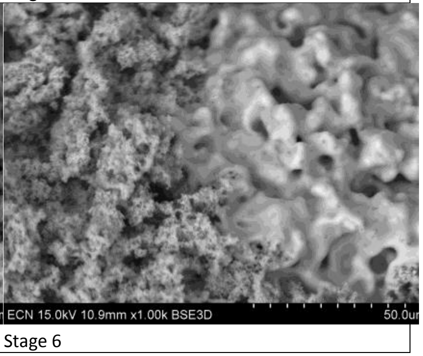
Stage 3



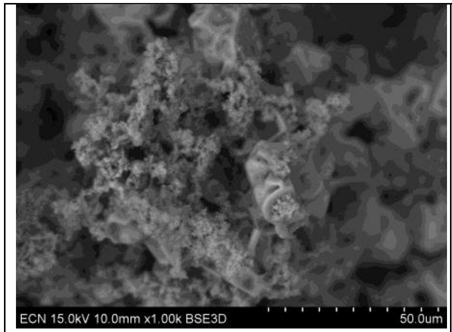
Stage 4



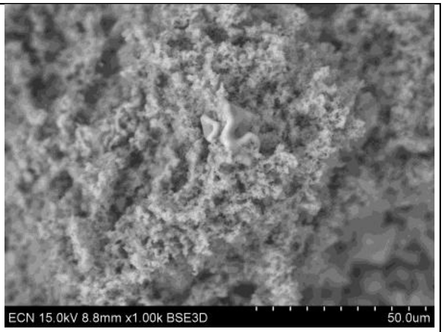
Stage 5



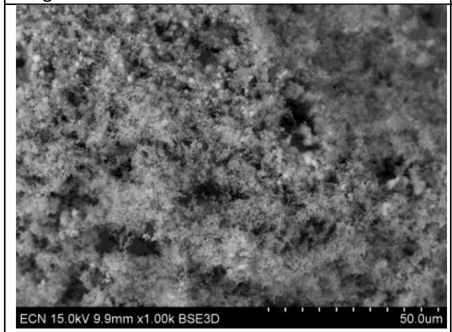
Stage 6



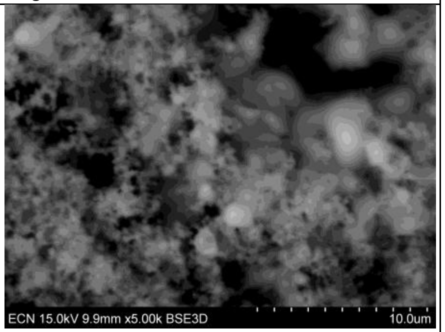
Stage 7



Stage 8



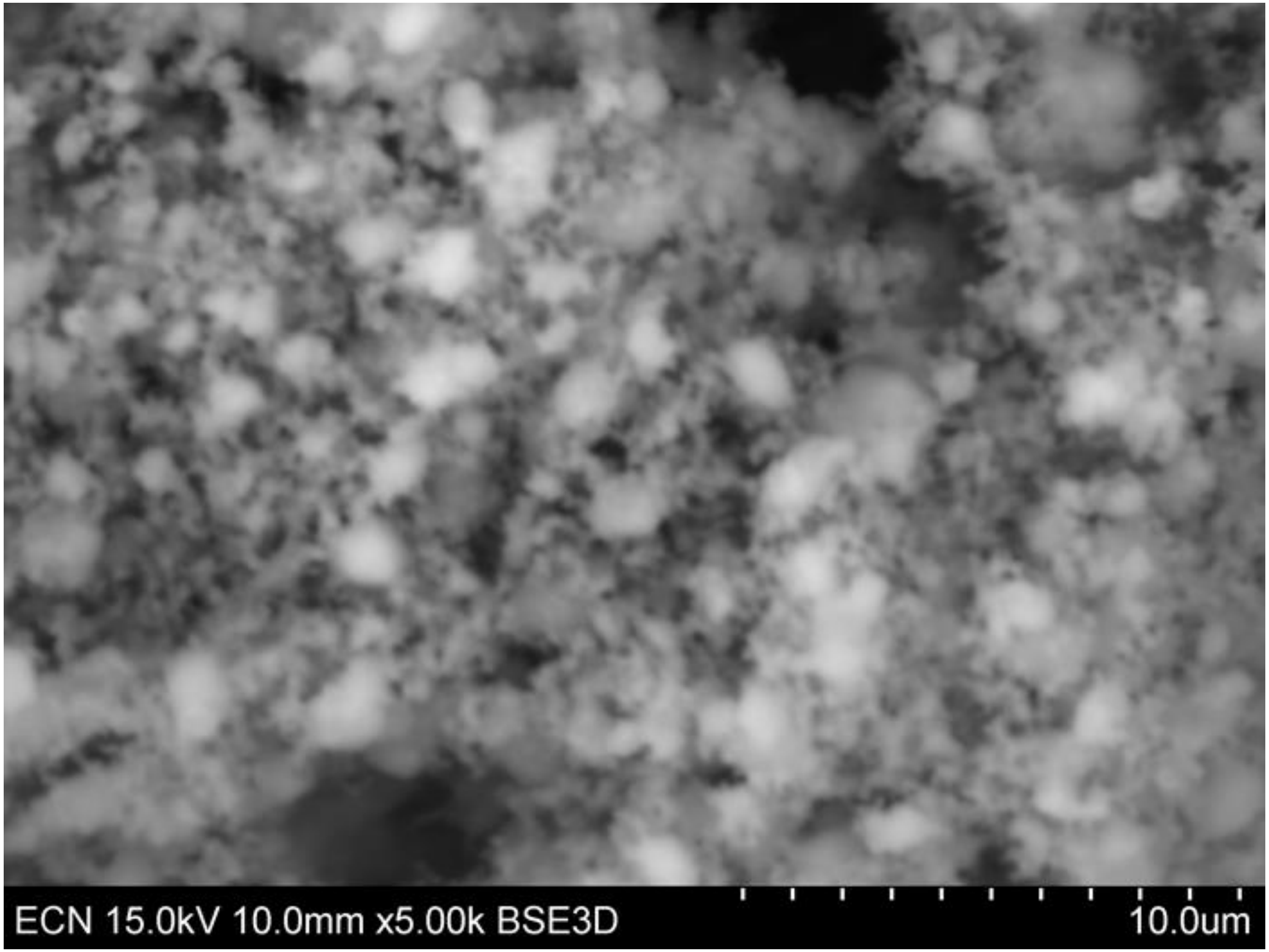
Stage 9



Stage 10

Results

dust morphology (2): superfines



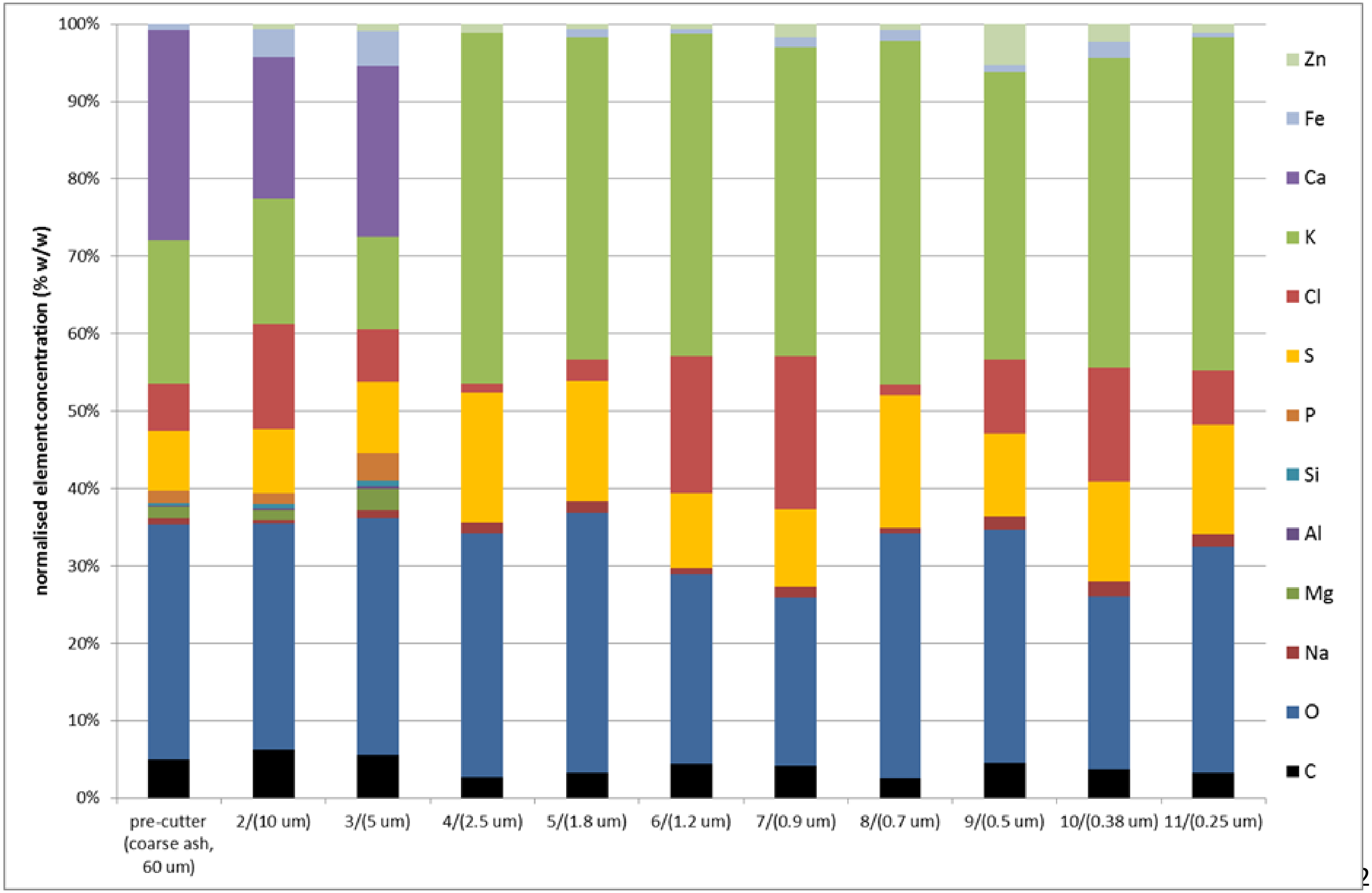
Results

dust morphology: discussion

- Pre-cutter contains coarse primarily mineral matter, with only very few char particles (later verified by low carbon contents measured).
- Material on the intermediate stage 2 contains several cenospheres, typical for aluminosilicates-based fly ashes in high temperature combustion environment. Next to those, also 10-20 micron-sized spongy mineral agglomerates are present.
- From stage 3 on, two morphologies are recognisable: highly fused yet porous, microcrystalline material with sharp edged walls or smooth, spherical shaped particles (larger than microcrystals).
- Occasionally (vide stage 6), parts of the surfaces formed by the sponge-like network appears to be melted or recrystallized into a more smooth continuous surface. SEM melting!
- All of the particulate has the typical appearance of condensed and partly molten (earth) alkali salts, often found in combustion systems, lacking the aluminosilicate mineral ashes which could act as the active or passive capture matrix for the (earth)alkalis.

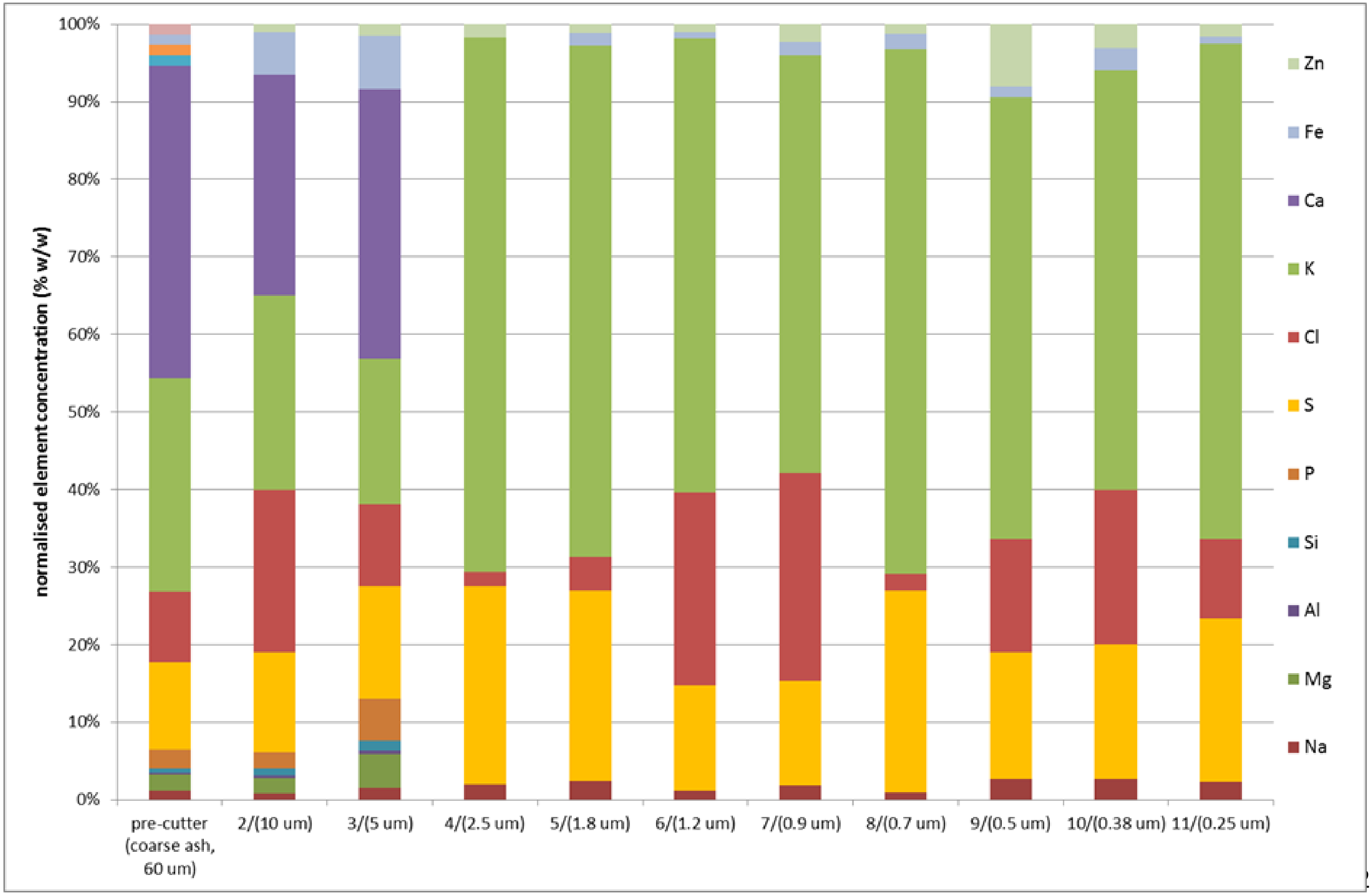
Results

dust compositions (1): overall, including light elements, K24/15 Dec



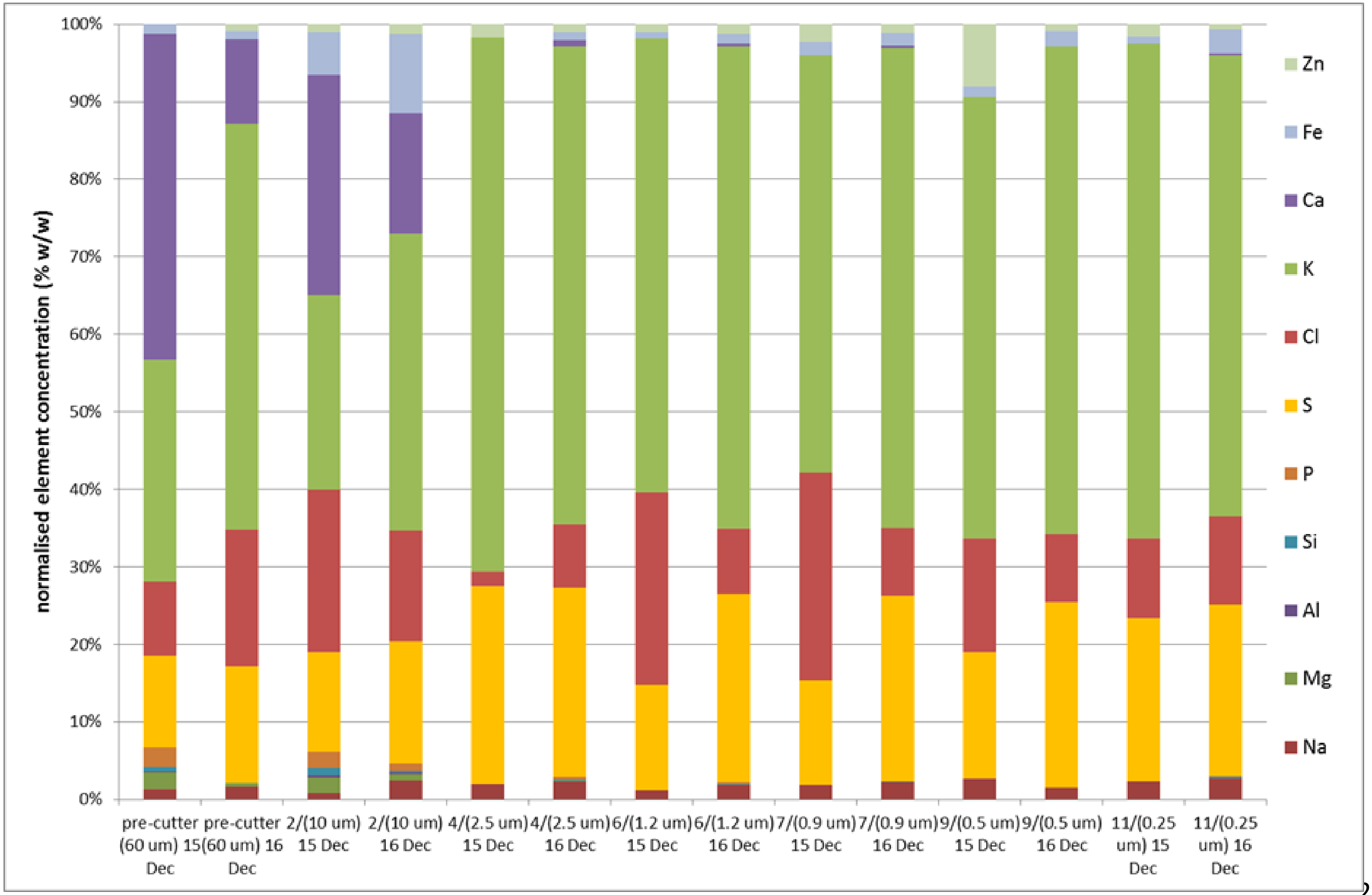
Results

dust compositions (2): O and C free, K24/Dec15



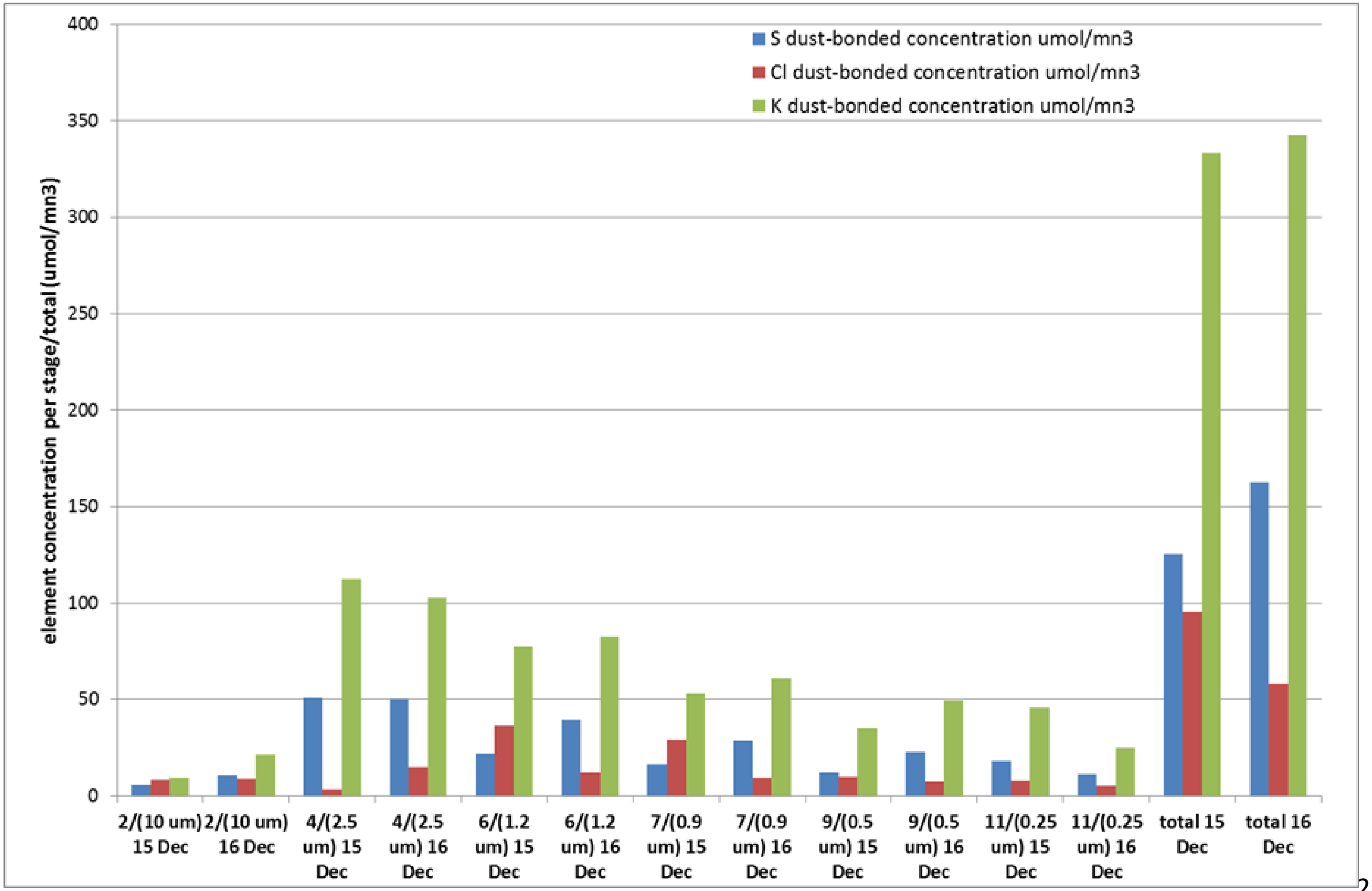
Results

dust compositions (2): O and C free,
K24/Dec15 vs K 24/Dec16



Results

dust compositions (2): S and Cl dust-bonded fluxes, K24/Dec15 vs K 24/Dec16



Results

dust compositions: discussion (1)

- The spongy, uniform matrix is composed of potassium-rich entities.
- Oxygen is distributed evenly throughout the matrix and shows only a few area of slightly increased concentrations.
- Sulphur is distributed very evenly through the matrix and shows very little variation.
- Chlorine shows much varying distribution, centralised in areas also showing increased concentrations of sodium, yet not showing significantly lower concentrations of potassium.
- Separate KCl and NaCl structures exist (particularly in the case of potassium characterised by larger diameter than the microcrystalline matrix) alongside the sulphates of both elements.
- These chlorine-enriched species are often clustered together but not homogeneously spread within the sulphurous matrix.
- A few Zn-enriched and coincide with both increased levels of Cl as well as lower levels of S, which might suggest that Zn is primarily in a chloride association.

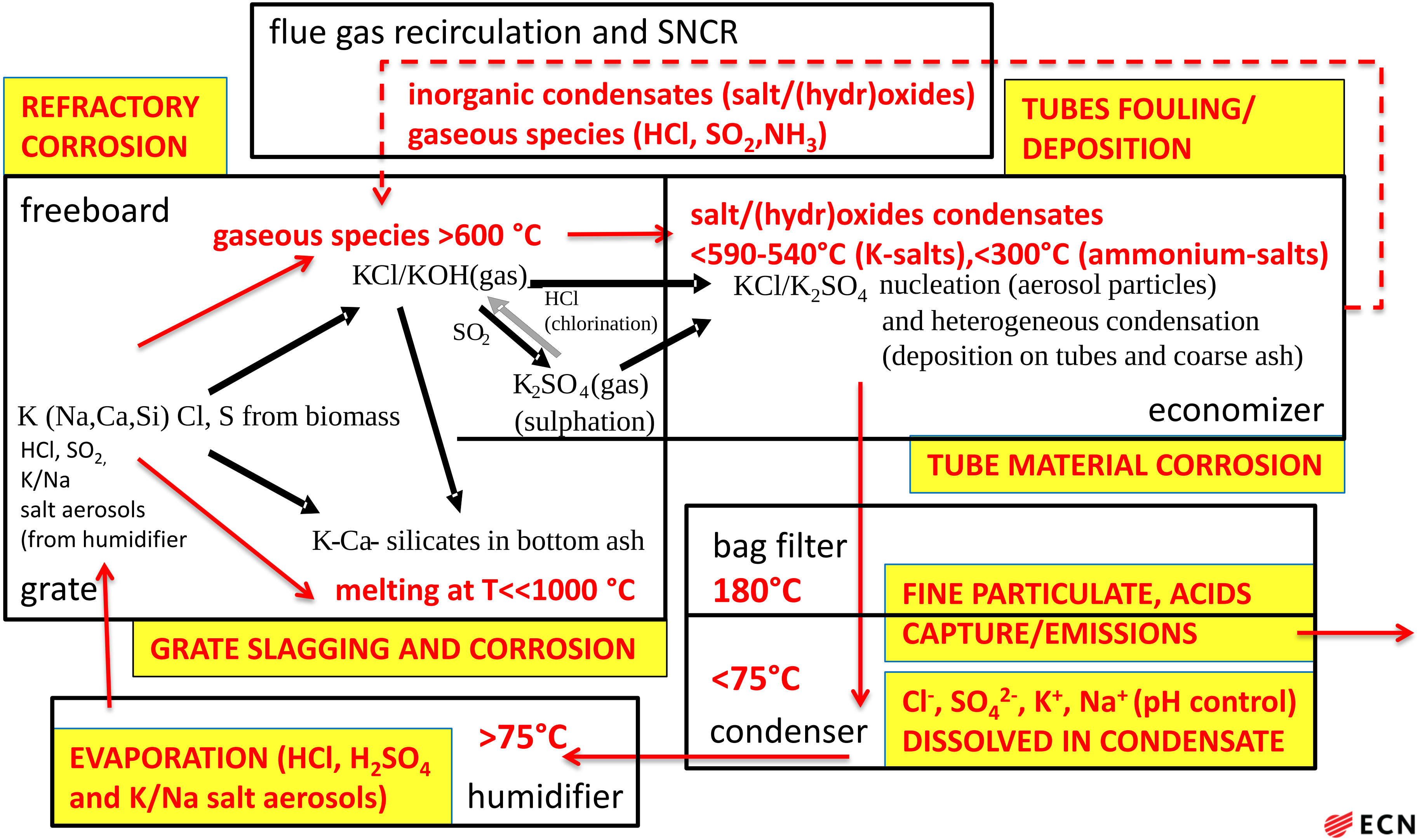
Results

dust compositions: discussion (2) K24 Dec15 vs Dec16

- No ammonium-based species have been found in the samples from Dec the 16th. This rules out the formation of very volatile and potentially corrosive ammonium chloride and sulphate.
- Compositions are quite comparable, however significant differences do appear.
  - Coarse and the supermicron ash both contain significantly lower calcium levels, now replaced with even more potassium.
  - Sodium levels, are increased slightly, yet significantly (approx. 10-30 % compared with day 1) particularly in the coarser and near-micron particles.
  - Sulphur levels are increased, while chlorides levels are generally lower.
- Molar concentration of fine-dust-bonded potassium is quite stable. This is well in-line with the minor fine dust concentration increase recorded on the second campaign day.
- Molar flux of sulphur increases ~30%, chlorine decreases ~40%.
- S/Cl ratio (S/Cl ~1.3 and S/Cl ~2.8 on Dec 15/Dec 16, respectively.

Biomass problem elements chemistry:

(earth) alkalis, Cl and S fate in SVP system



flue gas recirculation and SNCR

inorganic condensates (salt/(hydr)oxides)
gaseous species (HCl, SO_2,NH_3)

REFRACTORY CORROSION

TUBES FOULING/ DEPOSITION

freeboard

gaseous species >600 °C

KCl/KOH(gas)

SO_2

HCl (chlorination)

K_2SO_4(gas) (sulphation)

K (Na,Ca,Si) Cl, S from biomass

HCl, SO_2,
K/Na
salt aerosols
(from humidifier

K-Ca- silicates in bottom ash

melting at T<<1000 °C

grate

GRATE SLAGGING AND CORROSION

salt/(hydr)oxides condensates
<590-540°C (K-salts),<300°C (ammonium-salts)

KCl/K_2SO_4 nucleation (aerosol particles)
and heterogeneous condensation
(deposition on tubes and coarse ash)

economizer

TUBE MATERIAL CORROSION

bag filter
180°C

FINE PARTICULATE, ACIDS CAPTURE/EMISSIONS

<75°C

condenser

Cl^-, SO_4^{2-}, K^+, Na^+ (pH control) DISSOLVED IN CONDENSATE

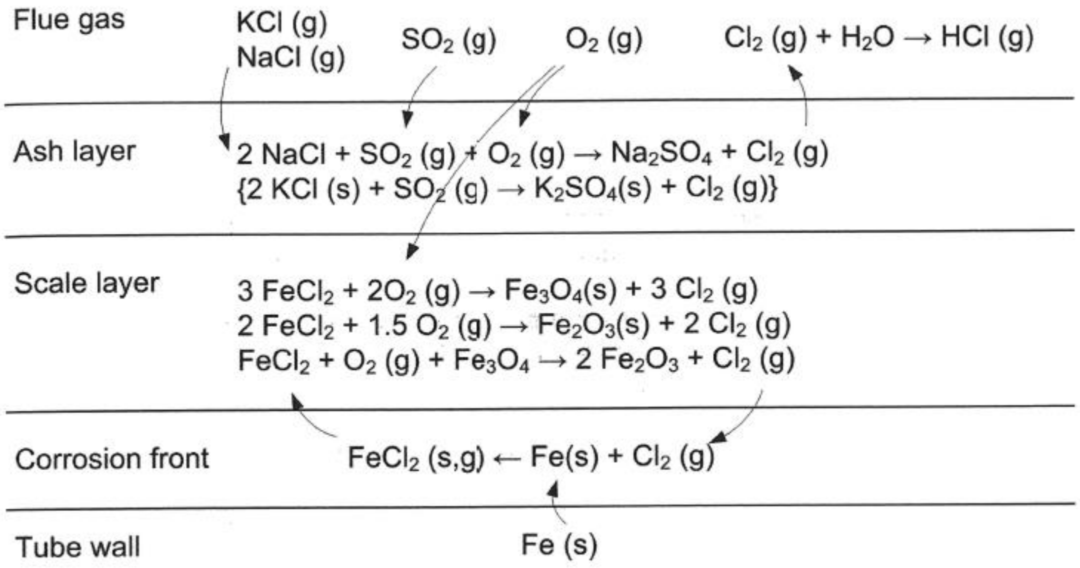
>75°C

humidifier

EVAPORATION (HCl, H_2SO_4 and K/Na salt aerosols)

Biomass problem elements chemistry:

(details of the S/Cl corrosion chemistry)



Flue gas

$KCl\ (g)$
$NaCl\ (g)$

$SO_2\ (g)$

$O_2\ (g)$

$Cl_2\ (g) + H_2O \rightarrow HCl\ (g)$

Ash layer

$2\ NaCl + SO_2\ (g) + O_2\ (g) \rightarrow Na_2SO_4 + Cl_2\ (g)$
$\{2\ KCl\ (s) + SO_2\ (g) \rightarrow K_2SO_4(s) + Cl_2\ (g)\}$

Scale layer

$3\ FeCl_2 + 2O_2\ (g) \rightarrow Fe_3O_4(s) + 3\ Cl_2\ (g)$
$2\ FeCl_2 + 1.5\ O_2\ (g) \rightarrow Fe_2O_3(s) + 2\ Cl_2\ (g)$
$FeCl_2 + O_2\ (g) + Fe_3O_4 \rightarrow 2\ Fe_2O_3 + Cl_2\ (g)$

Corrosion front

$FeCl_2\ (s,g) \leftarrow Fe(s) + Cl_2\ (g)$

Tube wall

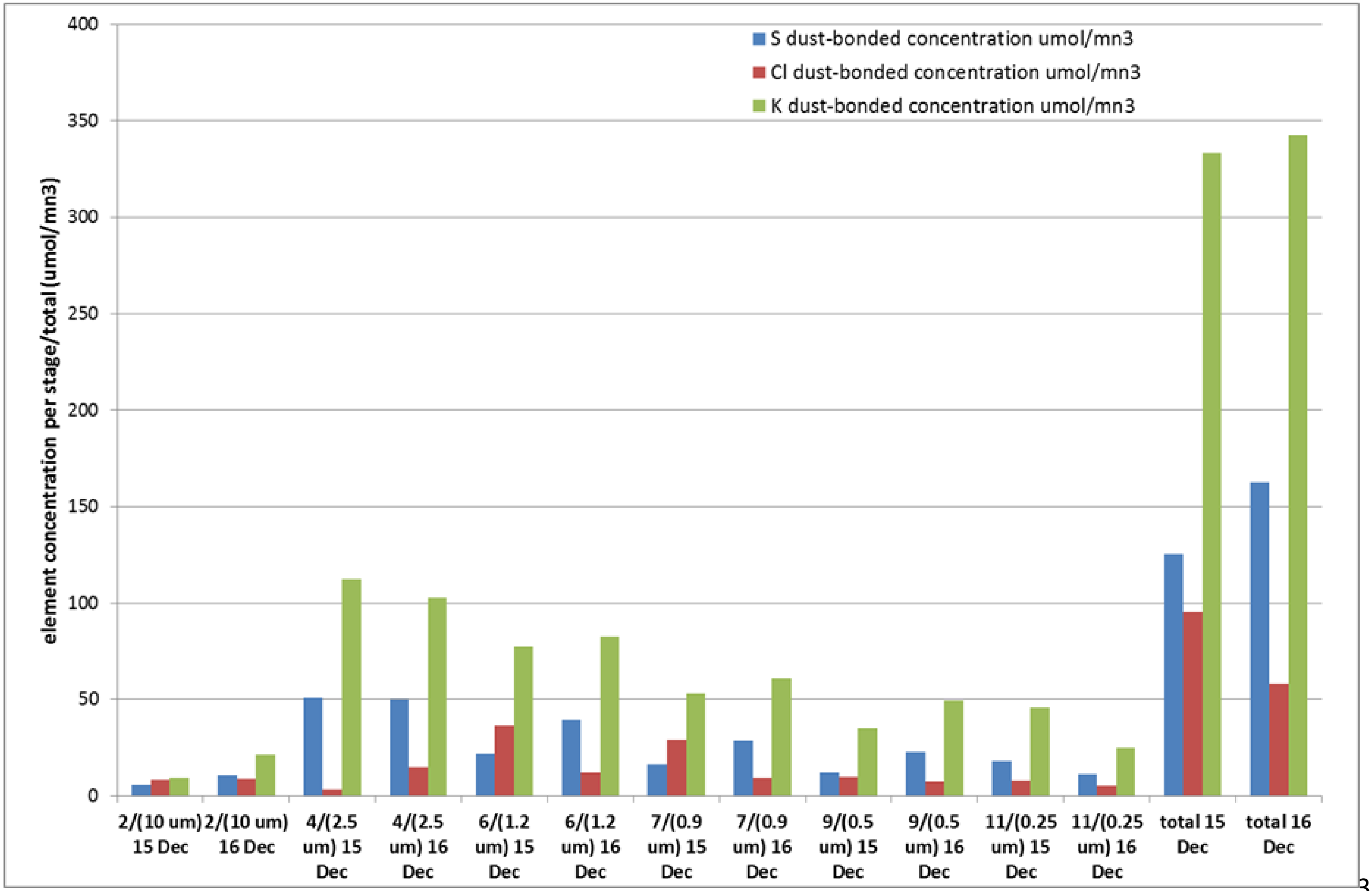
$Fe\ (s)$

S/Cl < 2: severe Cl corrosion
S/Cl < 4: intermediate Cl corrosion
S/Cl > 4: safe situation
but at high [SO_2] higher risk of S corrosion !

A. Robinson, H. Junker, S. Buckley, G. Sclippa and L. Baxter, “Interaction between coal and biomass when cofiring,” *Symposium (International) on Combustion,* vol. 27, pp. 1351-1359, 1998

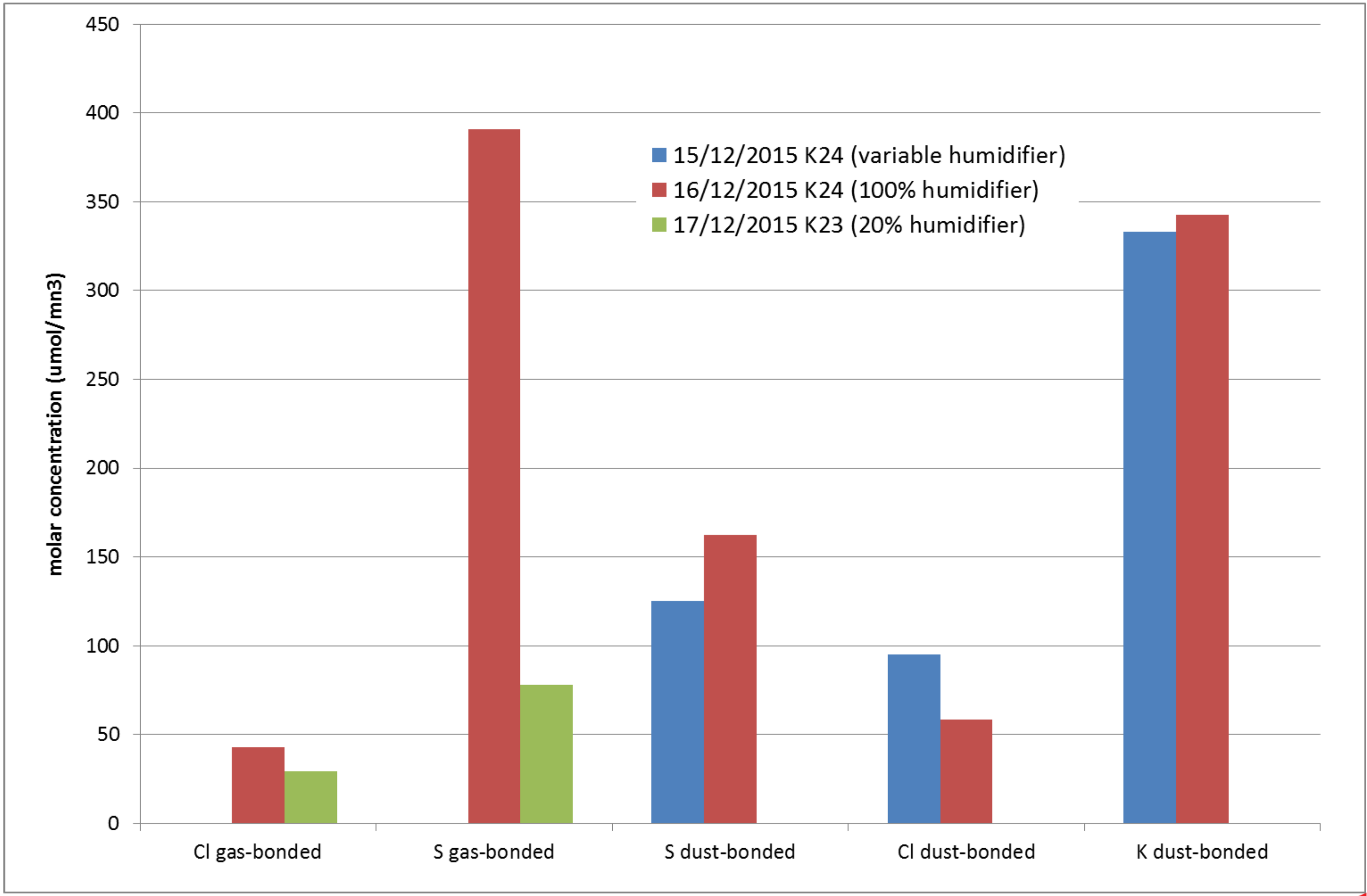
Results

dust compositions (2): S and Cl dust-bonded fluxes, K24/Dec15 vs K 24/Dec16



Results

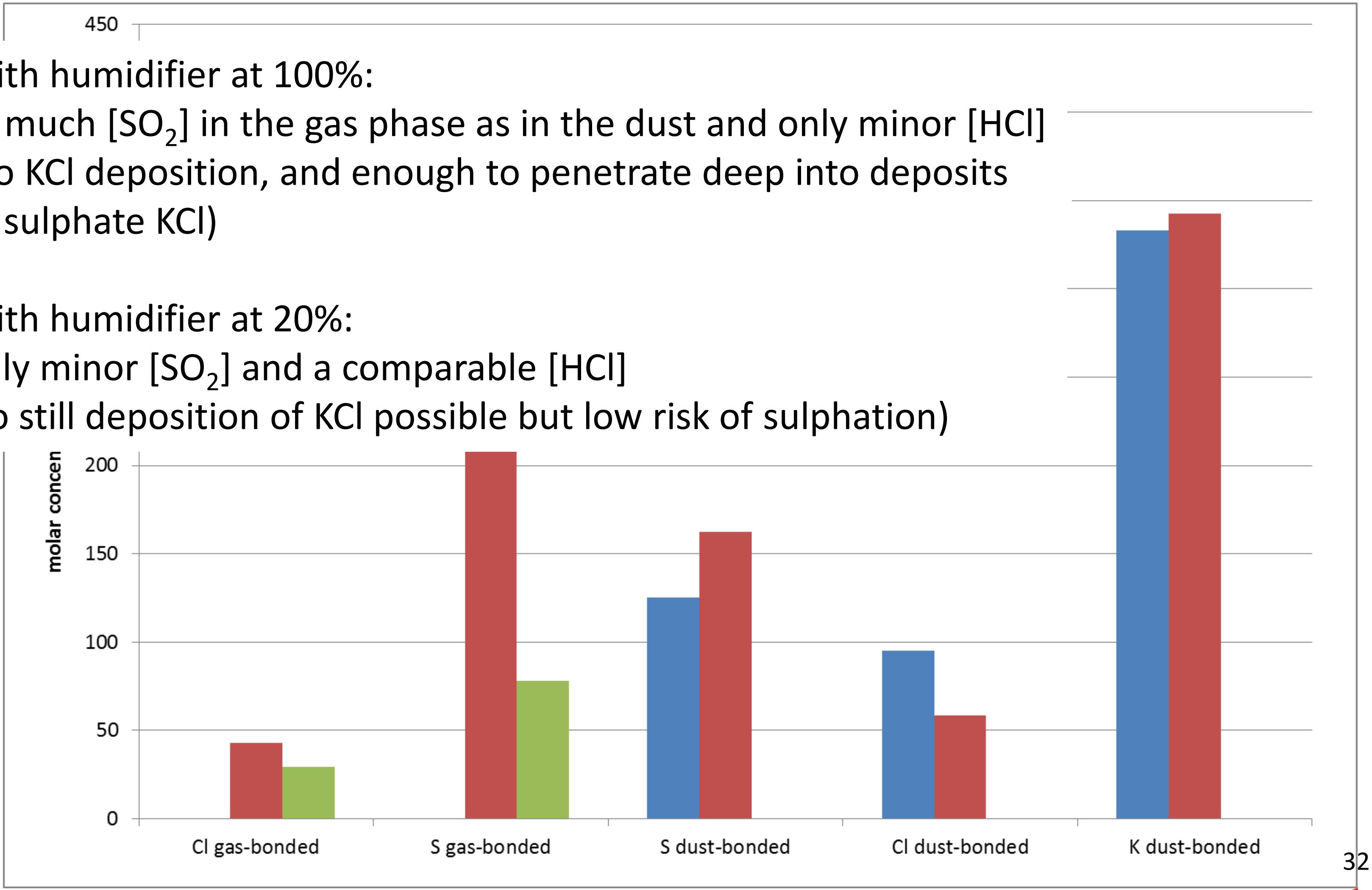
gas compositions (1): S and Cl gas-phase vs dust-bonded concentrations, K24/Dec15-16 vs K 23/Dec17



ECN

Results

gas compositions (1): S and Cl gas-phase vs dust-bonded concentrations, K24/Dec15-16 vs K 23/Dec17

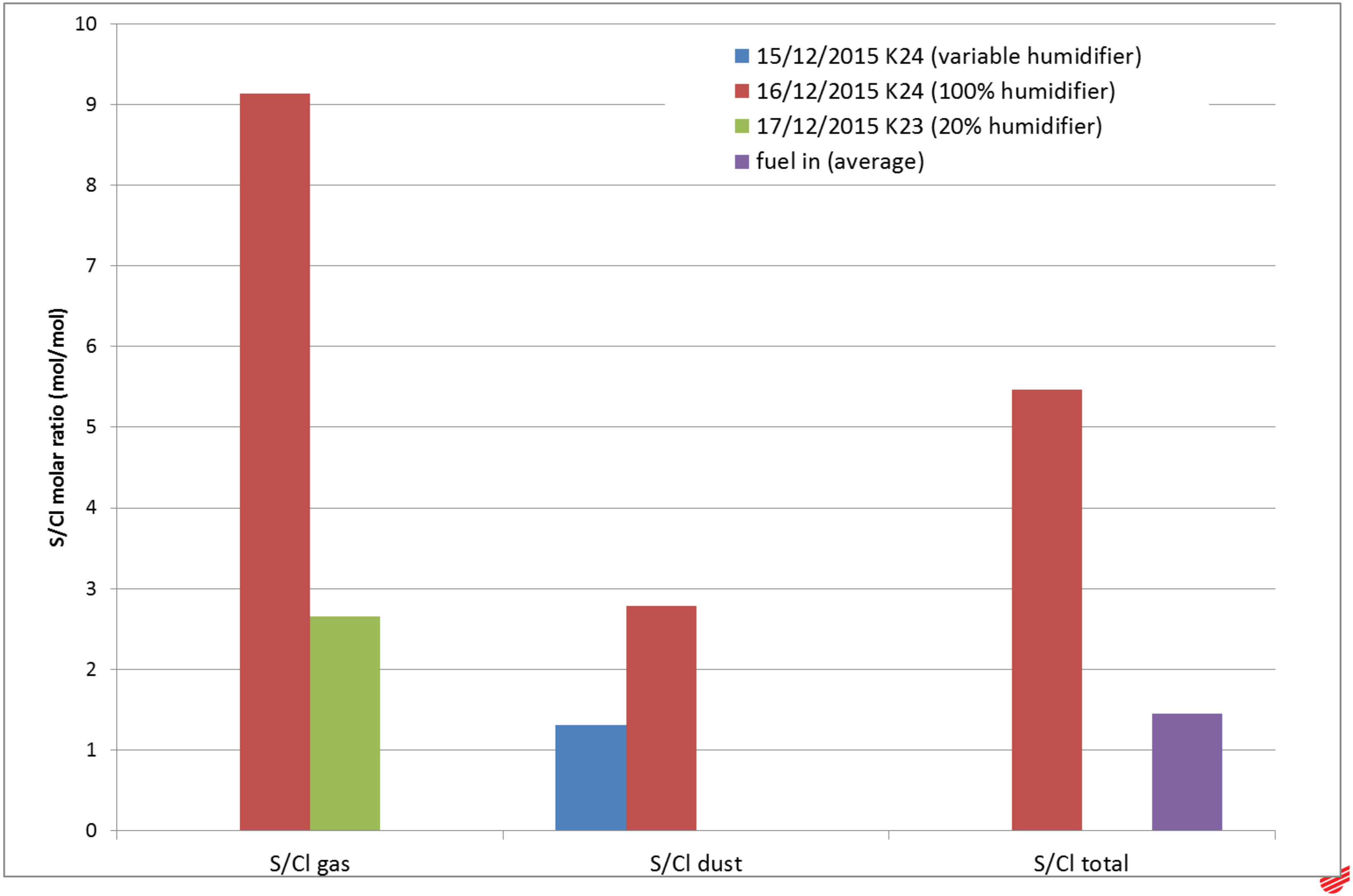


With humidifier at 100%:
as much [SO_2] in the gas phase as in the dust and only minor [HCl]
(no KCl deposition, and enough to penetrate deep into deposits
to sulphate KCl)

With humidifier at 20%:
only minor [SO_2] and a comparable [HCl]
(so still deposition of KCl possible but low risk of sulphation)

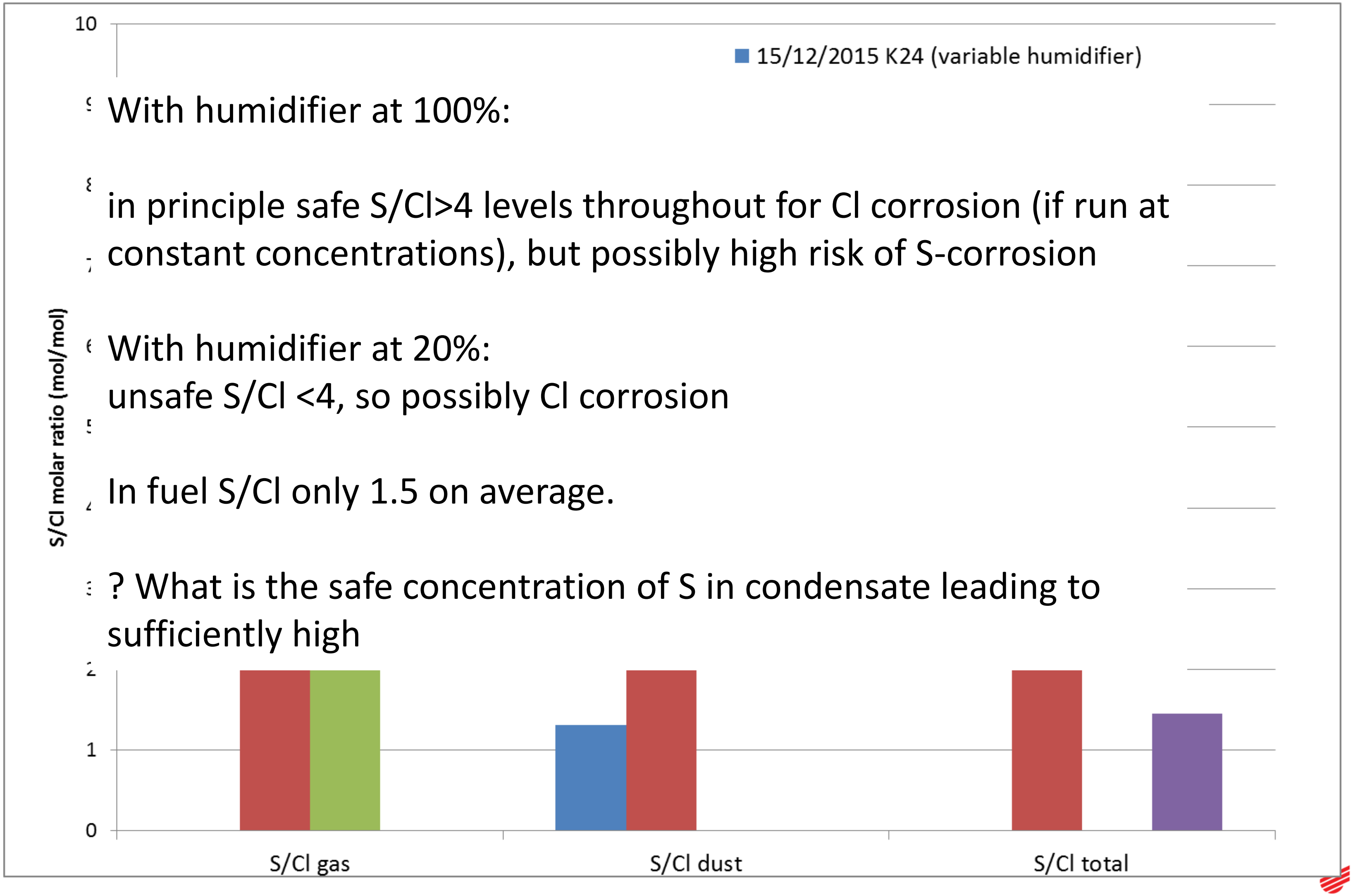
Results

gas compositions (2): S and Cl gas-phase vs dust-bonded concentrations, K24/Dec15-16 vs K 23/Dec17



Results

gas compositions (2): S and Cl gas-phase vs dust-bonded concentrations, K24/Dec15-16 vs K 23/Dec17



With humidifier at 100%:

in principle safe S/Cl>4 levels throughout for Cl corrosion (if run at constant concentrations), but possibly high risk of S-corrosion

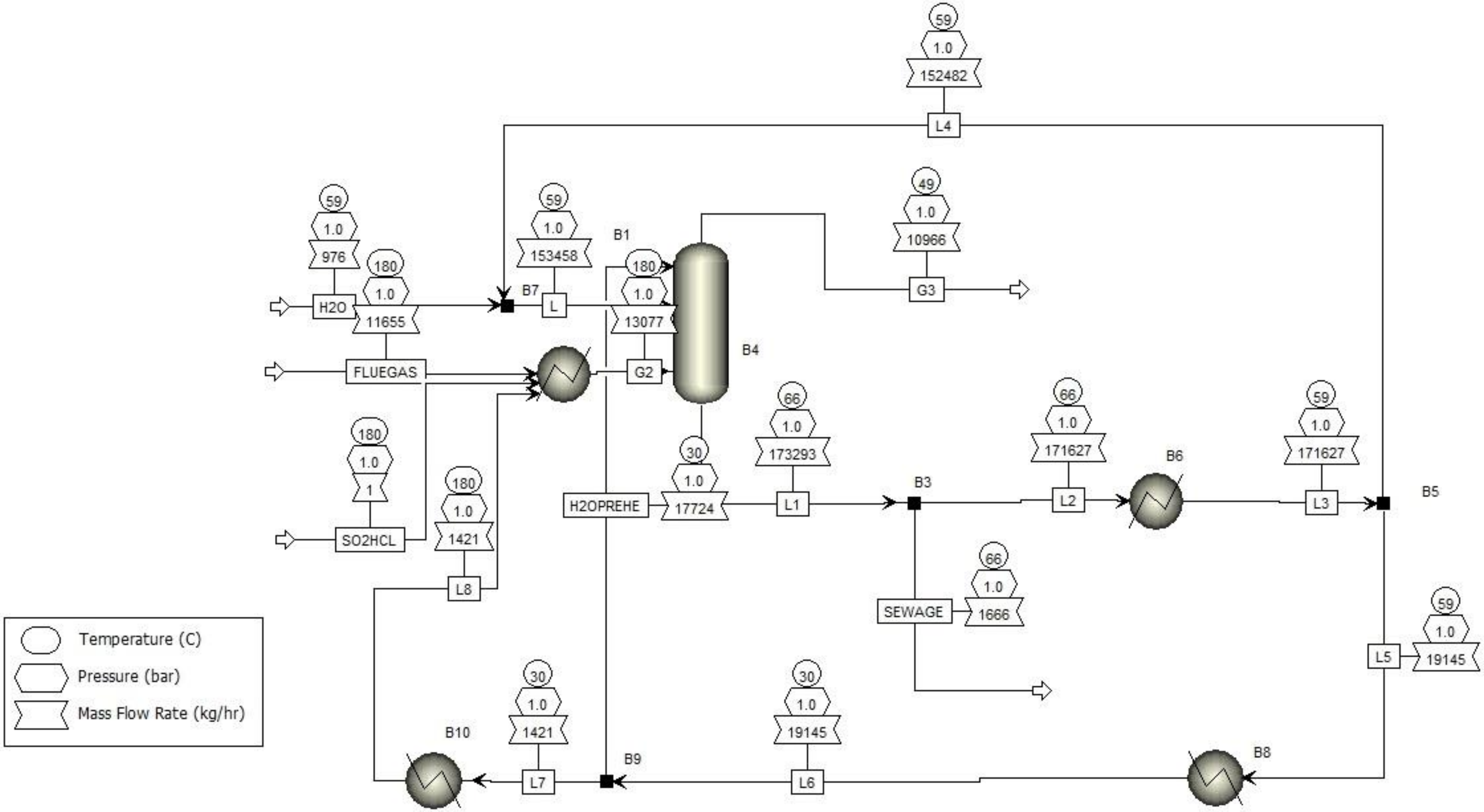
With humidifier at 20%:
unsafe S/Cl <4, so possibly Cl corrosion

In fuel S/Cl only 1.5 on average.

? What is the safe concentration of S in condensate leading to sufficiently high

Modelling the gas-phase and condensate SO2 and NH3

Modelling the gas-phase and condensate SO2 and NH3: *the definitive ASPEN model*



Modelling the gas-phase and condensate SO2 and NH3: *the definitive ASPEN model*

Model:

- ASPEN model of condensor/humidifier loop
- Includes evaporation/condensation in the absorber, recycle loop through the humidifier and bleed to sewer
- SO_2 (and SO_3) and HCl recycle as variable rate injection into flue gas, with live coupling with the condensor loop and fixed feed in from fuel
- Variable flue-gas NH_3 concentration, as simulation of ammonia slip

Status:

- Model set up and converged thermally and mass-flow wise
- Full ionic chemistry ($SO_{x\,,}$ HCl dissolution and oxidation) now implemented,
- pH balancing implemented, including NH_3 dissolution,
- minor problems still exist with ion balancing (@ < 10^{-6} mmol/kg levels in outgoing streams)
- Implementing salts “breakthrough” proven problematic due to phase change issues

Modelling the gas-phase and condensate SO2 and NH3: *cases run*

Cases run so far:

- all cases fixed thermal load of 11 MWth
- free flue gas-bonded acids (seed concentrations) at 25 [SO_2] and 5 mg/m_n^3 [HCl] (similar to measured during the campaign with humidifier)
- moisture contents 30% vol. [H_2O] (similar to measured during the campaign with humidifier)
- flue gas inlet T standard at 180°C (standard at SVP)
- 0, 0.2, 5, 20 of NH_3 (simulation of no and optimised SNCR) and 40 mg/m_n^3 of NH_3 (extrapolated historical slip under suboptimal SNCR)
- standard full humidifier load (100% = 1.4 m^3/h water evaporation) and purge rate of 1.7 m^3/h
- standard full humidifier load (100% = 1.4 m^3/h water evaporation) and purge rate increased to 2 m^3/h
- 30% increased flue gas flow (simulation of wetter fuel, ca. 48 instead of 40% moisture)
- flue gas inlet T decreased to 150°C (to simulate extra condensation drive)

Modelling the gas-phase and condensate SO2 and NH3: *cases run – the matrix considered here*

Case/model	14-04-2016 0mgnm3 NH3	15-03-2016 0.2 mgnm3 NH3	15-03-2016 5 mgnm3 NH3	15-03-2016 20mgnm3 NH3 1.7m3h	16-03-2016 20mgnm3 NH3 2.0m3h	12-04-2016 20 mgnm3 NH3 150 oC	12-04-2016 20 mgnm3 NH3 +30%	14-04-2016 40mgnm3 NH3
serie s name in charts	0 mg/mn3 NH3 @ 1.7 m3/h purge	0.2 mg/mn3 NH3 @ 1.7 m3/h purge	5 mg/mn3 NH3 @ 1.7 m3/h purge	20 mg/mn3 NH3 @ 1.7 m3/h purge	20mg/m3 NH3 @2.0 m3/h purge	20 mg/mn3 NH3 @ 1.7 m3/h purge 150 °C flue gas T	20 mg/mn3 NH3 @ 1.7 m3/h purge + 30% total flow	40 mg/mn3 NH3 @ 1.7 m3/h purge
humidifier load (m3/h condensate evaporation)	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
NH3 seed concentration (mg/mn3)	0	0.2	5	20	20	20	20	40
SO2 seed concentration (mg/mn3)	25	25	25	25	25	25	25	25
HCl seed concentration (mg/mn3)	5	5	5	5	5	5	5	5
flue gas crubber inlet T (°C)	180	180	180	180	180	150	180	180
flue gas moisture content (% vol.)	30	30	30	30	30	30	30	30
flue gas volume (% reference)	100	100	100	100	100	100	130	100
bleed/purge flow (m3/h)	1.7	1.7	1.7	1.7	2	1.7	1.7	1.7

Modelling the gas-phase and condensate SO2 and NH3: *results available*

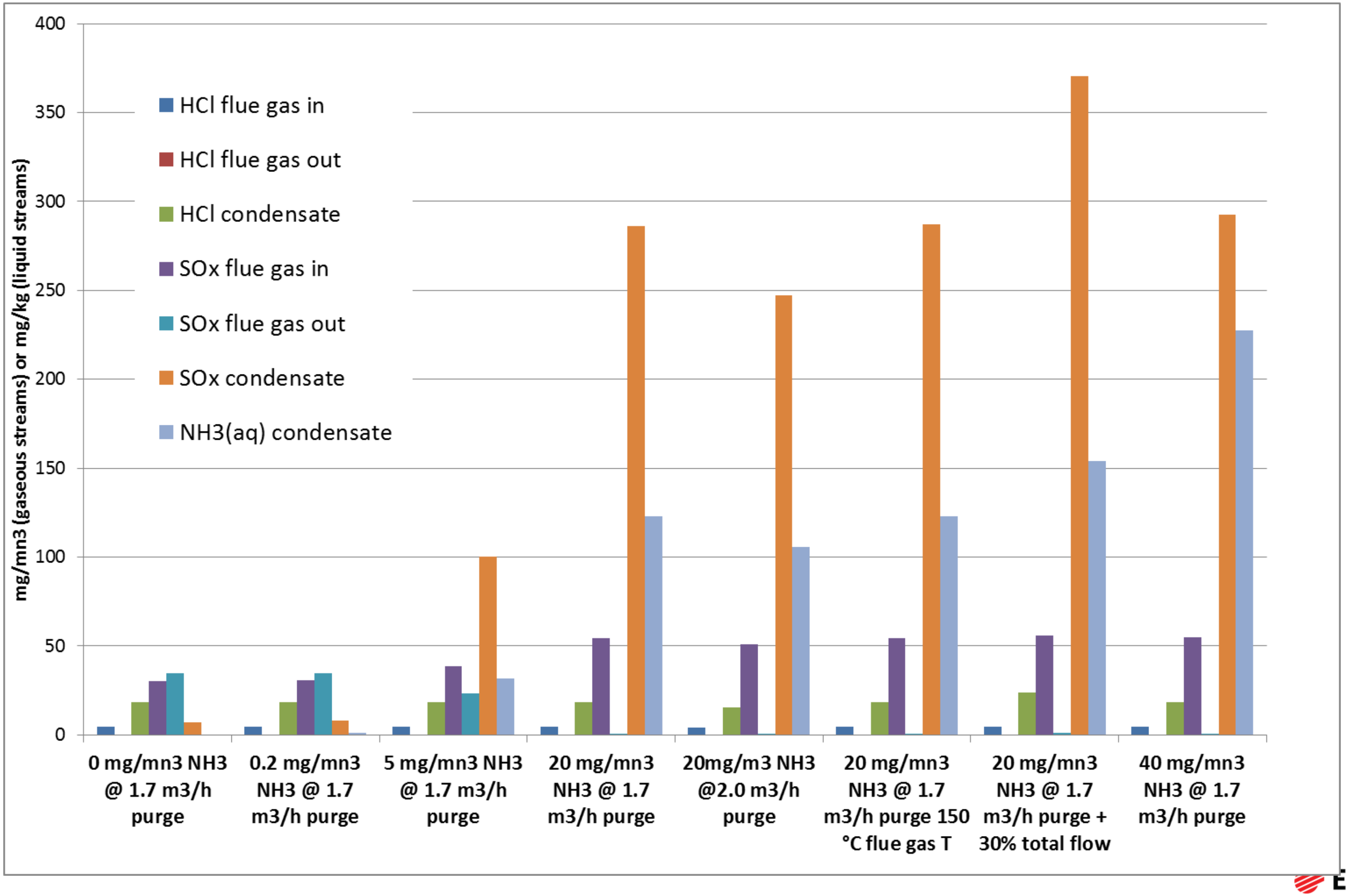
Results reported as equilibrium concentrations of (sum)SOx, HCl and NH_3:

- "Flue gas in" – raw flue gas at the scrubber inlet (in mg/m_n^3)
- "Flue gas out" – flue gas after scrubber/condensor, so also excluding water condensed out in the condensor loop
- "Condensate" – condensed fluid (water) injected into the humidifier loop
- "natural pH" (uncorrected = no NaOH injection) pH of the condensate

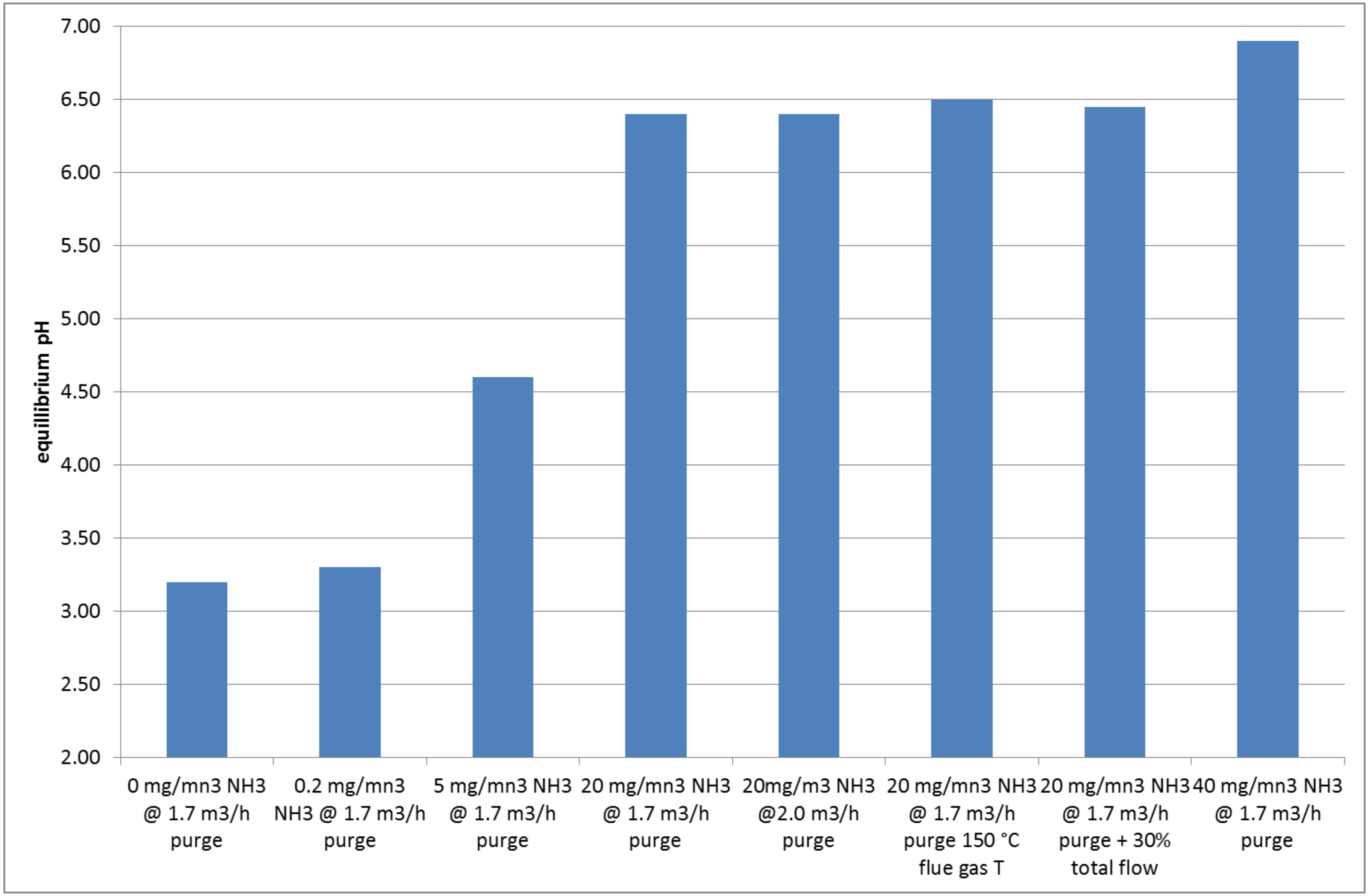
Also available but not directly relevant for the model:

- Fully resolved concentrations of all gaseous sulphurous, chlorine carbonates and ammonia species in all in-/out-going streams
- Humidifier condensate return stream
- Waste condensate stream (purge or sewer dump)

Modelling the gas-phase and condensate SO2 and NH3: *results graphically (dissolved and gaseous species)*



Modelling the gas-phase and condensate SO2 and NH3: *results graphically (uncorrected, natural pH)*



Modelling the gas-phase and condensate SO2 and NH3: *nummerical results*

case	14-04-2016 0mgnm3 NH3	15-03-2016 0.2 mgnm3 NH3	15-03-2016 5 mgnm3 NH3	15-03-2016 20mgnm3 NH3 1.7m3h	16-03-2016 20mgnm3 NH3 2.0m3h	12-04-2016 20 mgnm3 NH3 150 oC	12-04-2016 20 mgnm3 NH3 +30%	14-04-2016 40mgnm3 NH3
series name	0 mg/mn3 NH3 @ 1.7 m3/h purge	0.2 mg/mn3 NH3 @ 1.7 m3/h purge	5 mg/mn3 NH3 @ 1.7 m3/h purge	20 mg/mn3 NH3 @ 1.7 m3/h purge	20mg/m3 NH3 @2.0 m3/h purge	20 mg/mn3 NH3 @ 1.7 m3/h purge 150 °C flue gas T	20 mg/mn3 NH3 @ 1.7 m3/h purge + 30% total flow	40 mg/mn3 NH3 @ 1.7 m3/h purge
HCl flue gas in	4.42	4.42	4.42	4.42	4.11	4.42	4.53	4.42
HCl flue gas out	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HCl condensate	18.19	18.21	18.21	18.20	15.47	18.20	23.68	18.20
SOx flue gas in	30.44	30.51	38.45	54.40	51.05	54.51	55.71	54.98
SOx flue gas out	34.69	34.59	23.36	0.86	0.86	0.87	1.01	0.24
SOx condensate	7.07	7.95	100.47	285.98	247.02	287.24	370.37	292.31
NH3(aq) condensate	0.00	1.29	31.95	122.95	105.73	123.00	154.13	227.50

Modelling the gas-phase and condensate SO2 and NH3: *discussion, no SNCR*

Without ammonia slip:

- only with SO_2 (i.e. no SO_3) in the flue gas:
- all HCl dissolves, but only a minor share of SOx
- hence low HCl in flue gas, but SOx high after water condensation in scrubber
- [HCl]condensate > [SOx]condensate (18 vs 7-8 mg/kg)
- Natural (uncorrected) pH ~3.5

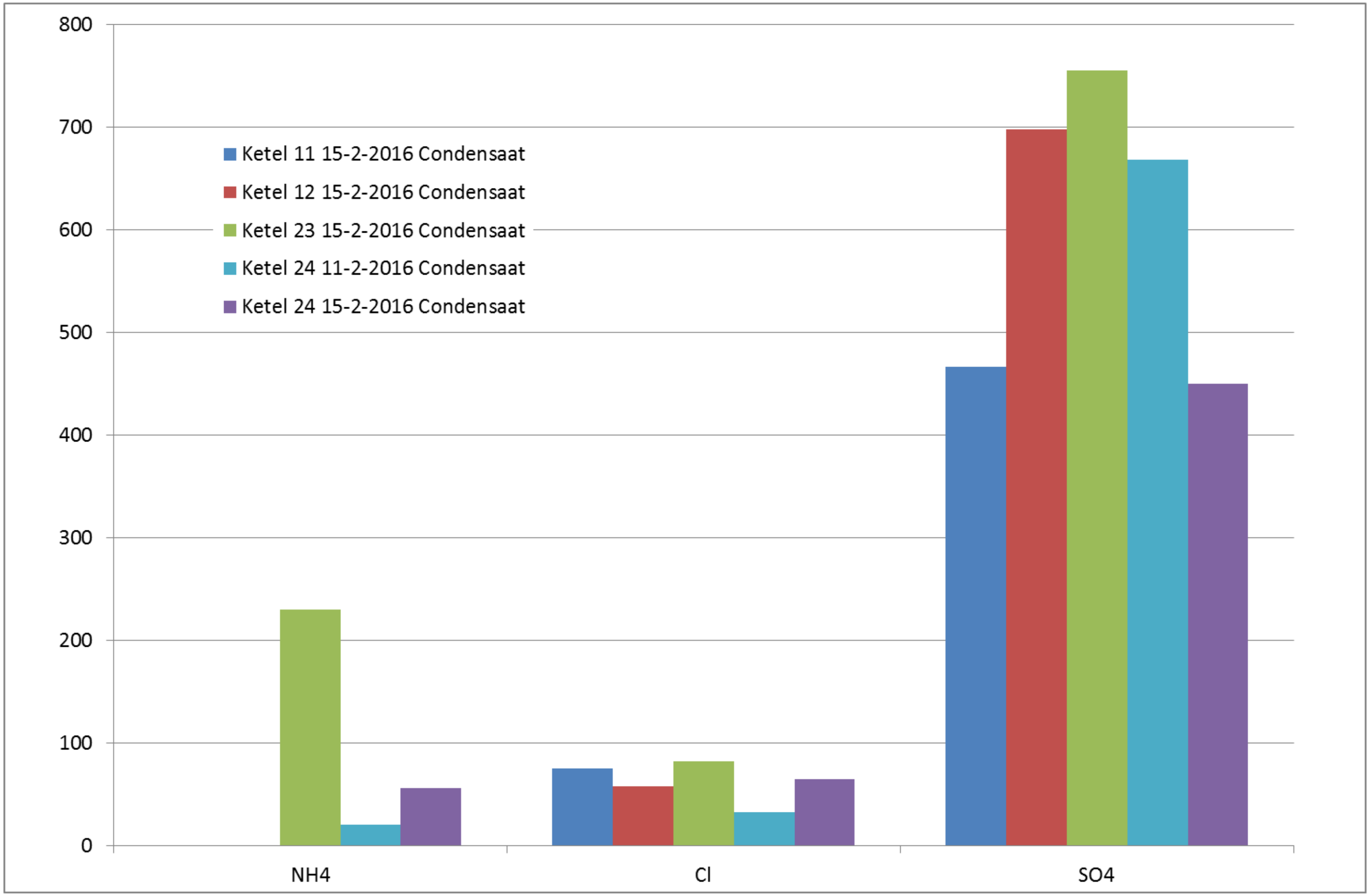
Modelling the gas-phase and condensate SO2 and NH3: *discussion, with SNCR*

With NH_3 slip:

- At $[NH_3]$ 0.2 mg/m_n^3 only very minor impact on SOx in all streams
- At $[NH_3]$ 5.o mg/m_n^3 big impact on SOx in the condensate, but small impact on flue gas concentration
- At $[NH_3]$ 20 mg/m_n^3 very big impact on condensate, now SOx(aq) in condensate ~300 mg/kg
- At $[NH_3]$ 20 mg/m_n^3 >2x SOx enrichment in raw flue gas (now at ~60 mg/m_n^3)
- But significantly lower emissions (flue gas out), thanks to better scrubbing
- $[NH_4^-]$ in the condensate around 120 mg/kg
- Increasing condensate discharge from 1.7 to 2.0 m^3/h decreases concentration of dissolved species in the condensate and in the raw flue gas <u>proportionally</u>
- Increasing total flue gas flow by 30% increases SO_x in the condensate proportionally and increases slightly flue gas SOx concentration
- Decreasing flue gas inlet T to 150°C has only minor effect on all species
- Increasing NH_3 slip to $[NH_3]$ 40 mg/m_n^3 increases $[NH_4^-]$ to ~300 mg/kg **but does not cause additional SOx uptake in the condensate**
- natural pH of the condensate without SNCR < 3.5, increases and stabilises quickly around 6.5-7 if ammonia slip 20-40 mg/m_n^3

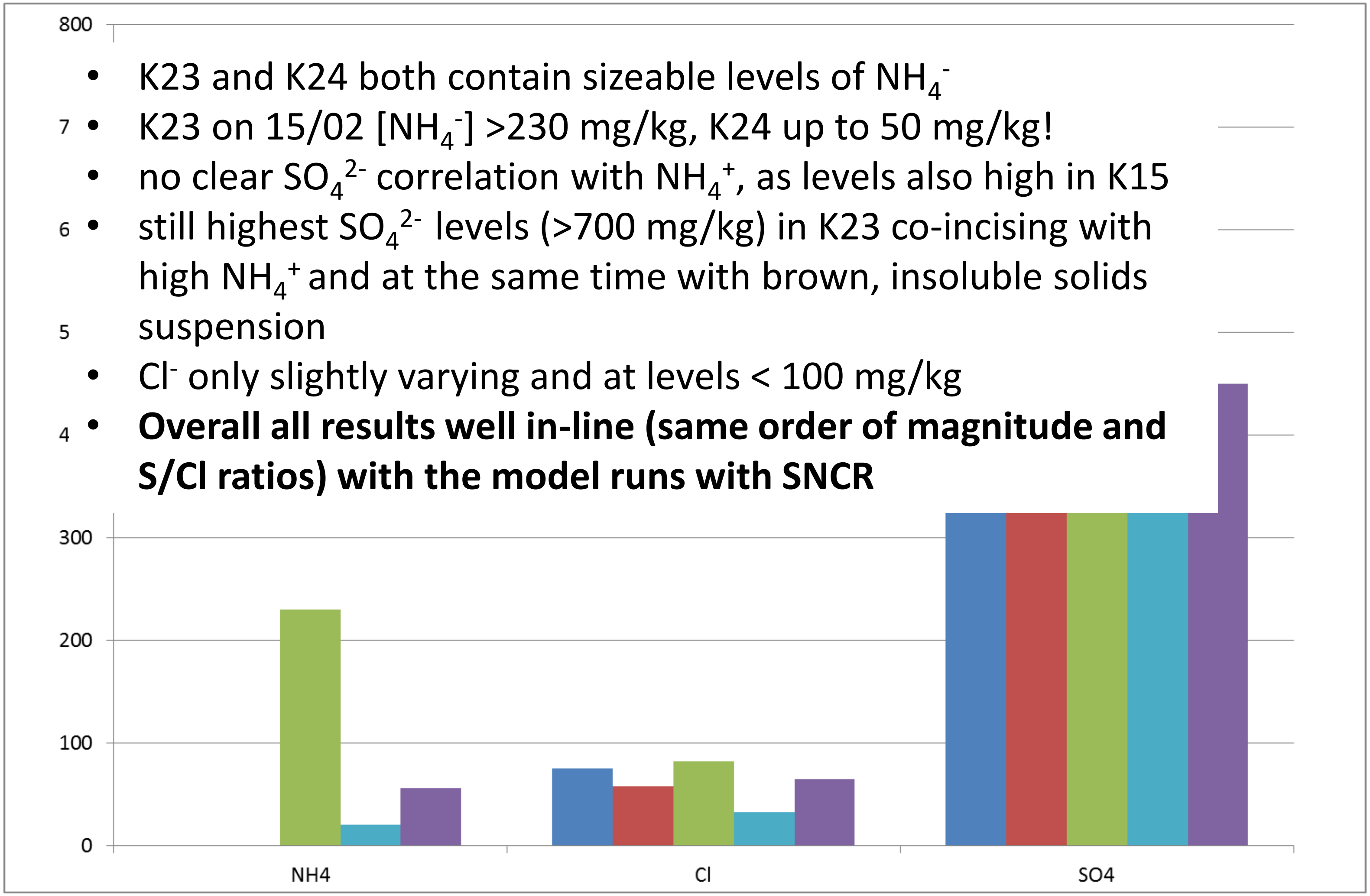
Condensates compositions 15-2-2016:

comparison with model results



Condensates compositions 15-2-2016:

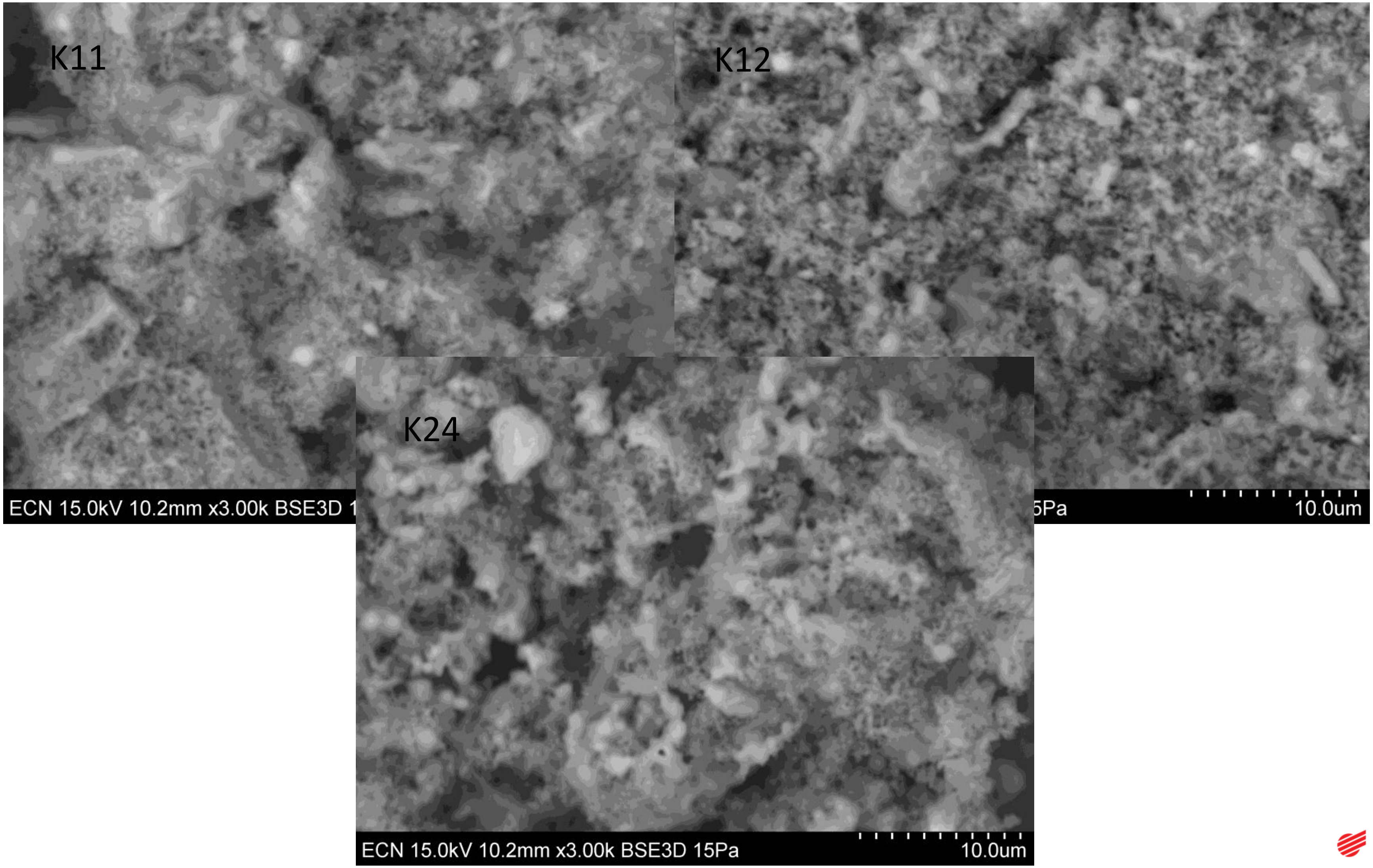
comparison with model results



- K23 and K24 both contain sizeable levels of NH_4^-
- K23 on 15/02 [NH_4^-] >230 mg/kg, K24 up to 50 mg/kg!
- no clear SO_4^{2-} correlation with NH_4^+, as levels also high in K15
- still highest SO_4^{2-} levels (>700 mg/kg) in K23 co-incising with high NH_4^+ and at the same time with brown, insoluble solids suspension
- Cl^- only slightly varying and at levels < 100 mg/kg
- **Overall all results well in-line (same order of magnitude and S/Cl ratios) with the model runs with SNCR**

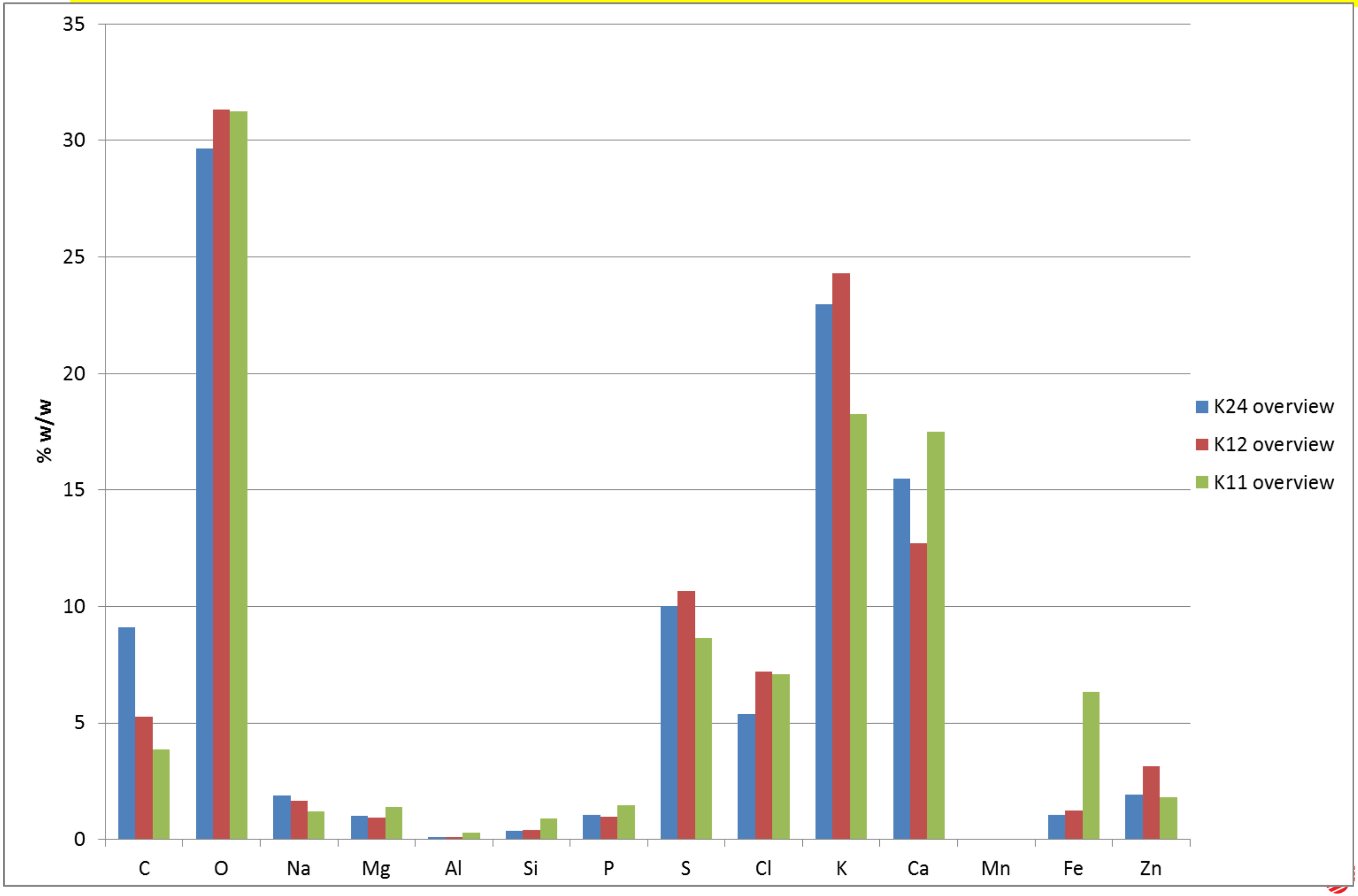
Fly ashes analyses

Fly ashes 16/02/2016: morphology



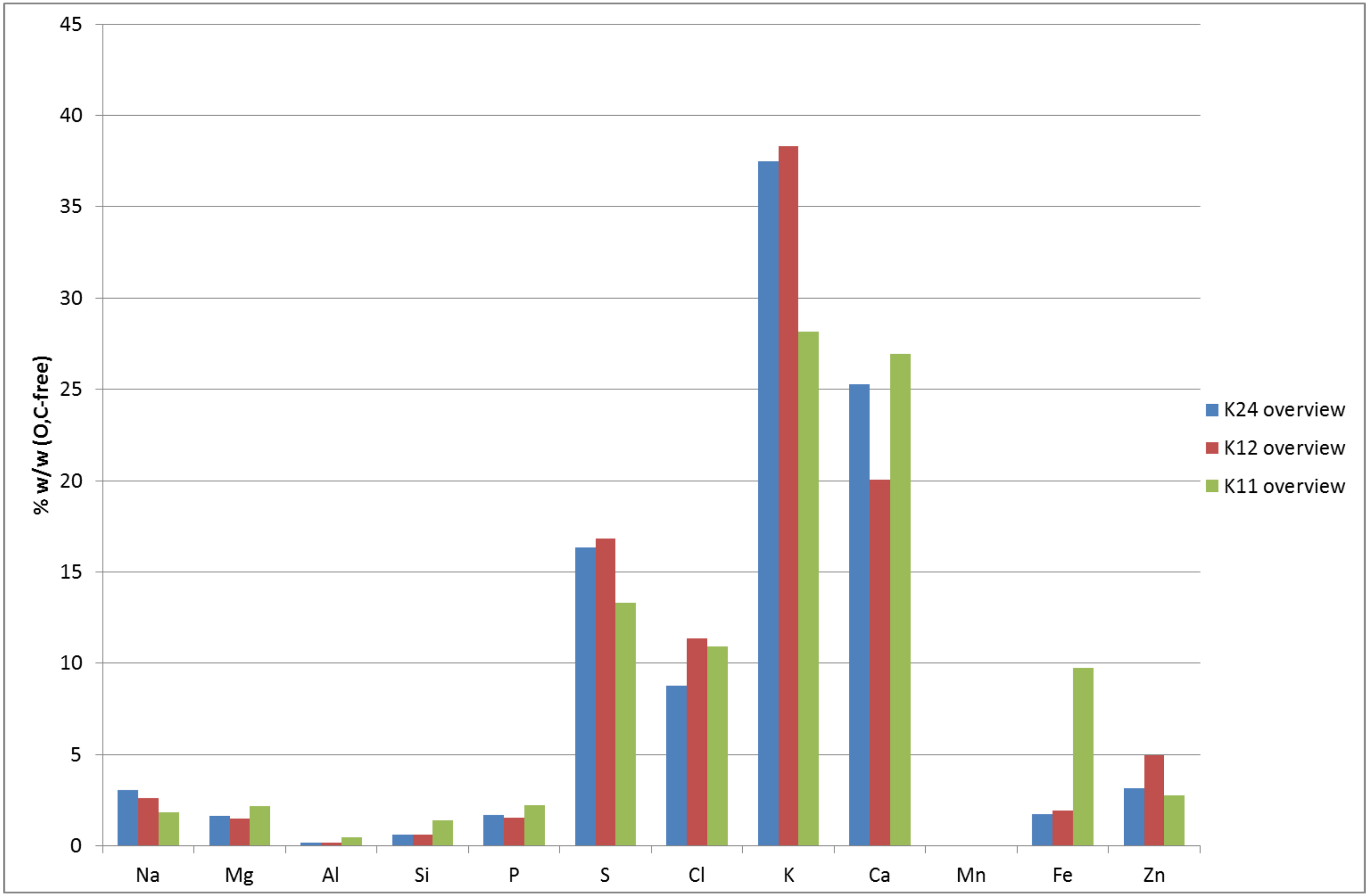
Fly ashes 16/02/2016:

general composition, all elements



Fly ashes 16/02/2016:

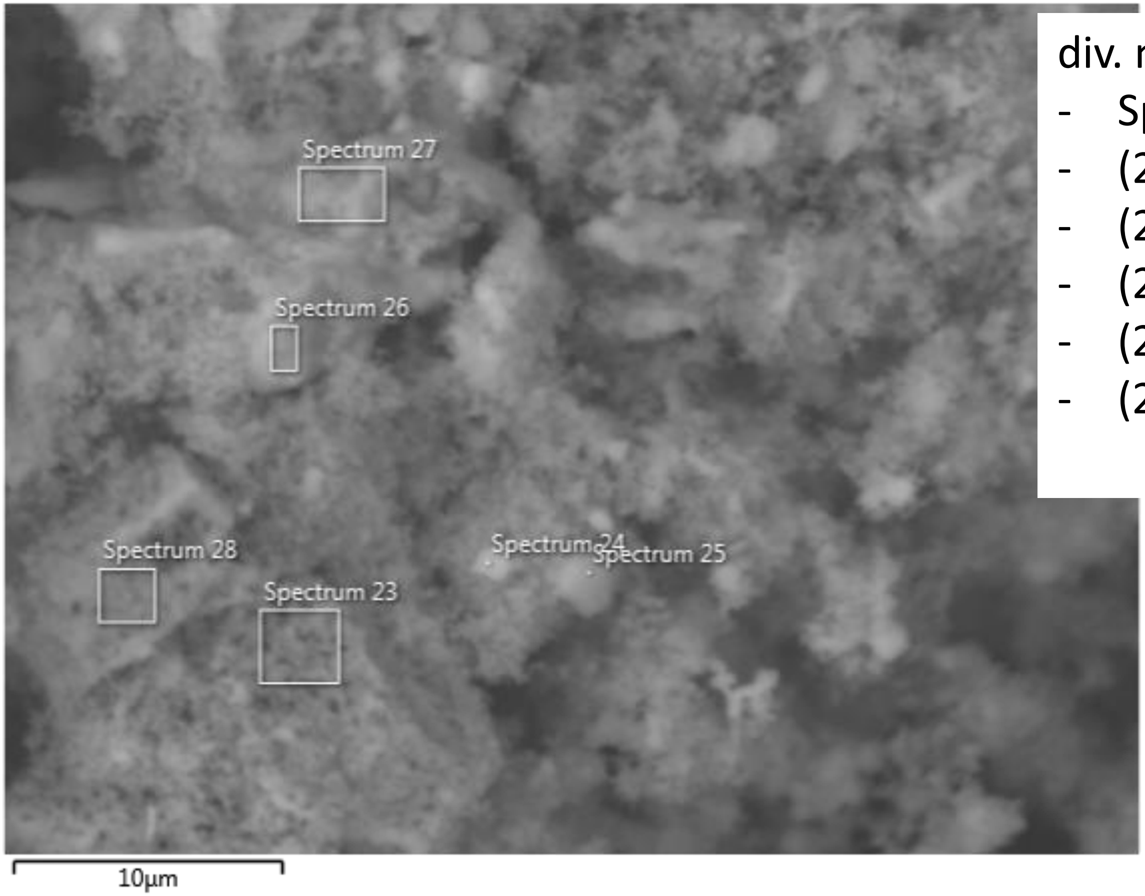
general composition, C,O-free



Fly ashes 16/02/2016:

K11 in details

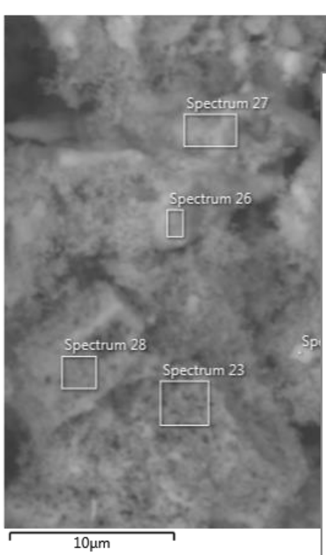
No.11

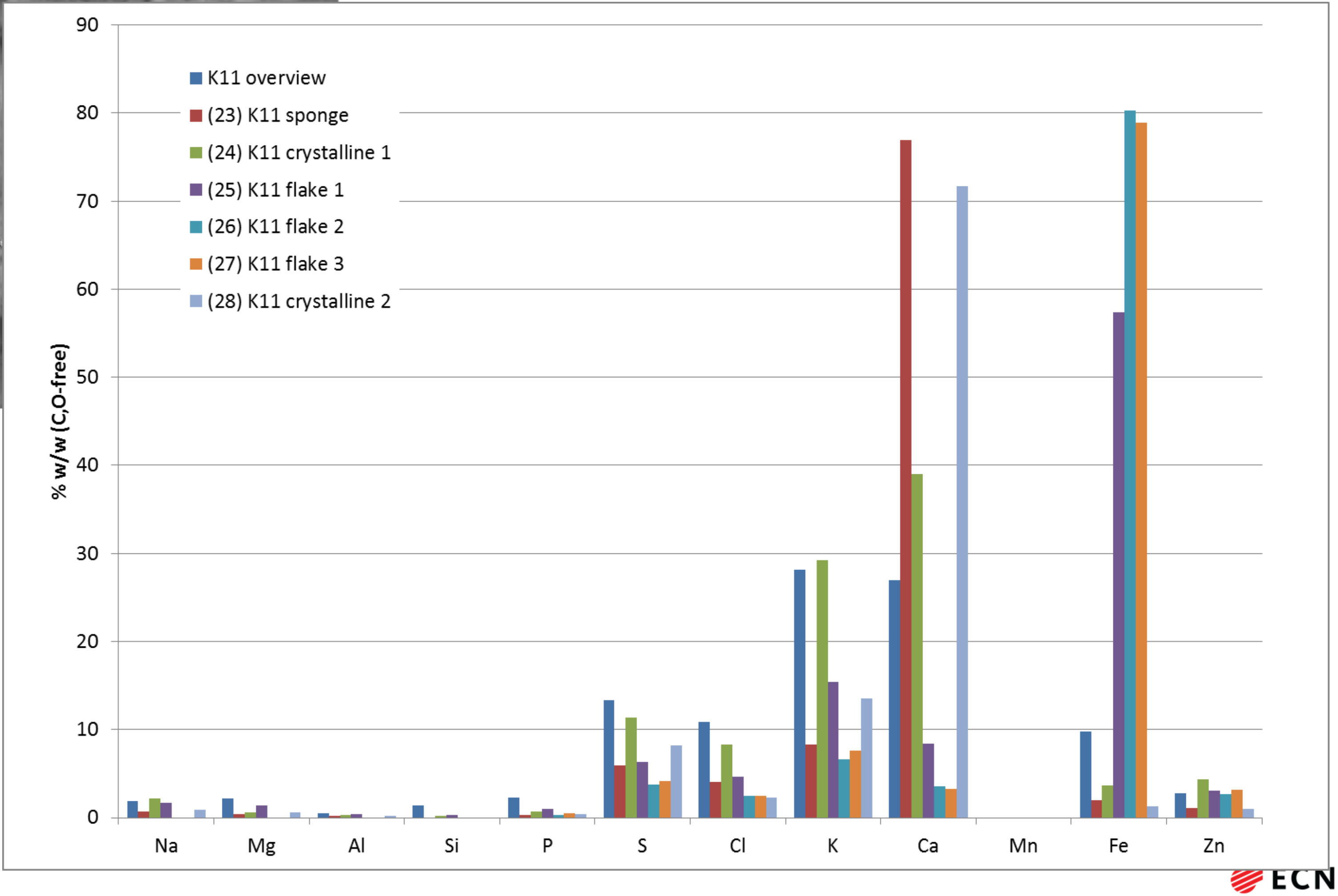


div. morphologies:
- Sponge (23)
- (24) crystalline 1
- (25) flake 1
- (26) flake 2
- (27) K11 flake 3
- (28) K11 crystalline 2

Fly ashes 16/02/2016:

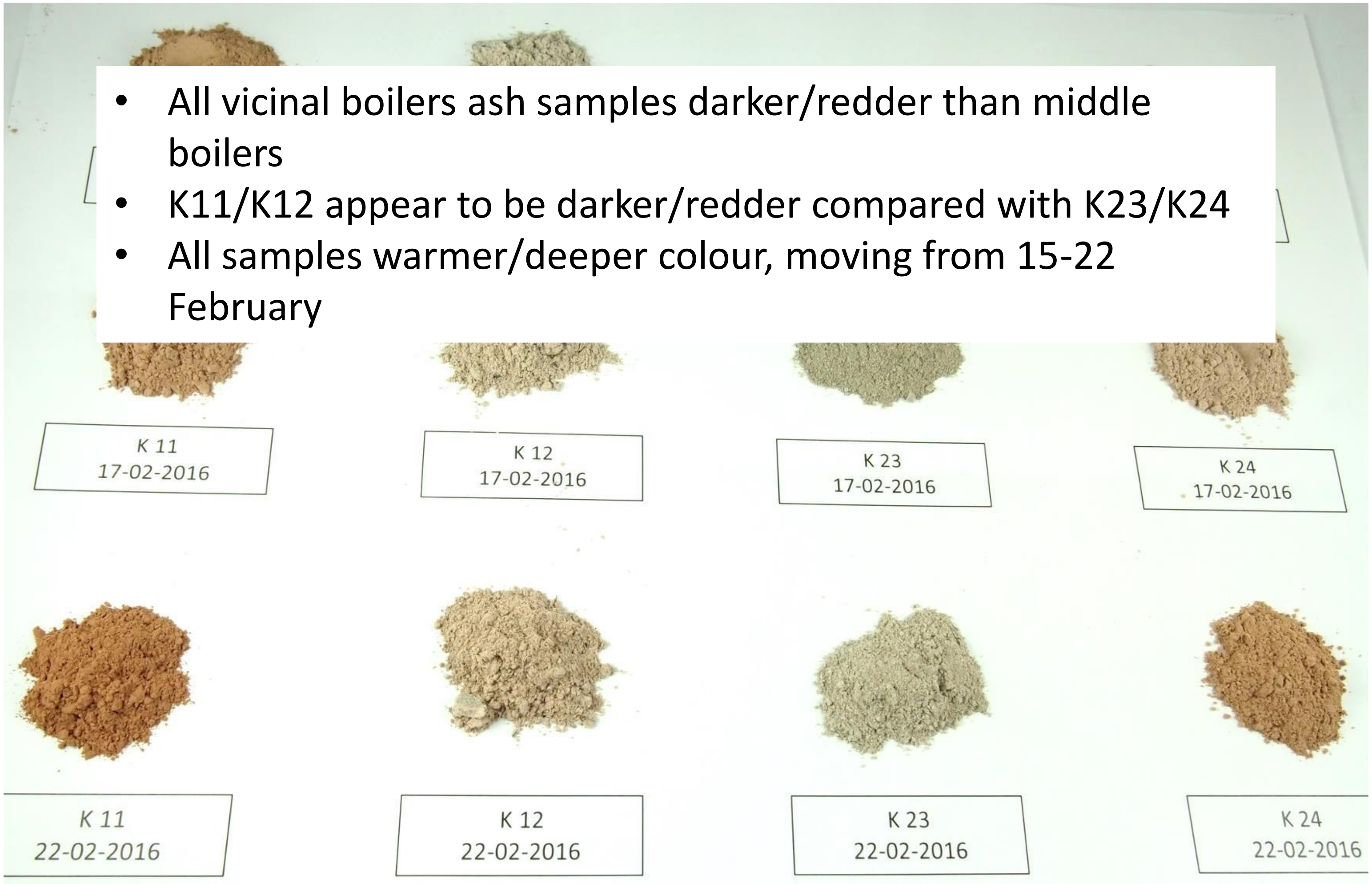
K11 in details





Fly ashes 15-17-22/02/2016:

photographic record (at WB 5200K)



- All vicinal boilers ash samples darker/redder than middle boilers
- K11/K12 appear to be darker/redder compared with K23/K24
- All samples warmer/deeper colour, moving from 15-22 February

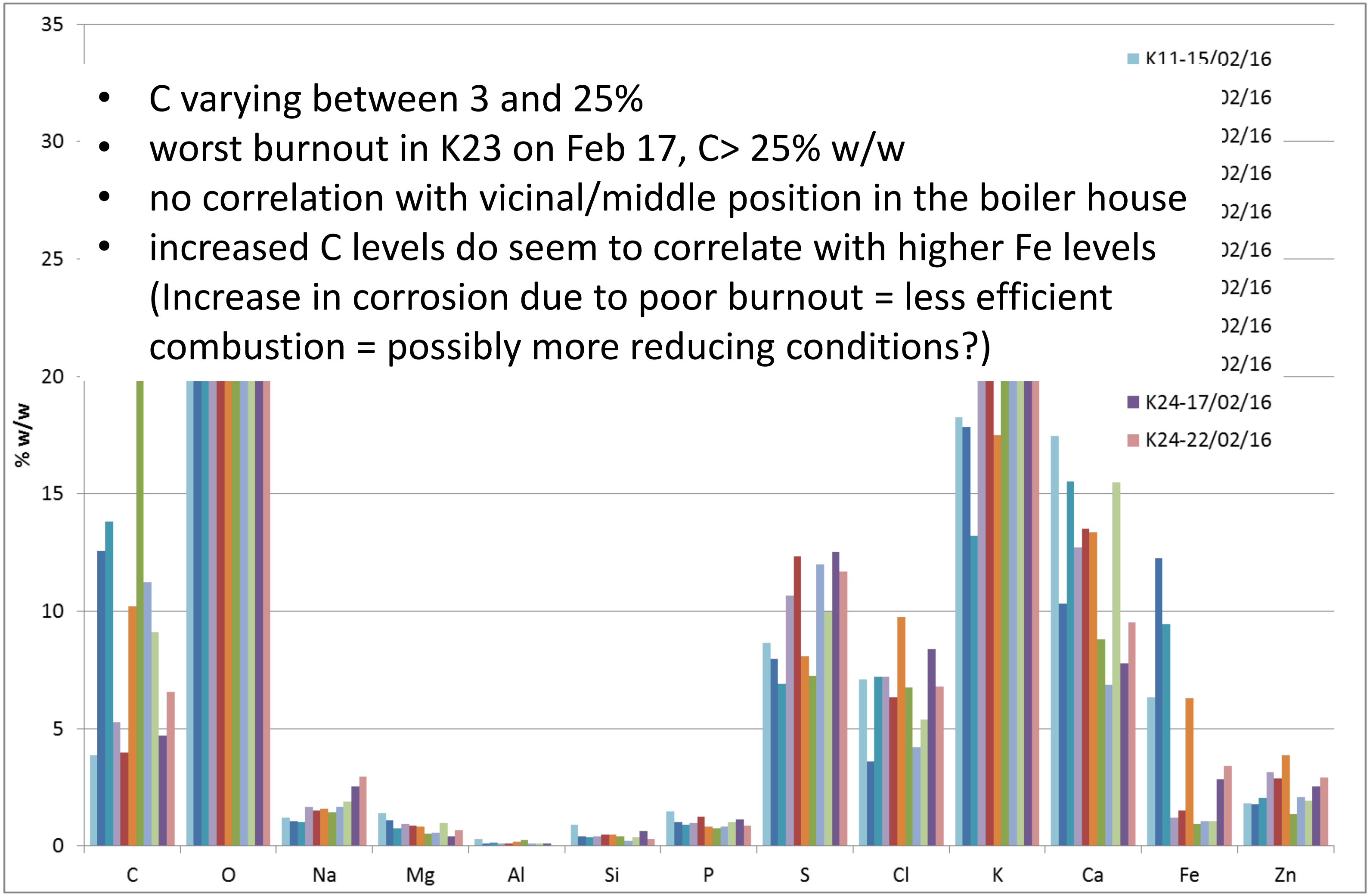
Fly ashes 15-17-22/02/2016:

general composition, numerical results

	K11-17/02/16	K12-17/02/16	K23-17/02/16	K24-17/02/16	K11-22/02/16	K12-22/02/16	K23-22/02/16	K24-22/02/16	K24-15/02/16	K12-15/02/16	K11-15/02/16
C	12.58	3.99	25.76	4.71	13.81	10.2	11.22	6.55	9.1	5.28	3.88
O	29.92	28.22	24.84	25.86	28.64	27.02	31.58	30.4	29.65	31.33	31.23
Na	1.05	1.52	1.43	2.54	1.01	1.59	1.68	2.95	1.89	1.67	1.21
Mg	1.08	0.86	0.54	0.41	0.77	0.83	0.56	0.68	1	0.95	1.41
Al	0.13	0.12	0.27	0.1	0.14	0.17	0.1	0	0.11	0.12	0.3
Si	0.43	0.49	0.41	0.63	0.36	0.51	0.21	0.3	0.37	0.41	0.92
P	1.01	1.25	0.76	1.15	0.91	0.85	0.84	0.89	1.04	0.98	1.46
S	7.98	12.33	7.24	12.54	6.91	8.08	12.01	11.7	10	10.68	8.64
Cl	3.62	6.34	6.76	8.38	7.23	9.74	4.2	6.81	5.39	7.21	7.08
K	17.86	26.99	20.88	30.48	13.2	17.51	27.61	23.58	22.96	24.28	18.26
Ca	10.32	13.5	8.79	7.8	15.51	13.35	6.88	9.53	15.48	12.71	17.48
Fe	12.24	1.53	0.94	2.85	9.44	6.29	1.05	3.43	1.06	1.23	6.33
Zn	1.77	2.88	1.37	2.56	2.06	3.87	2.07	2.94	1.94	3.16	1.81

Fly ashes 15-17-22/02/2016:

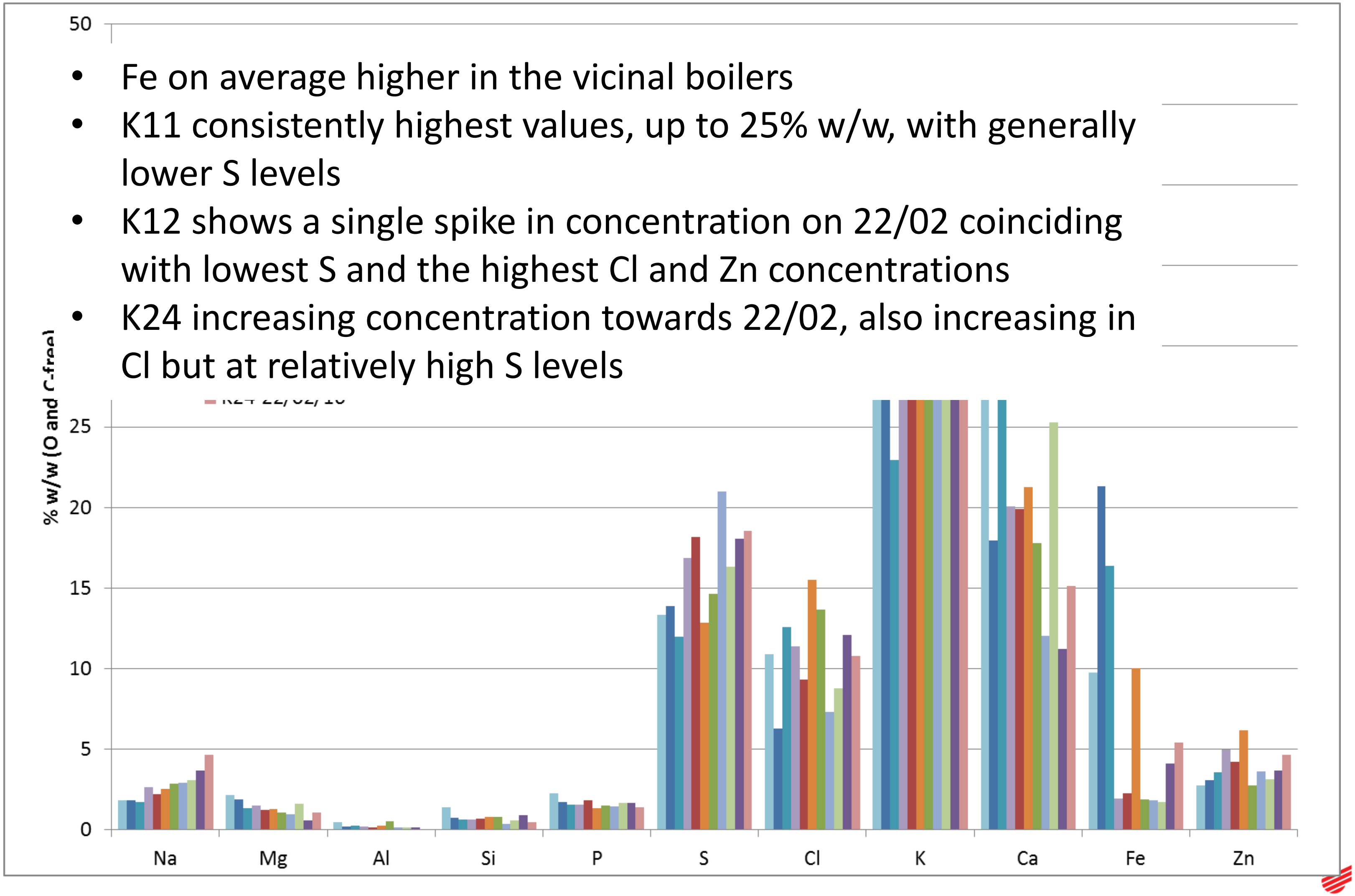
general composition, all elements



- C varying between 3 and 25%
- worst burnout in K23 on Feb 17, C> 25% w/w
- no correlation with vicinal/middle position in the boiler house
- increased C levels do seem to correlate with higher Fe levels (Increase in corrosion due to poor burnout = less efficient combustion = possibly more reducing conditions?)

Fly ashes 15-17-22/02/2016:

general composition, C,O-free

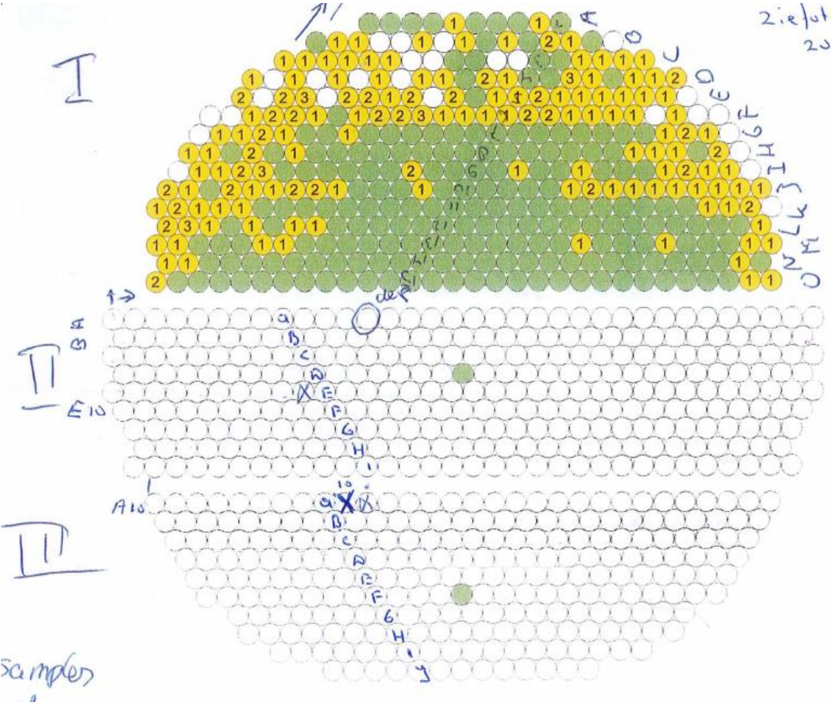


- Fe on average higher in the vicinal boilers
- K11 consistently highest values, up to 25% w/w, with generally lower S levels
- K12 shows a single spike in concentration on 22/02 coinciding with lowest S and the highest Cl and Zn concentrations
- K24 increasing concentration towards 22/02, also increasing in Cl but at relatively high S levels

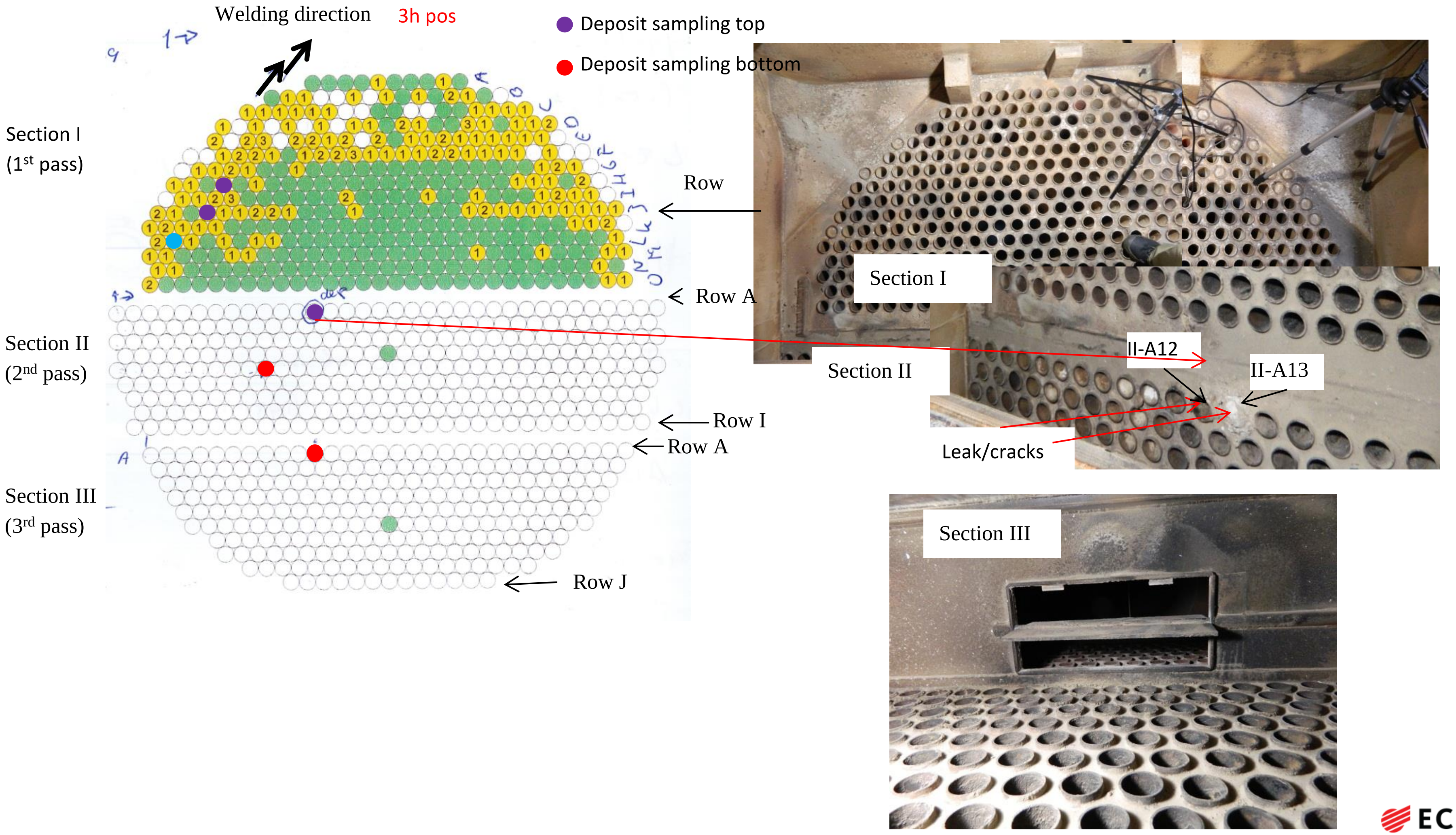
ECO inspection and ash deposits analyses

Boiler inspection 14/03/2016:
general

- Inspected:
  - Top/bottom sections K11 economiser
  - General photographic record Top side
  - Limited photographic record bottom sections
- Sampled and analysed (SEM/EDX)
  - Loose/chunk material inlet of 1st pass
  - Pipe wall deposits from selected pipes 1 2nd and 3rd pass
- General observations
  - bruin/dark grey deposits in the 1st pass inlet (bottom) blocking the flow
  - limited deposition in the 1st top section
  - 2nd pass top/bottom section limited deposition, but several pipes blocked completely, associated with leaks and cracks (A13 deposit sampled)
  - 3rd pass limited deposition and corrosion



Boiler inspection 14/03/2016: inspection/sampling locations



Welding direction

3h pos

● Deposit sampling top

● Deposit sampling bottom

Section I
(1st pass)

Section II
(2nd pass)

Section III
(3rd pass)

Row

Row A

Row I

Row A

Row J

Section I

Section II

II-A12

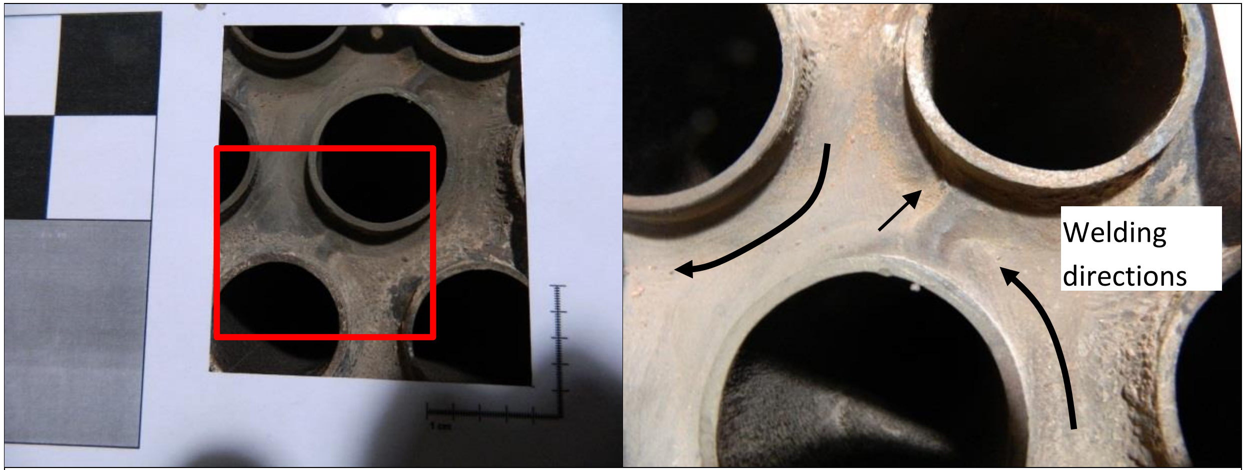
II-A13

Leak/cracks

Section III

Boiler inspection 14/03/2016:

detailed pictures 1st pass



Pipe I-L2

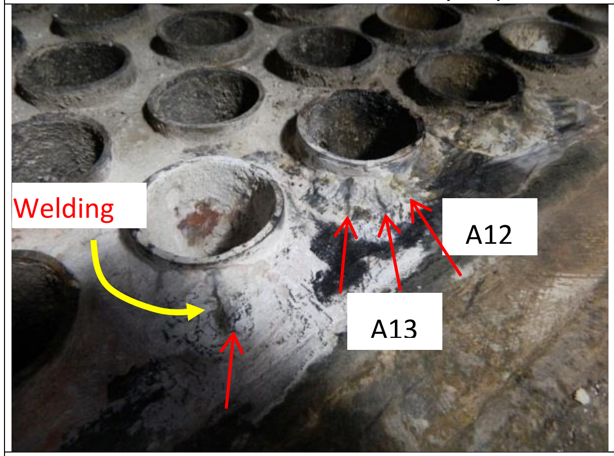
Pipe I-J4

I-G3

Boiler inspection 14/03/2016:

detailed pictures 2nd pass

Heavy deposit and sampling, Pipe A12

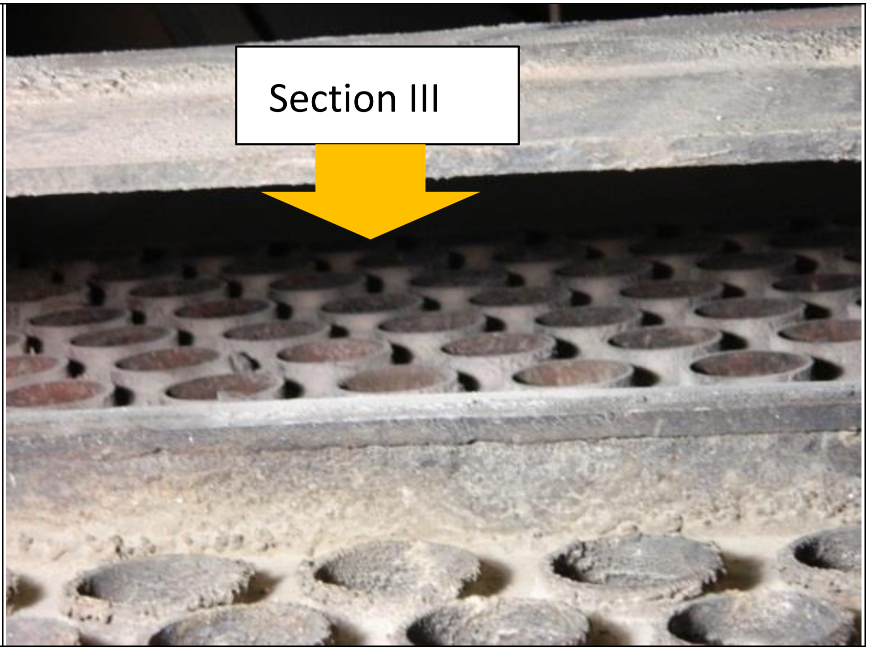


Pipe A12 and A13 (red arrows indicate crack)

A13 after grinding

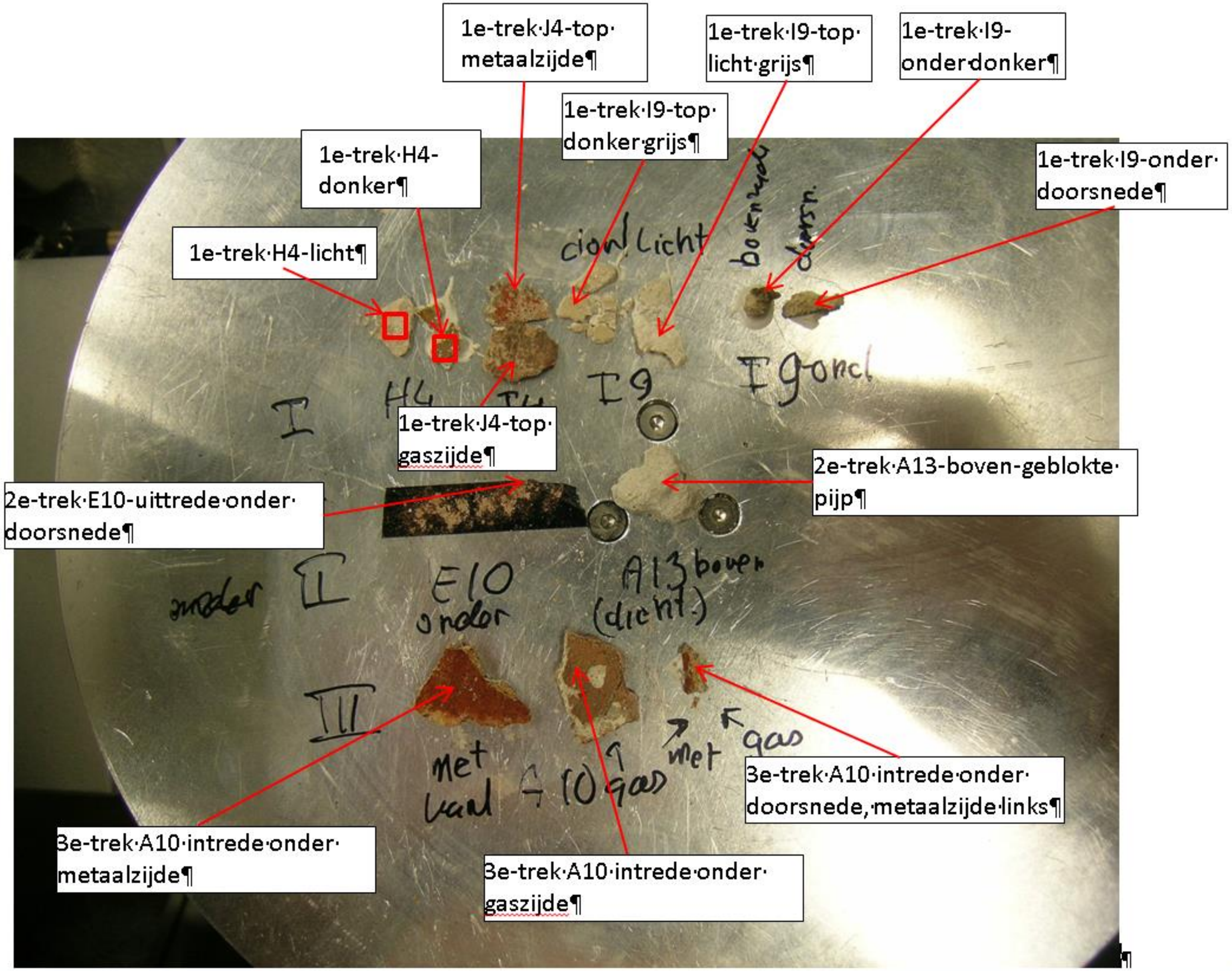
Boiler inspection 14/03/2016:

detailed pictures 3rd pass



Boiler inspection 14/03/2016:

SEM/EDX samples



1e-trek J4-top metaalzijde

1e-trek I9-top licht grijs

1e-trek I9-onder donker

1e-trek I9-top donker grijs

1e-trek H4-donker

1e-trek I9-onder doorsnede

1e-trek H4-licht

1e-trek J4-top gaszijde

2e-trek A13-boven-geblokte pijp

2e-trek E10-uittrede onder doorsnede

3e-trek A10 intrede onder doorsnede, metaalzijde links

3e-trek A10 intrede onder metaalzijde

3e-trek A10 intrede onder gaszijde

Boiler inspection 14/03/2016:

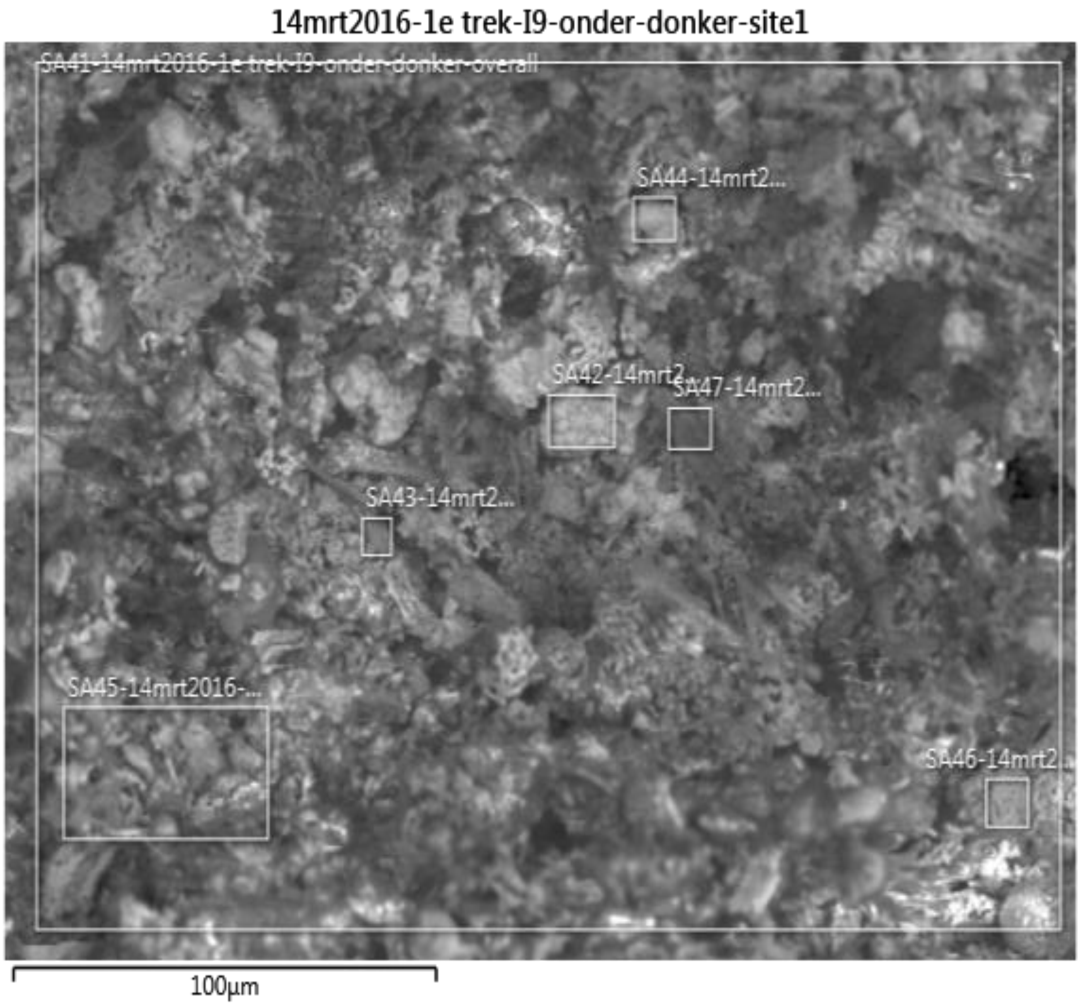
deposit morphologies 1st pass

Chunks/sticky material blocking the pipes:

- Coarse material!
- Clearly containing microcrystalline salt material
- But also chunks of char material
- Fused yet porous material
- Likely impacted as plastic/molten material
- No secondary melt (due to char burning) indications

Boiler inspection 14/03/2016:

deposit morphologies 1st pass

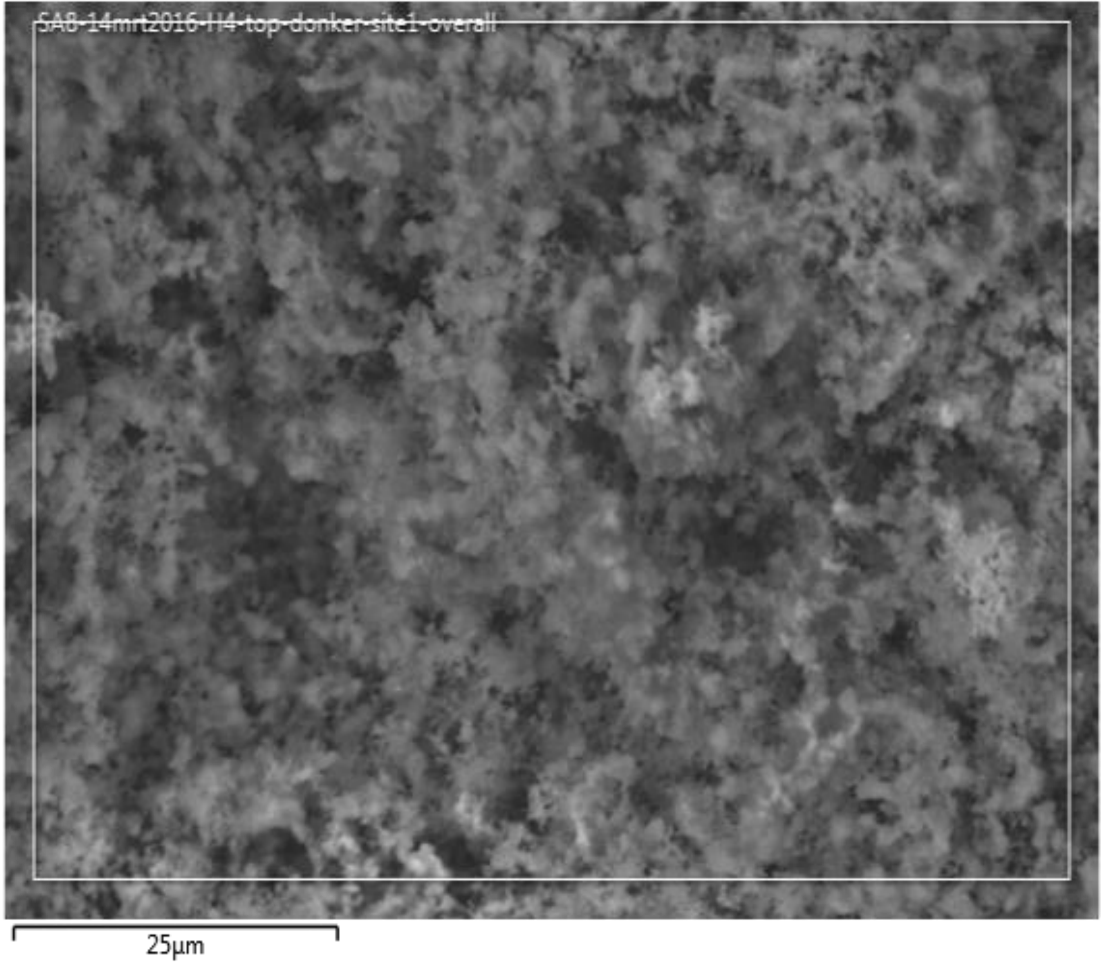


Chunky/fused deposit from I9 pipe (bottom side):

- Dark grey/brown colour
- Clearly containing microcrystalline salt material
- Visible chunks of char material (and high in carbon, vide infra)
- Fused and non-porous material
- No plastic/molten material evident

Boiler inspection 14/03/2016:
deposit morphologies 1st pass

14mrt2016-H4-top-donker-site1



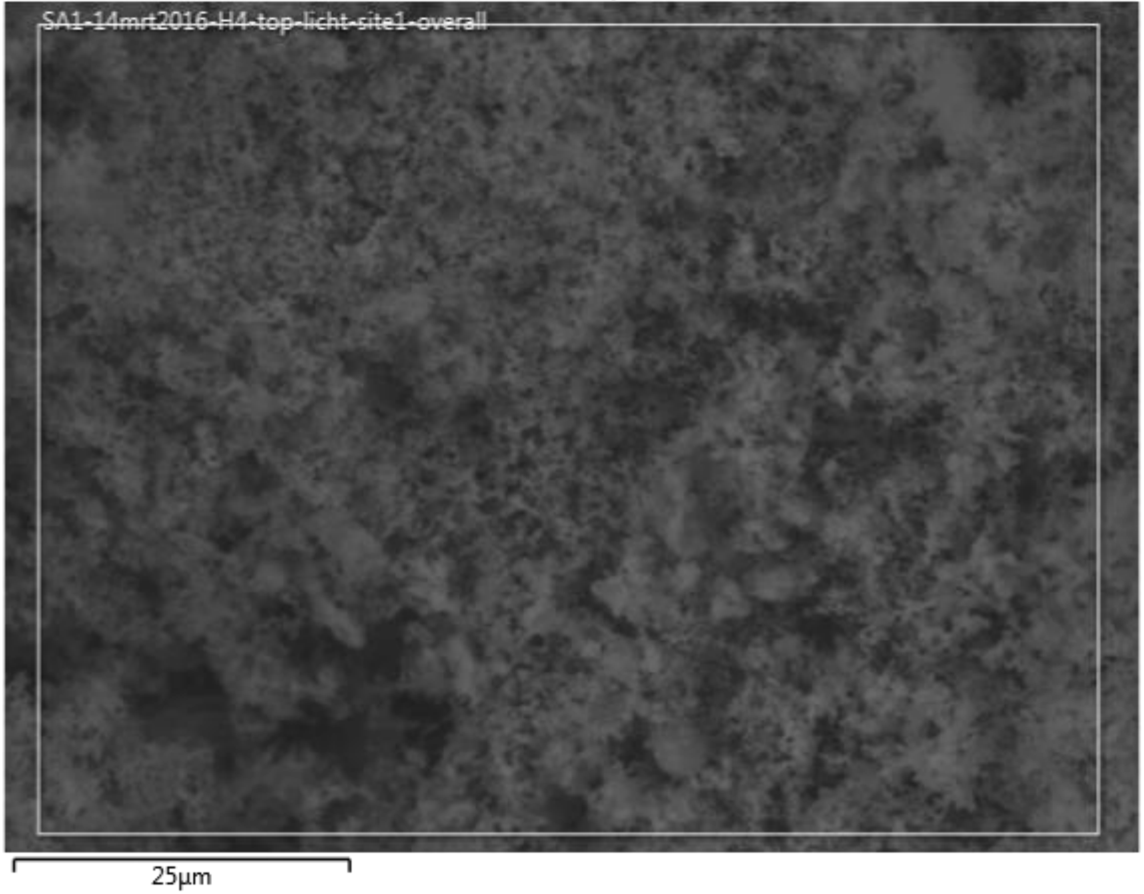
Powdery deposit from H4 pipe (top side):

- Dark grey/brown colour
- Clearly containing microcrystalline salt material
- No visible chunks of char material (yet high in carbon, vide infra)
- Fused yet porous material
- No plastic/molten material evident

Boiler inspection 14/03/2016:

deposit morphologies 1st pass

14mrt2016-H4-top-licht-site1

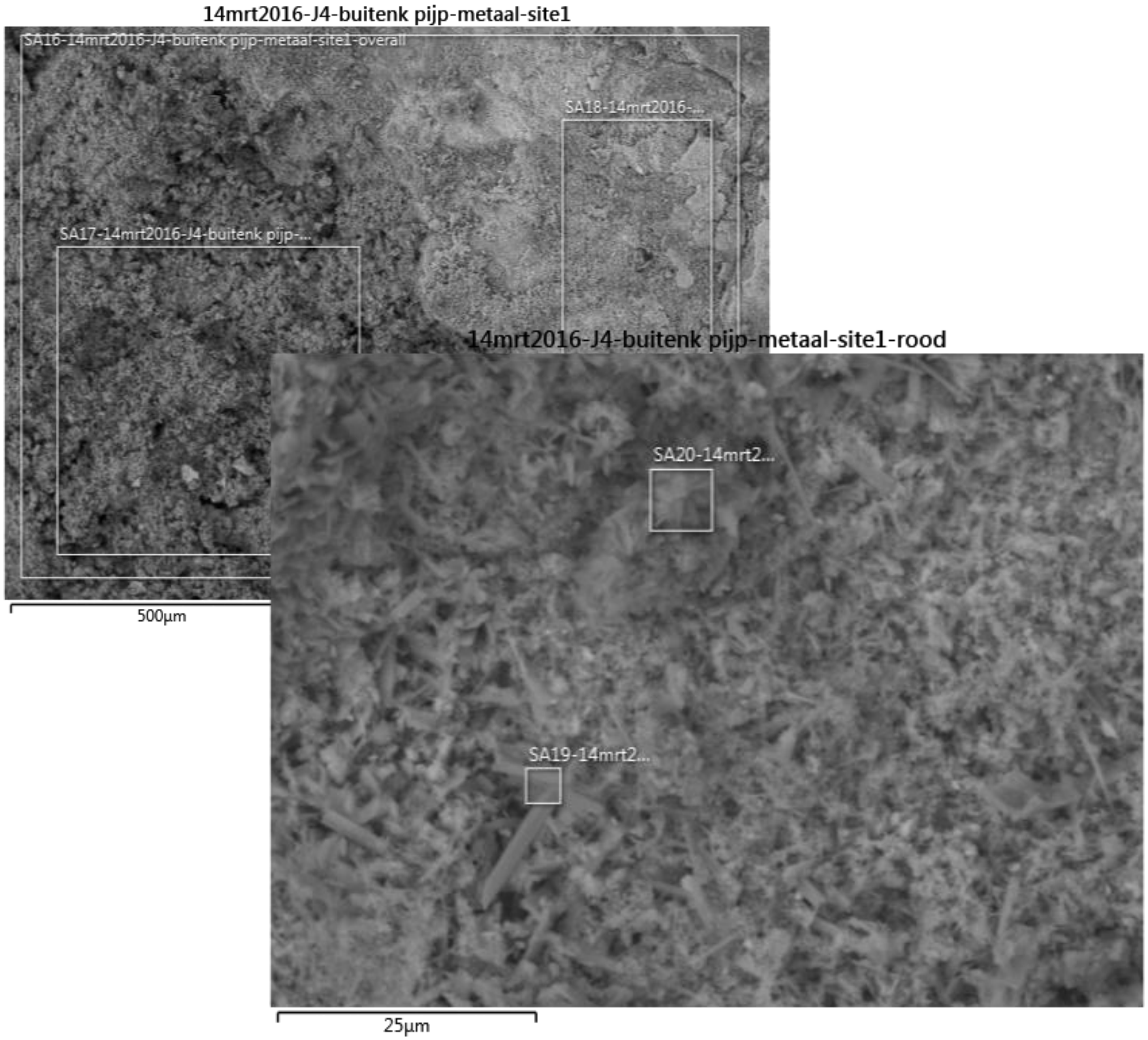


Powdery deposit from H4 pipe (top side):

- Light grey colour
- Clearly containing microcrystalline salt material
- No chunks of char material
- Fused yet porous material
- No plastic/molten material evident

Boiler inspection 14/03/2016:

deposit morphologies 1st pass

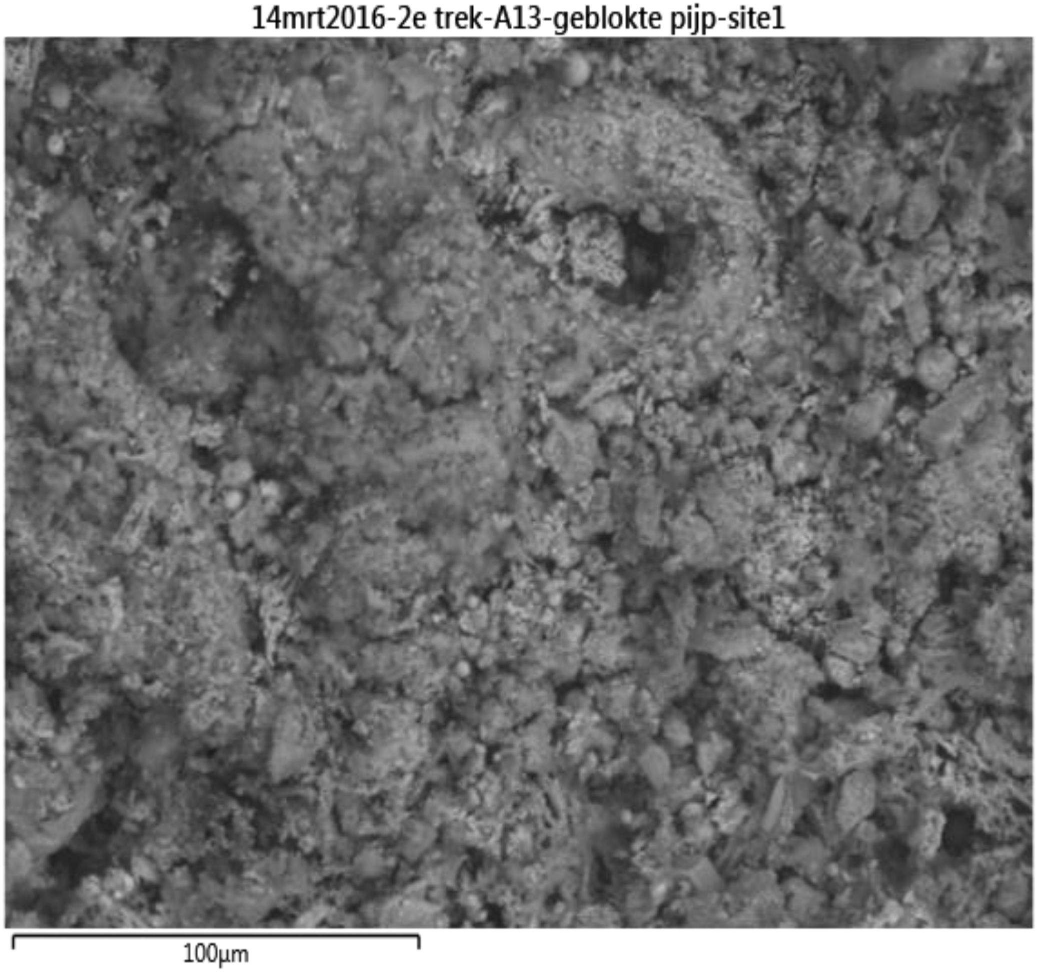


Flake-like, fragile deposit from J4 pipe (top side), pipe-wall-side :

- Red/brown colour
- Clearly containing microcrystalline salt material
- No chunks of char material
- Flakes of Fe-rich material (oxide layer) enclosed in salt
- Fused yet porous material
- No plastic/molten material evident

Boiler inspection 14/03/2016:

deposit morphologies 2nd pass



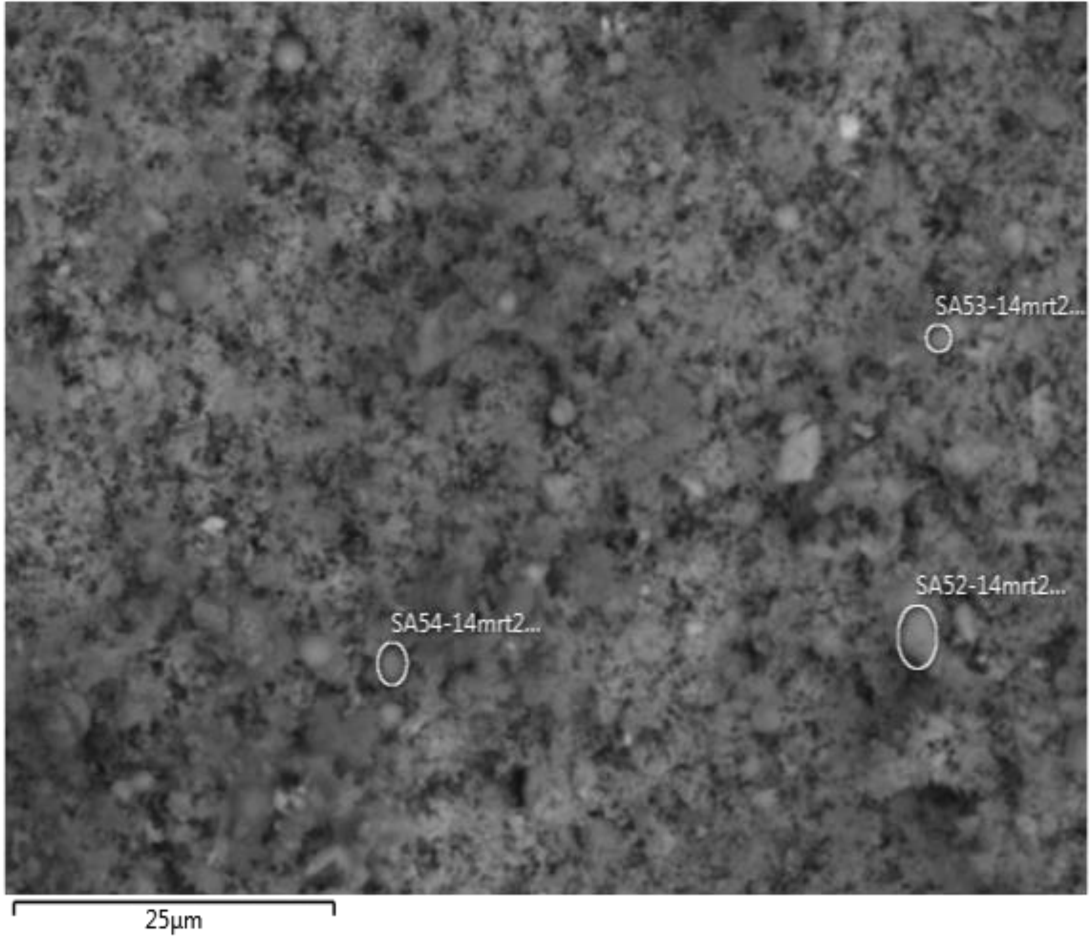
Powdery/chunky deposit from A13 pipe (top side), blocking the gas flow :

- Light colour
- Clearly containing microcrystalline salt material
- No chunks of char material
- Flakes of Fe-rich material (oxide layer) enclosed in salt
- Fused yet porous material
- No plastic/molten material evident

Boiler inspection 14/03/2016:

deposit morphologies 3rd pass

14mrt2016-3e trek A10-onder intrede-gaszijde-site1



Powdery deposit from A10 pipe (bottom, flue gas side):

- Light colour
- Containing only microcrystalline salt material
- No chunks of char material
- No flakes of Fe-rich material (oxide layer) enclosed in salt
- Porous and very slightly fused material
- No plastic/molten material evident

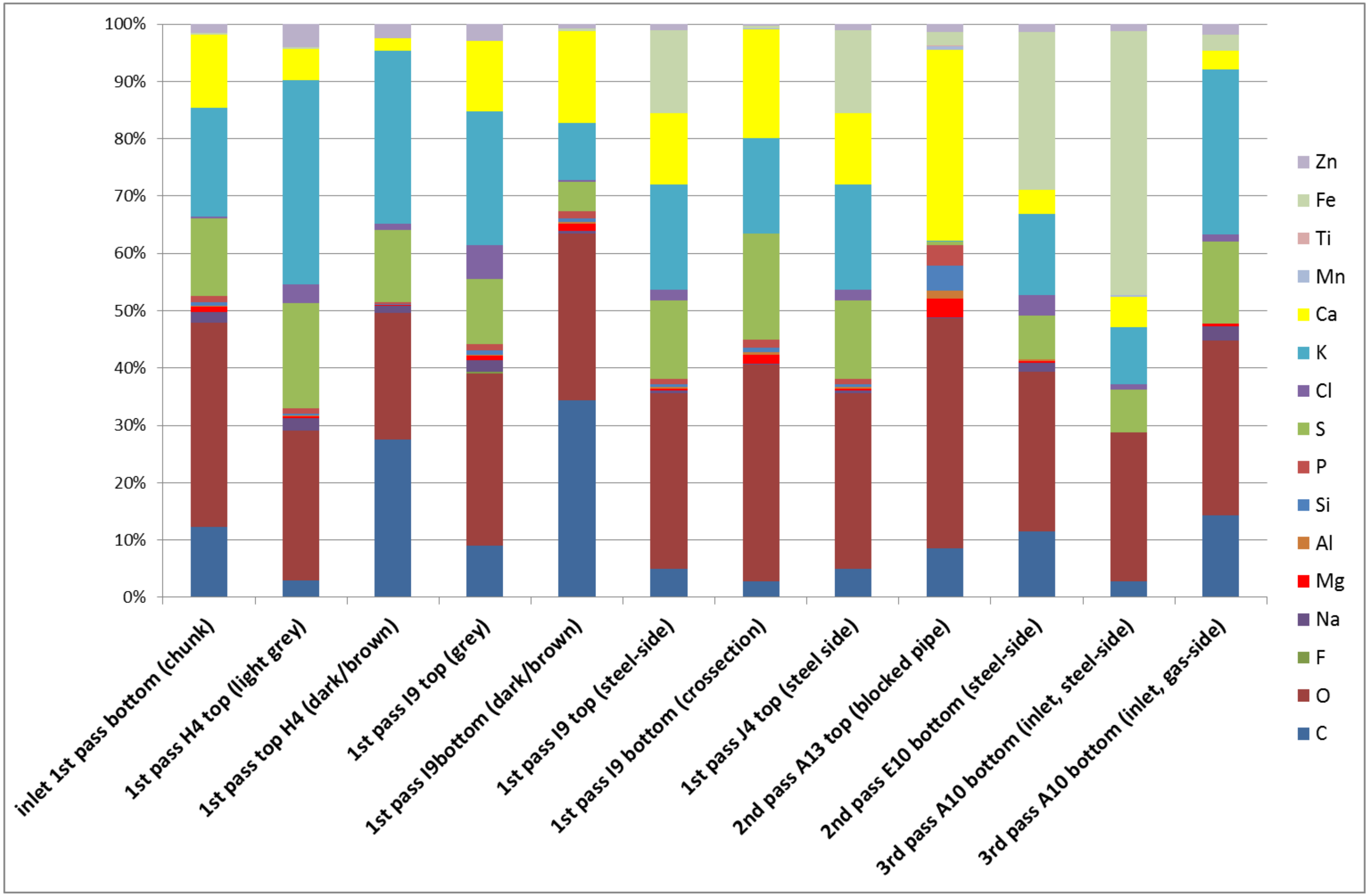
Boiler inspection 14/03/2016:

deposit compositions, numerical

	K11 ECO deposits and ashes 14/03/16												K11 fly ashes		
Sample	inlet 1st pass bottom (chunk)	1st pass H4 top (light grey)	1st pass top H4 (dark/brown)	1st pass I9 top (grey)	1st pass I9bottom (dark/brown)	1st pass I9 top (steel-side)	1st pass I9 bottom (crossection)	1st pass J4 top (steel side)	2nd pass A13 top (blocked pipe)	2nd pass E10 bottom (steel-side)	3rd pass A10 bottom (inlet, steel-side)	3rd pass A10 bottom (inlet, gas-side)	fly ash K11-17/02/16 1	fly ash K11-17/02/16 2	fly ash K11-17/02/16 3
C	12.21	2.93	27.59	9.04	34.37	4.9	2.76	4.9	8.55	11.43	2.71	14.35	8.18	17.19	10.3
O	35.62	26.18	21.98	29.98	29.09	30.71	37.79	30.71	40.09	27.93	26.1	30.42	30.58	29.32	29.68
F	0	0	0	0.35	0	0	0	0	0	0	0	0	0	0	0
Na	1.95	2.2	1.25	2.06	0.55	0.42	0.2	0.42	0.21	1.55	0	2.5	1.24	0.9	1.12
Mg	0.98	0.29	0.15	0.78	1.15	0.41	1.56	0.41	3.2	0.37	0	0.45	1.23	0.85	1.15
Al	0.11	0.15	0.09	0.17	0.26	0.27	0.38	0.27	1.5	0.31	0	0	0.28	0	0.23
Si	0.57	0.32	0.07	0.63	0.64	0.47	0.85	0.47	4.28	0	0	0	0.7	0.22	0.59
P	1.17	0.87	0.35	1.09	1.33	0.97	1.43	0.97	3.54	0	0	0	1.19	0.9	1.09
S	13.56	18.33	12.65	11.4	5.1	13.69	18.51	13.69	0.65	7.53	7.46	14.31	8.85	7.04	8.69
Cl	0.19	3.33	1.04	5.93	0.24	1.81	0	1.81	0.02	3.56	0.97	1.23	4.15	3.13	4.06
K	19.08	35.55	30.19	23.37	10.01	18.36	16.61	18.36	0.25	14.15	9.84	28.88	20.06	15.72	19.3
Ca	12.72	5.45	2.21	12.35	16.1	12.5	18.92	12.5	33.17	4.18	5.4	3.25	11.8	8.61	11.36
Mn	0	0	0	0	0	0	0.21	0	0.74	0	0.24	0	0	0	0
Ti	0	0	0	0	0	0	0	0	0.12	0	0	0	0	0	0
Fe	0.35	0.33	0	0	0.39	14.45	0.48	14.45	2.31	27.61	46.12	2.85	9.77	14.59	10.4
Zn	1.49	4.06	2.45	2.86	0.78	1.05	0.29	1.05	1.37	1.38	1.16	1.77	1.97	1.53	2.04

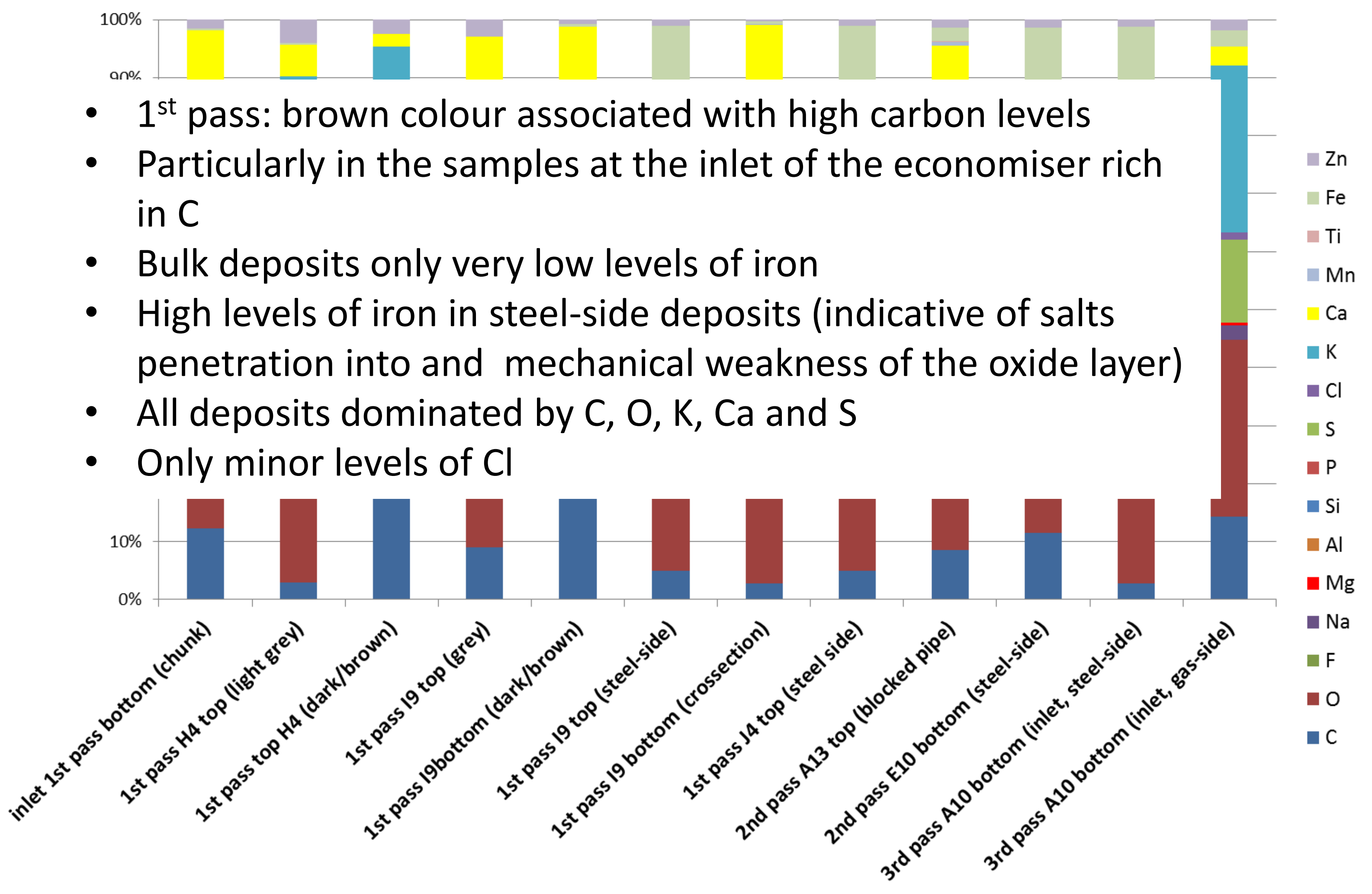
Boiler inspection 14/03/2016:

deposit compositions, all elements



Boiler inspection 14/03/2016:

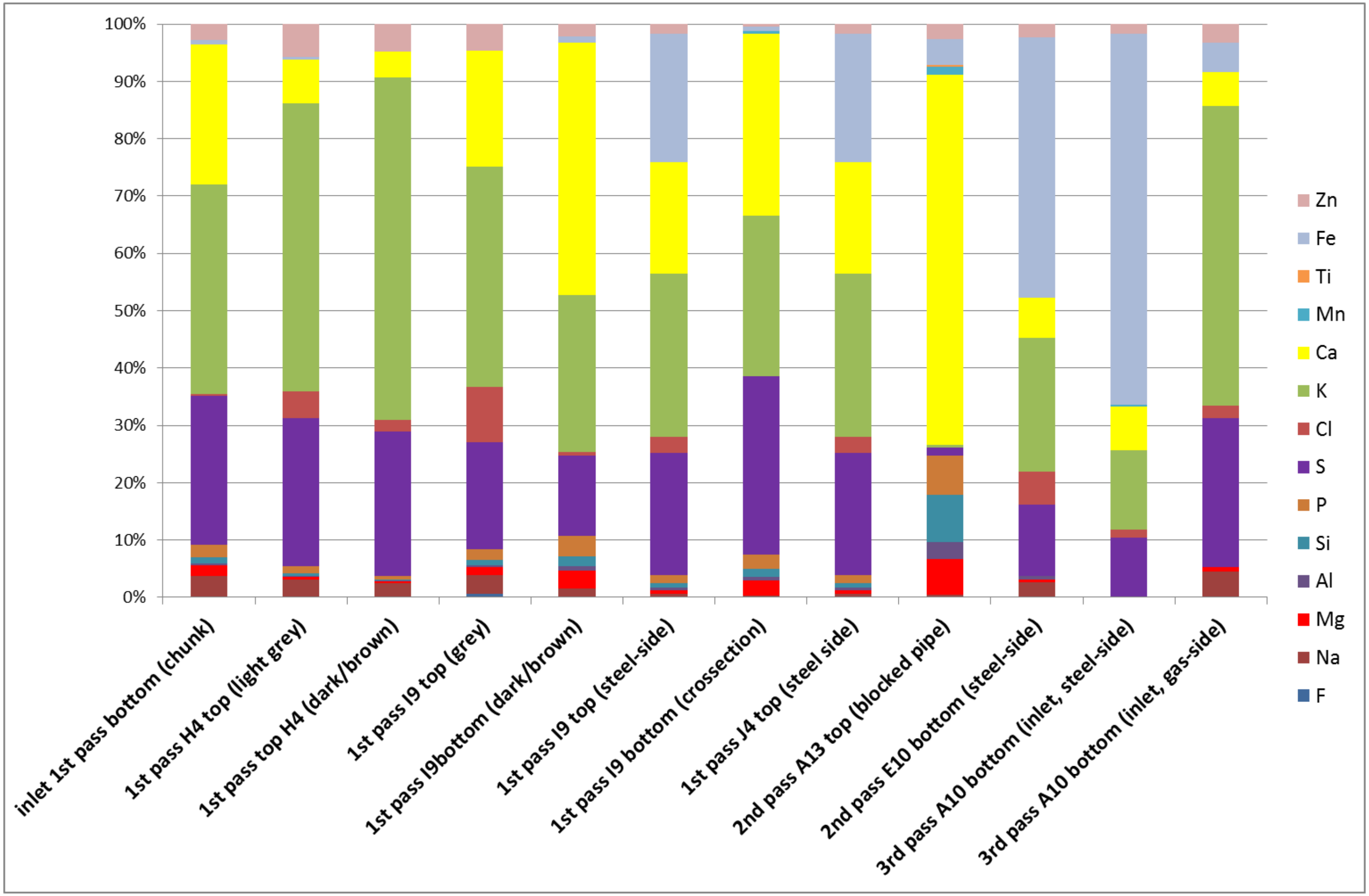
deposit compositions, all elements



- 1st pass: brown colour associated with high carbon levels
- Particularly in the samples at the inlet of the economiser rich in C
- Bulk deposits only very low levels of iron
- High levels of iron in steel-side deposits (indicative of salts penetration into and mechanical weakness of the oxide layer)
- All deposits dominated by C, O, K, Ca and S
- Only minor levels of Cl

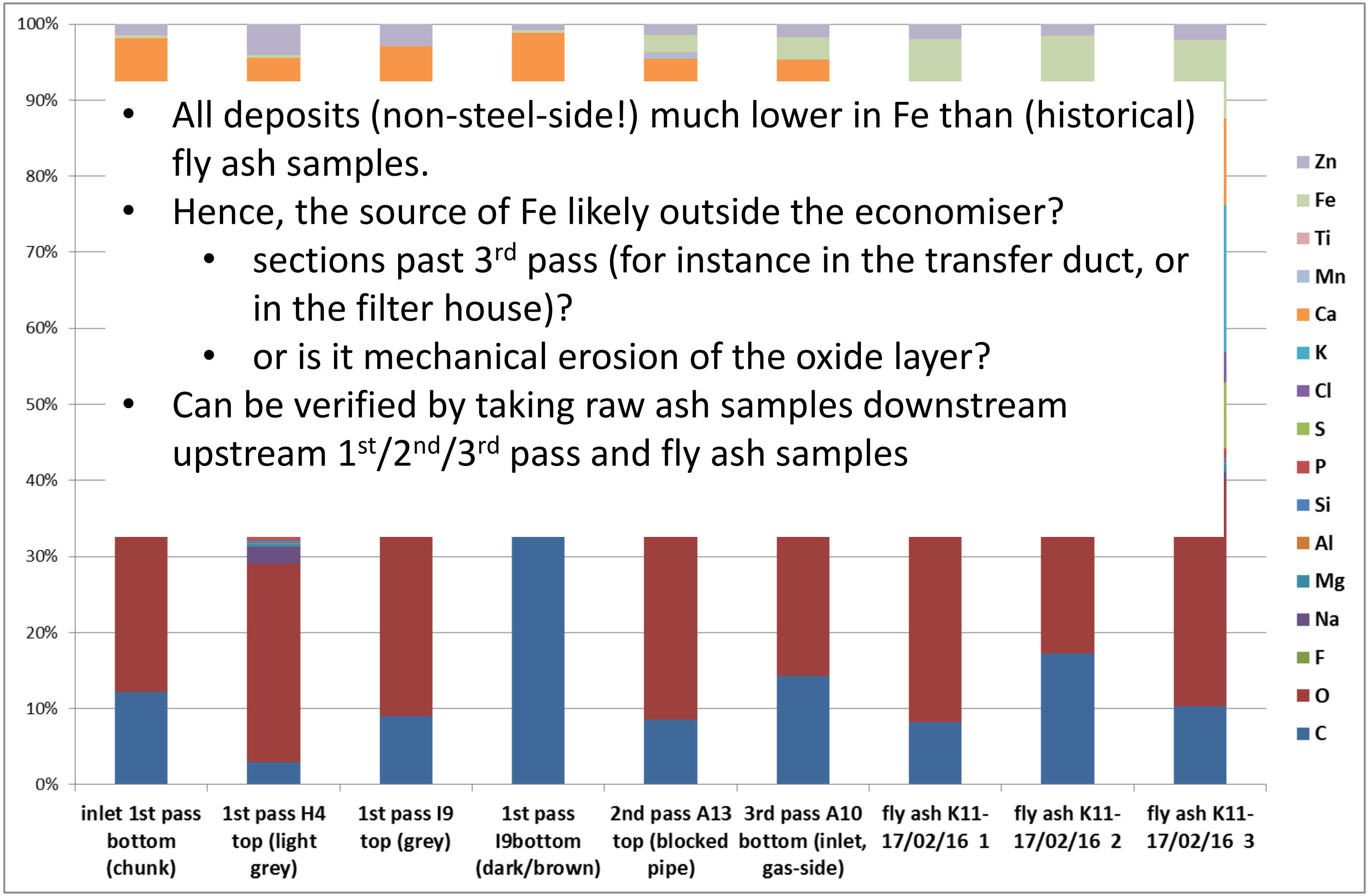
Boiler inspection 14/03/2016:

deposit compositions, ash forming elements



Boiler inspection 14/03/2016:

deposit compositions compared with fly ash



- All deposits (non-steel-side!) much lower in Fe than (historical) fly ash samples.
- Hence, the source of Fe likely outside the economiser?
  - sections past 3rd pass (for instance in the transfer duct, or in the filter house)?
  - or is it mechanical erosion of the oxide layer?
- Can be verified by taking raw ash samples downstream upstream 1st/2nd/3rd pass and fly ash samples

Boiler inspection 14/03/2016:

deposit compositions compared with fly ash

- All deposits (non-steel-side!) much lower in Fe than (historical) fly ash samples.
- Hence, the source of Fe likely outside the economiser?
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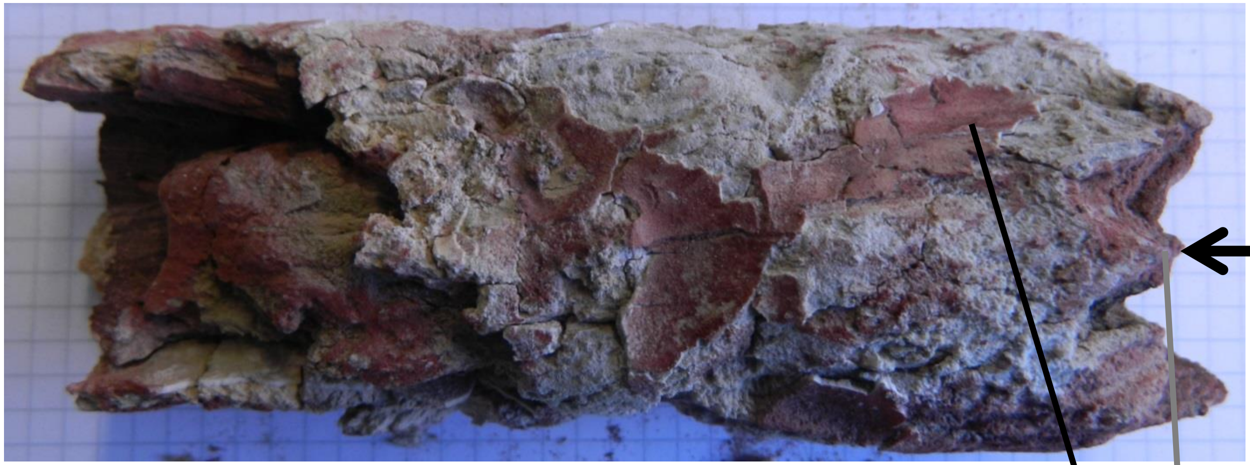
    - or is it mechanical erosion of the oxide layer?
- Can be verified by taking raw ash samples downstream upstream 1st/2nd~~/3rd~~ pass and fly ash samples
- Proposed approach:
    - 2-3 days measurement campaign
    - CI impactor for dust sampling but no dew point measurement
    - New, deeper penetrating and isokinetic probe necessary (same principle as for the earlier campaign, ca. 5-7 kEUR) (maken!)
    - Man-effort comparable to Dec campaign (week 20?)
    - Analyses to be agreed on, but SEM/EDX and gravimetry as a minimum

Boiler inspection 14/04/2016:

whole deposit from K23

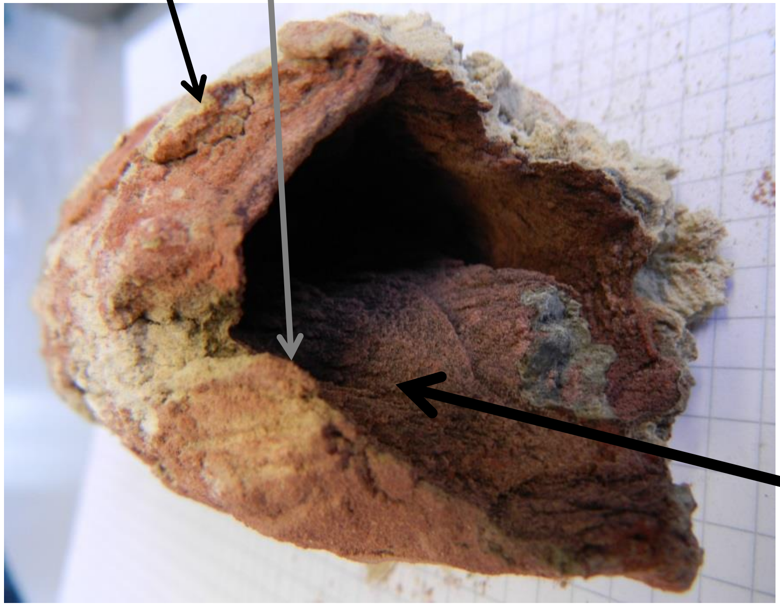


flue gas flow

Whole-deposit sample from K23 ECO
Complete with:

- oxide layer (tube-side)
- gas-side deposits protruding into the flow

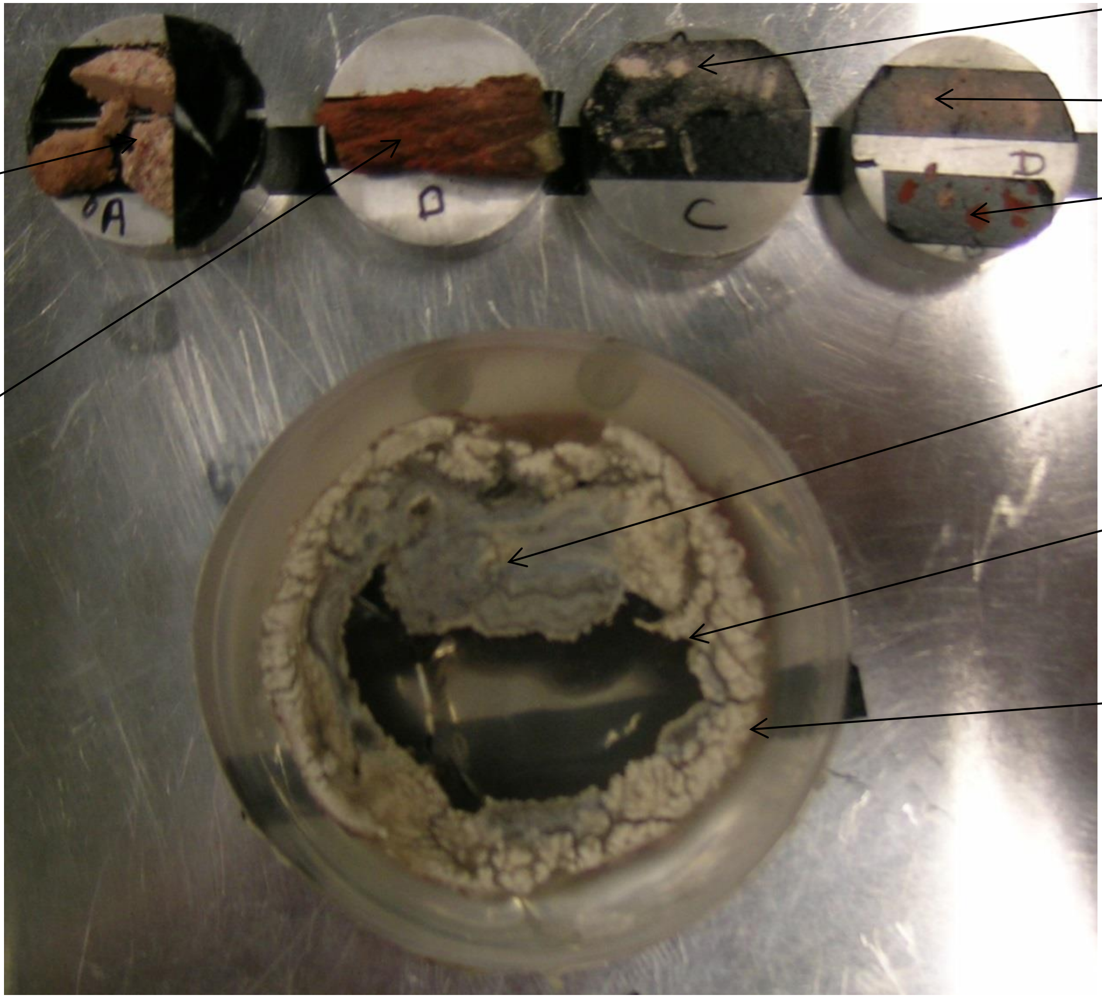
Sample origin: unsure
Material embedded in epoxy resin
and cross-sectioned for SEM/EDX analyses



flue gas flow

Boiler inspection 14/04/2016:

whole deposit from K23 and fly ashes K23



grey K12 fly ash

red K12 bulk fly ash

red K12 fly ash flakes

dried wet
ash deposit
K23

loose piece
gas-side
"stalactite"

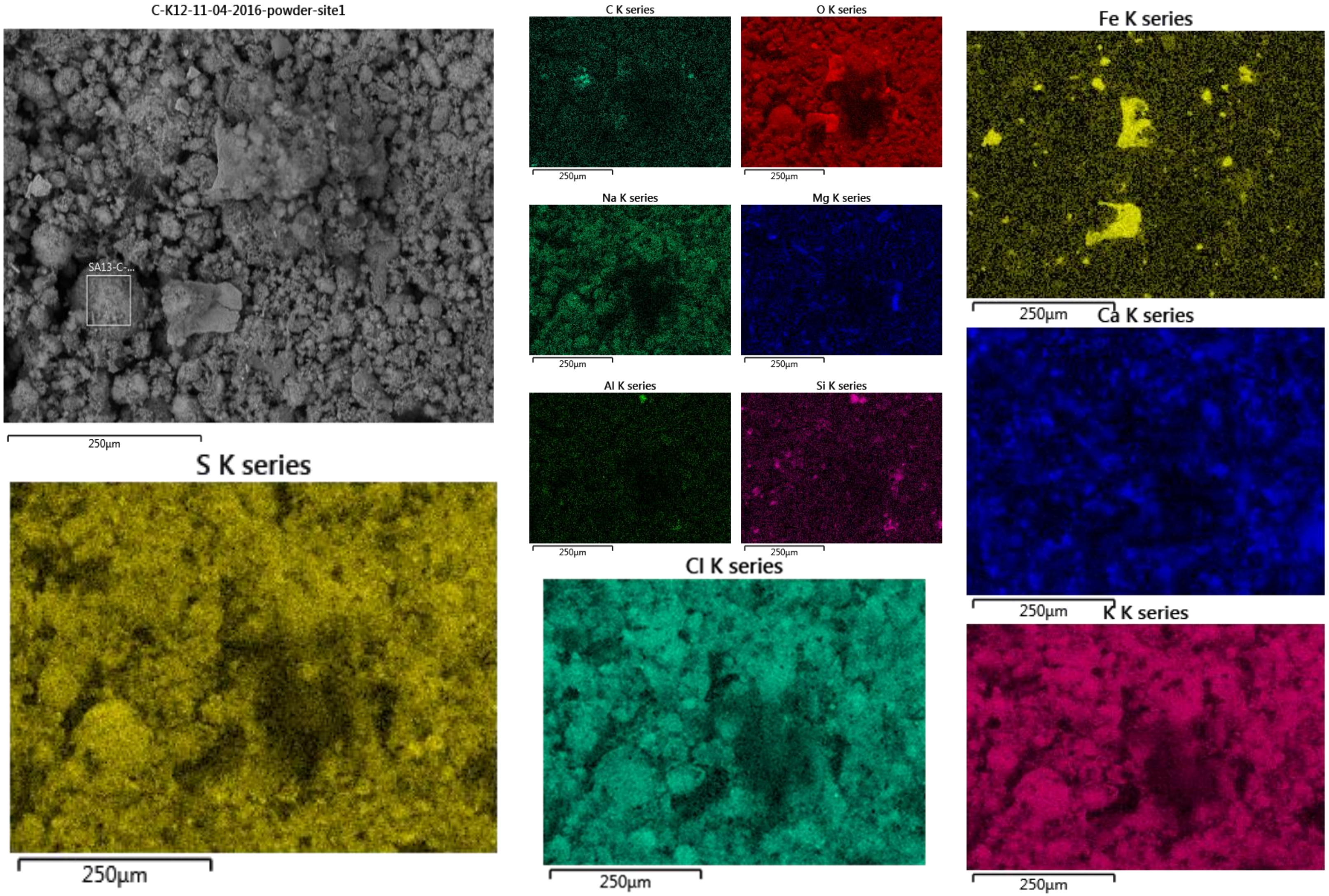
cross-section
deposit body

cross-section
gas-side

cross-section
pipe-side

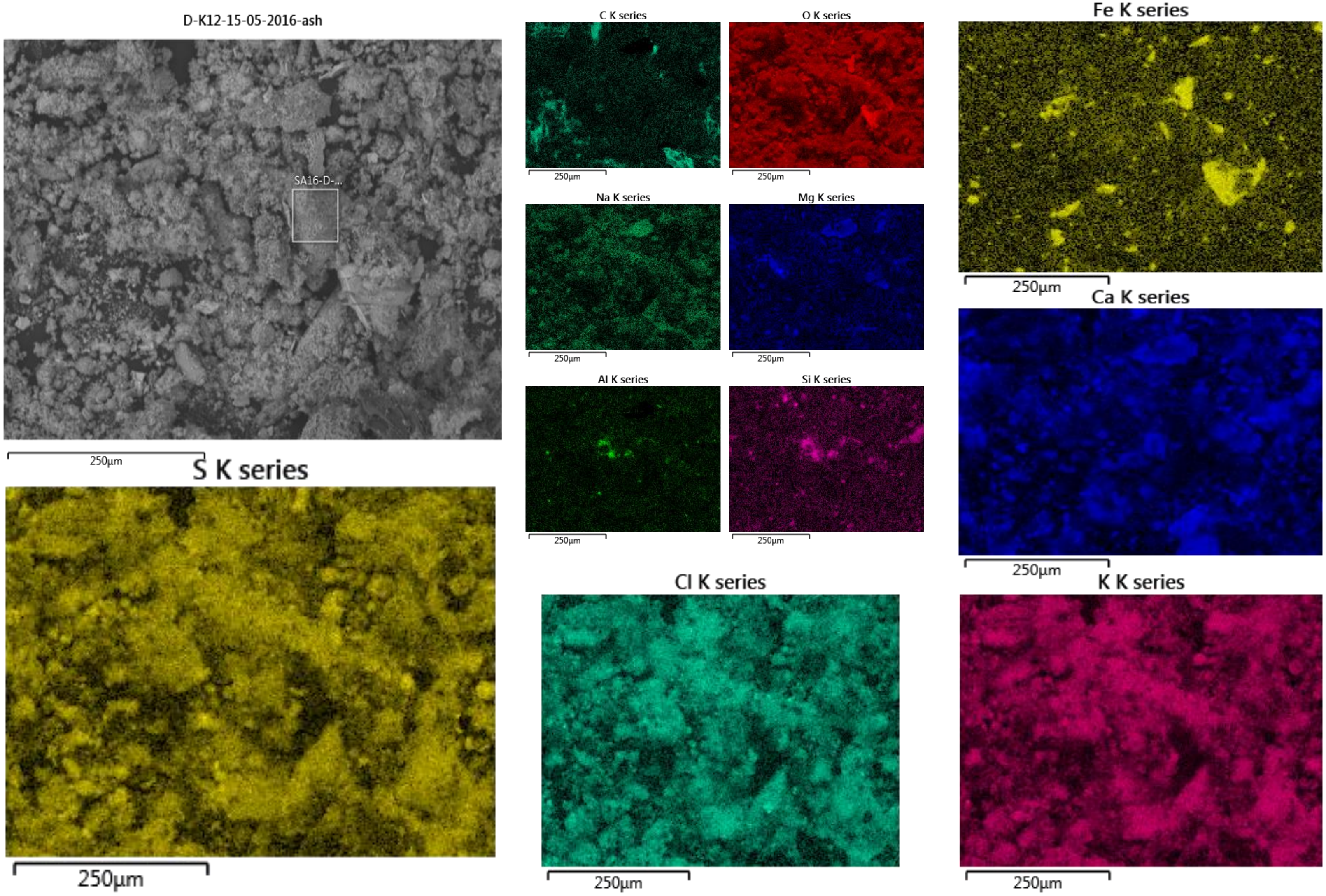
Boiler inspection 14/04/2016:

fly ashes K12 grey ash (bulk)



Boiler inspection 14/04/2016:

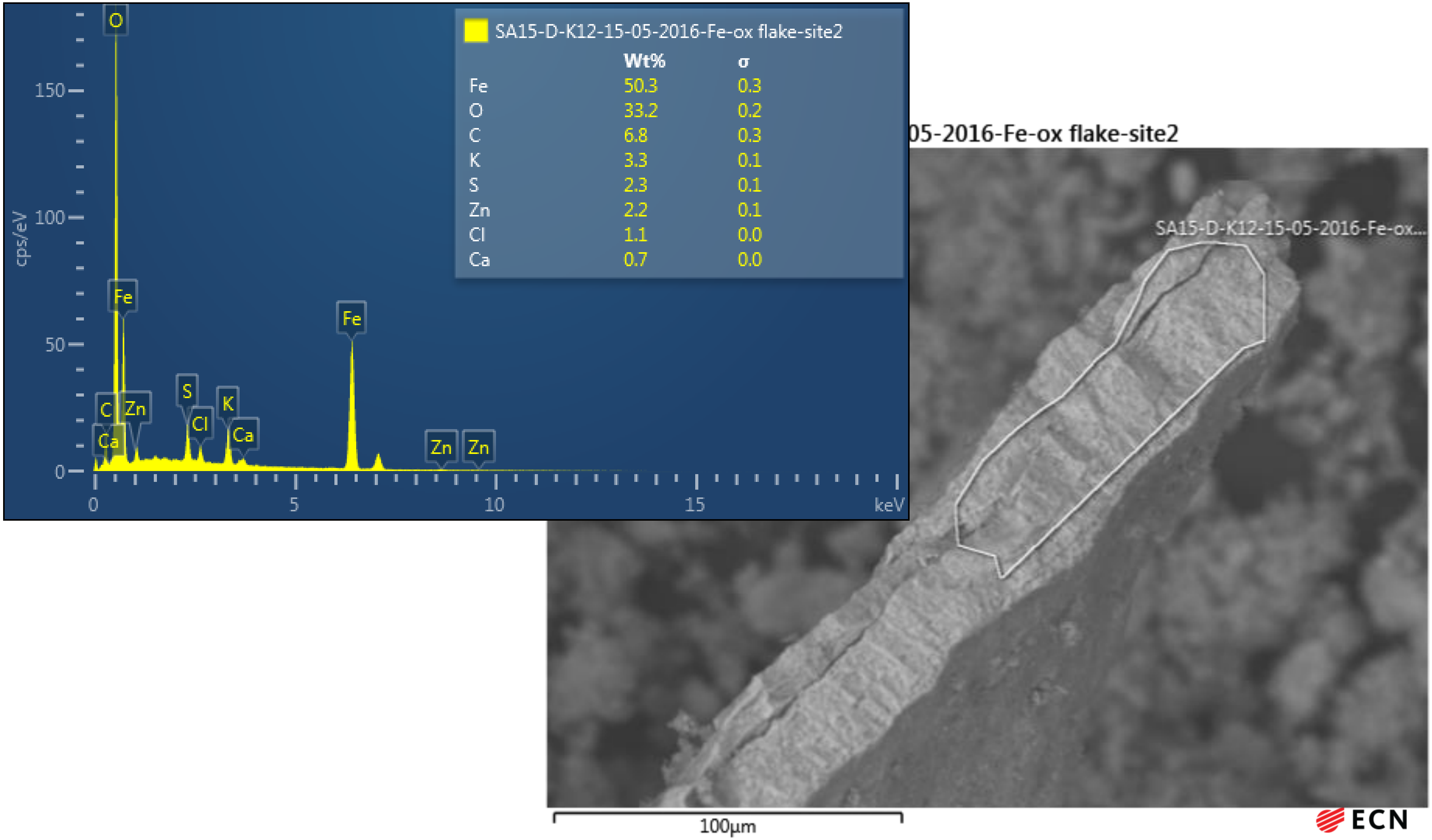
fly ashes K12 red ash (bulk)



ECN

Boiler inspection 14/04/2016:

fly ashes K12 red ash (flakes)

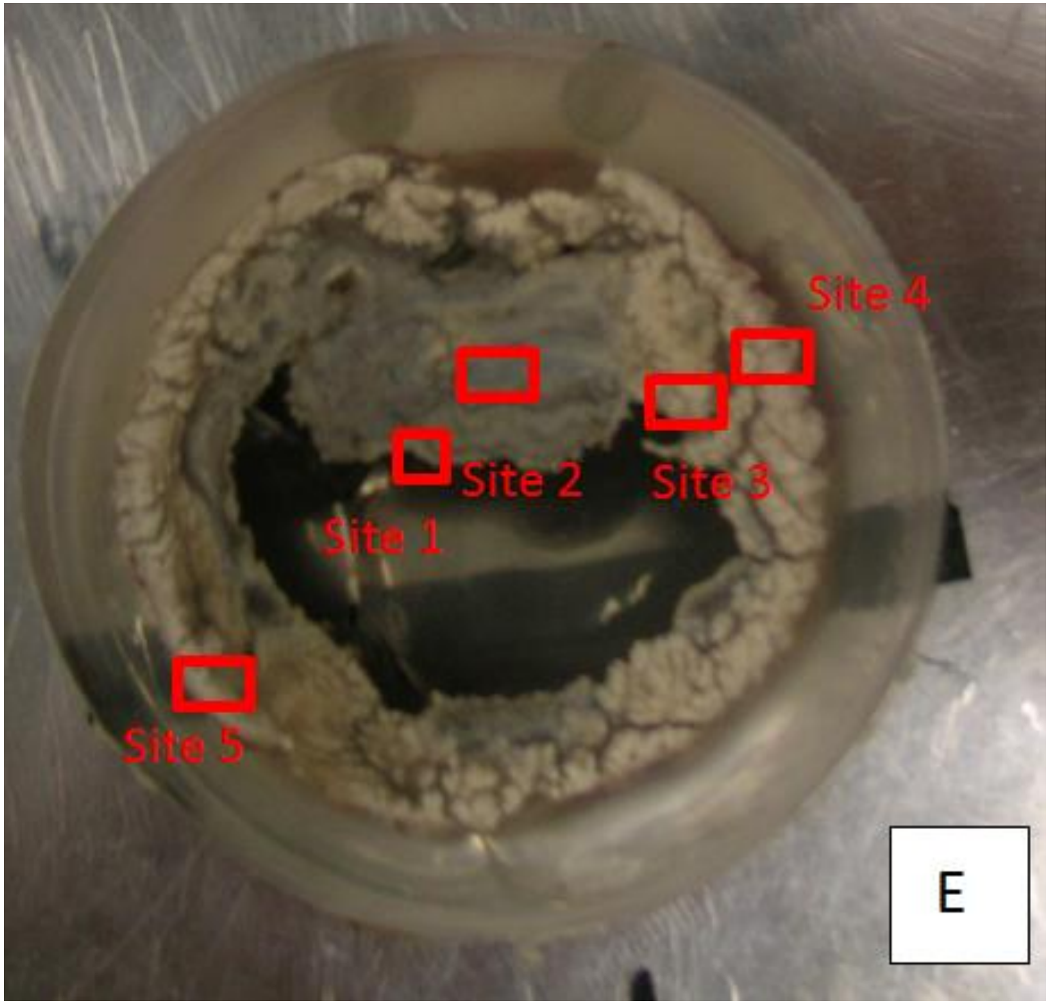


SA15-D-K12-15-05-2016-Fe-ox flake-site2

	Wt%	σ
Fe	50.3	0.3
O	33.2	0.2
C	6.8	0.3
K	3.3	0.1
S	2.3	0.1
Zn	2.2	0.1
Cl	1.1	0.0
Ca	0.7	0.0

Boiler inspection 14/04/2016:

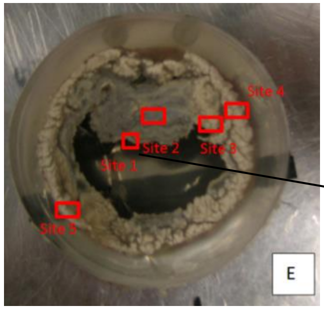
whole deposit cross-section

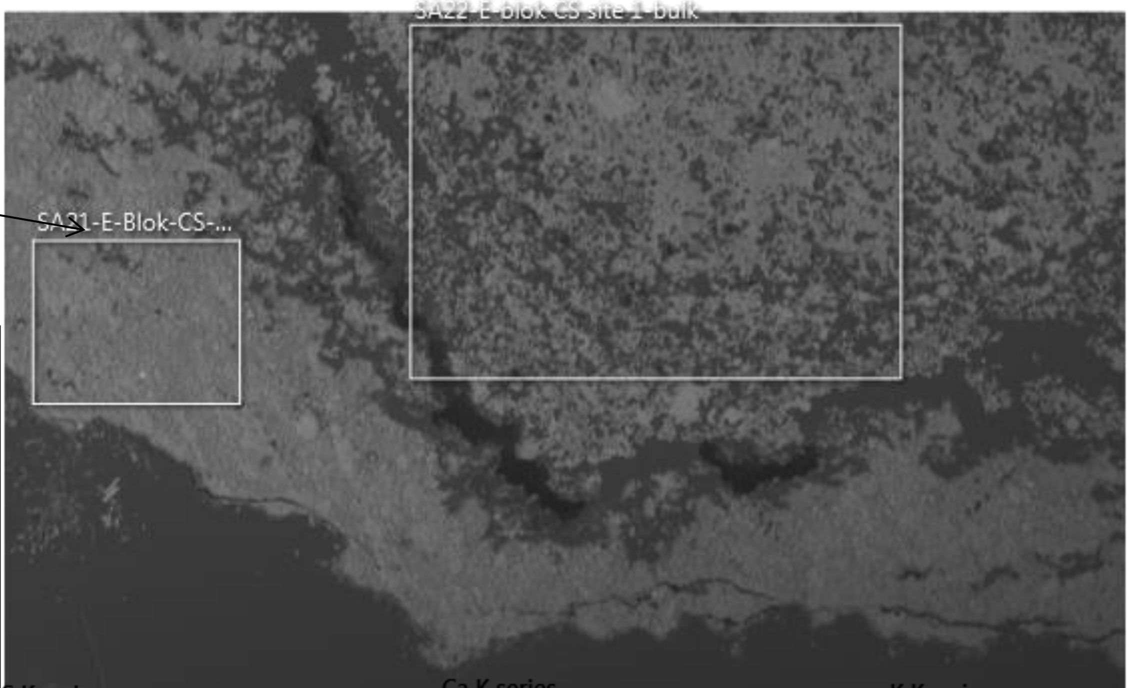


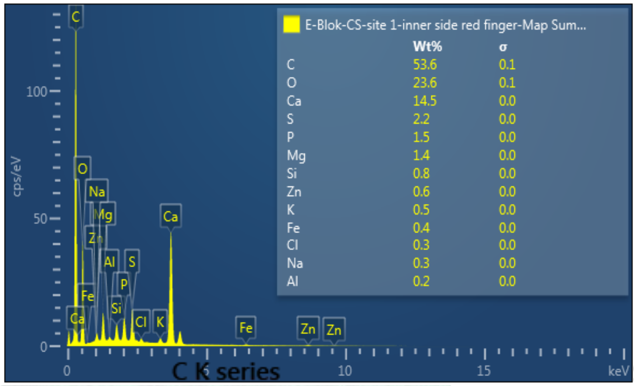
EDX site CS E:
Site 1: gas-side red finger (stalactite)
Site 2: centre red finger (stalactite)
Site 3: bright area bulk deposit
Site 4: interface tube 1
Site 5: interface tube 2

Boiler inspection 14/04/2016:

whole deposit cross-section stalactite – gas side

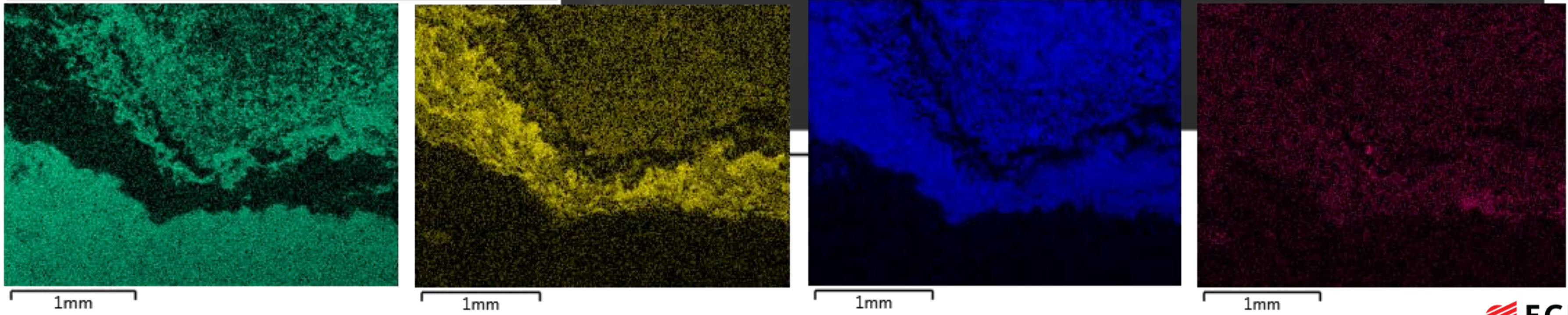






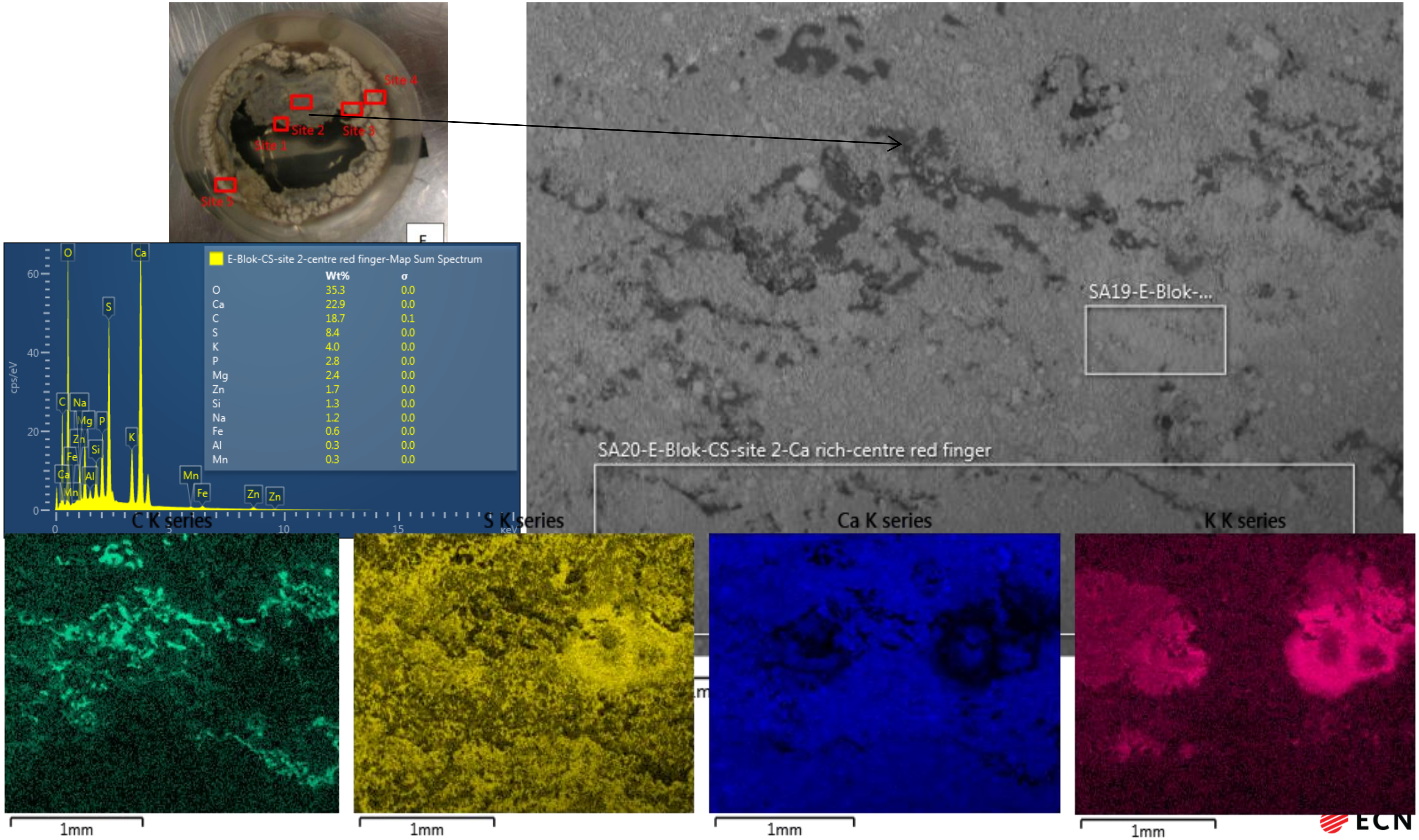
🟨 E-Blok-CS-site 1-inner side red finger-Map Sum...

	Wt%	σ
C	53.6	0.1
O	23.6	0.1
Ca	14.5	0.0
S	2.2	0.0
P	1.5	0.0
Mg	1.4	0.0
Si	0.8	0.0
Zn	0.6	0.0
K	0.5	0.0
Fe	0.4	0.0
Cl	0.3	0.0
Na	0.3	0.0
Al	0.2	0.0



Boiler inspection 14/04/2016:

whole deposit cross-section – stalactite bulk (inner side)

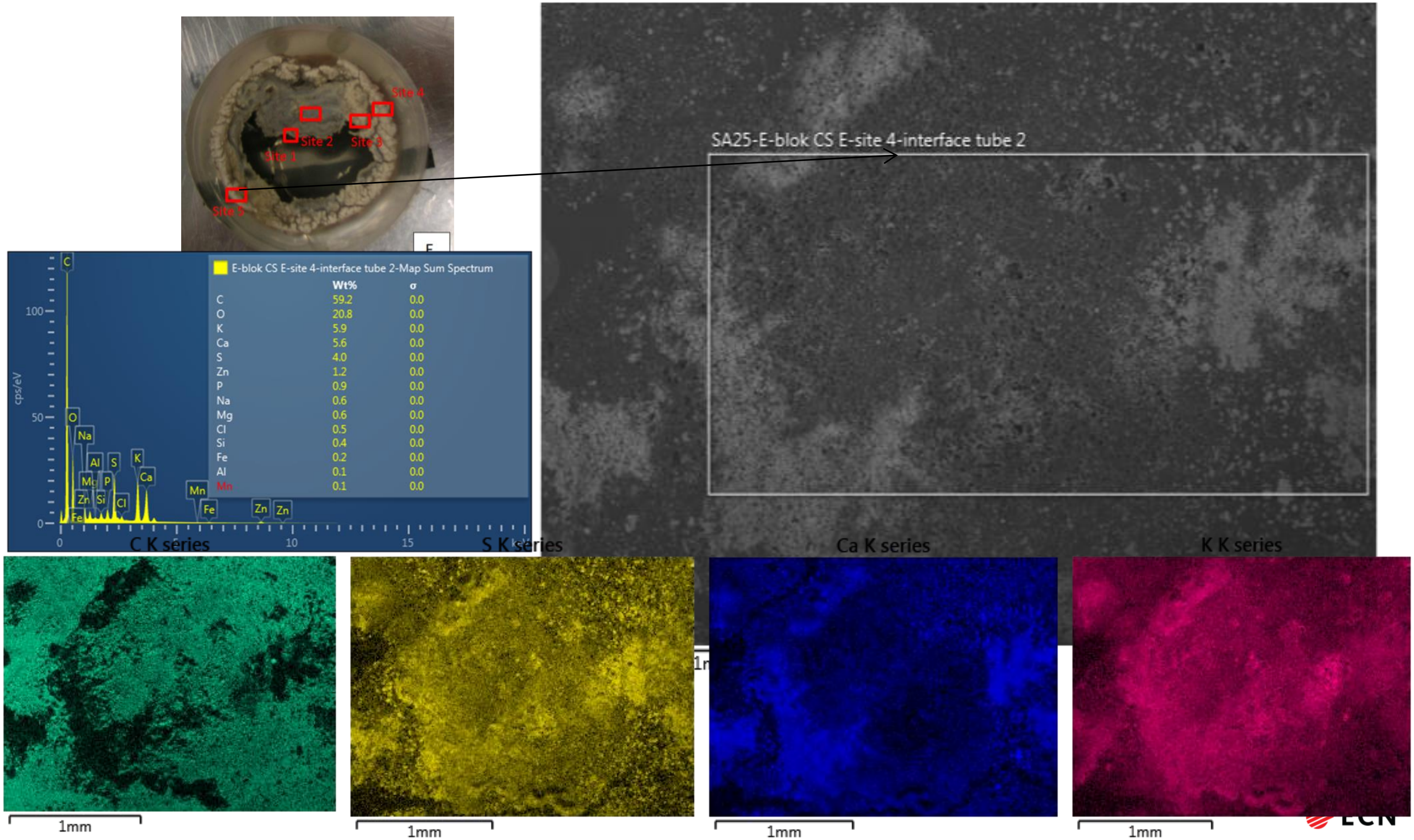


E-Blok-CS-site 2-centre red finger-Map Sum Spectrum

	Wt%	σ
O	35.3	0.0
Ca	22.9	0.0
C	18.7	0.1
S	8.4	0.0
K	4.0	0.0
P	2.8	0.0
Mg	2.4	0.0
Zn	1.7	0.0
Si	1.3	0.0
Na	1.2	0.0
Fe	0.6	0.0
Al	0.3	0.0
Mn	0.3	0.0

Boiler inspection 14/04/2016:

whole deposit cross-section – tube interface (inner side)

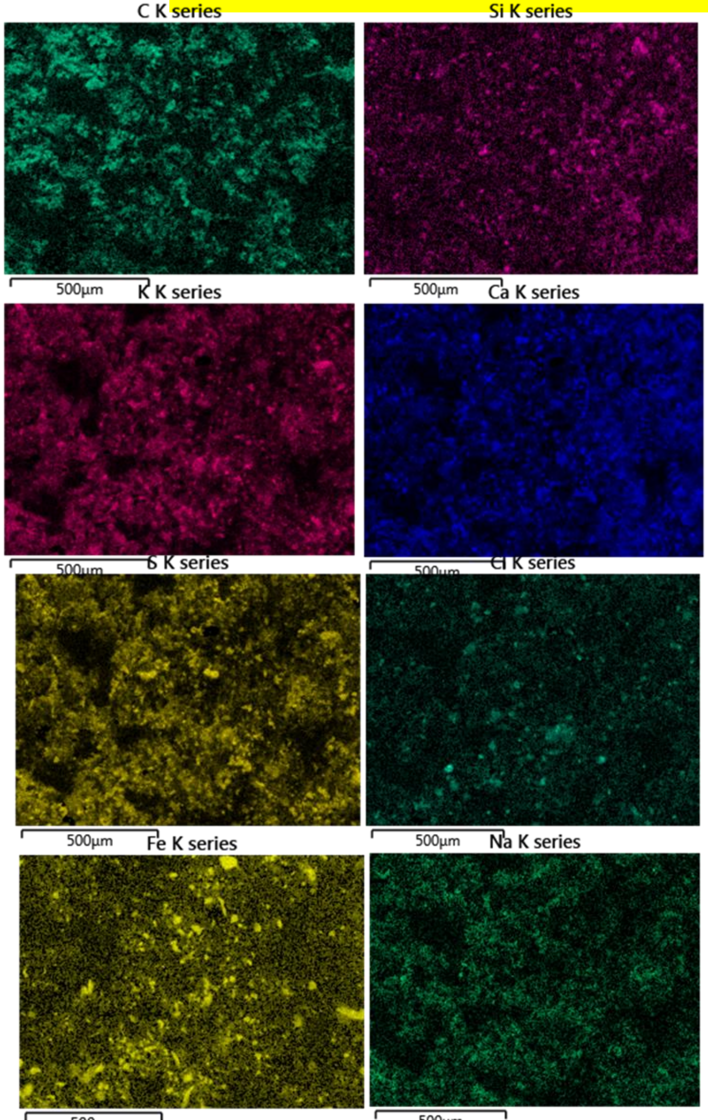


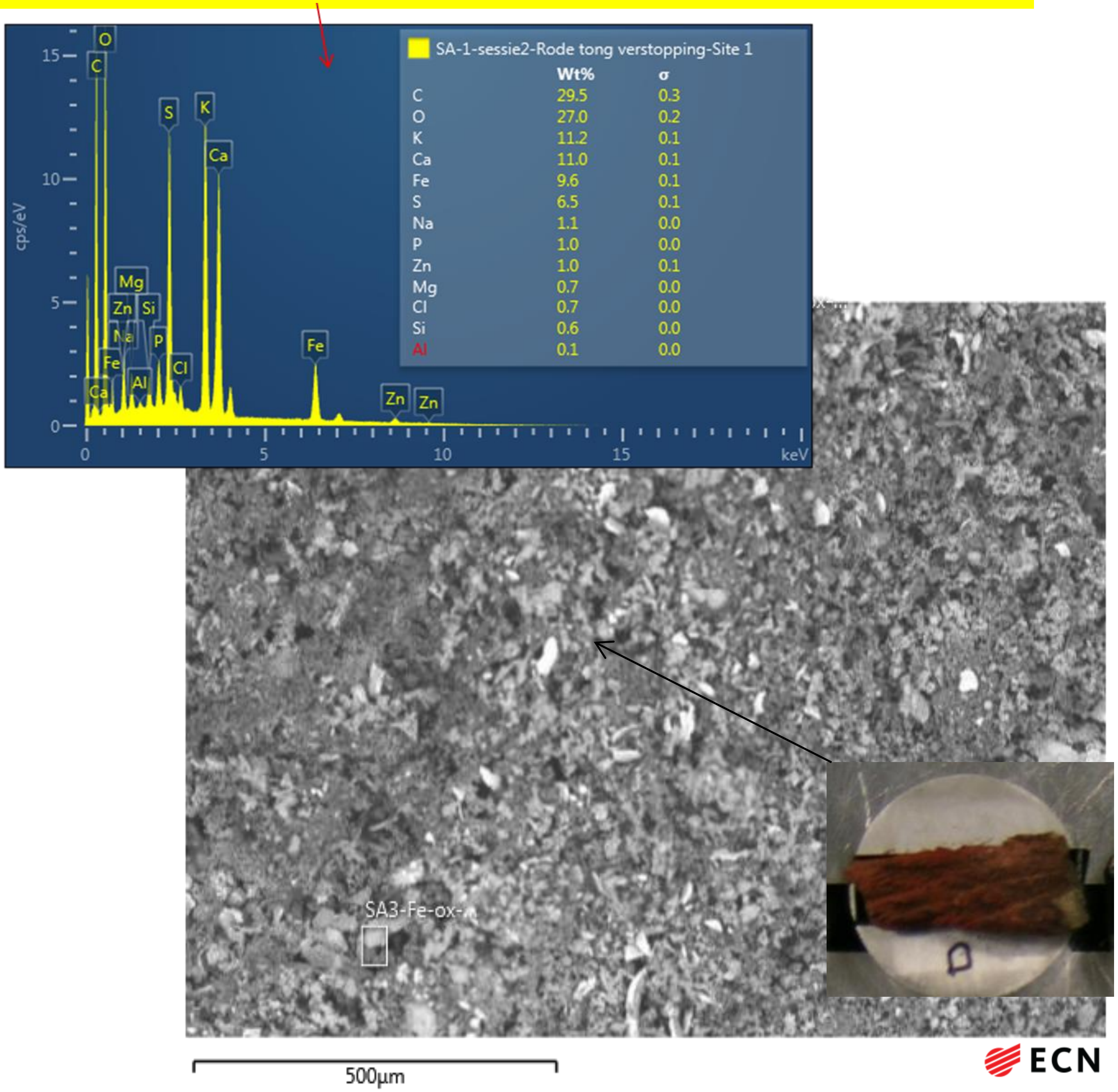
E-blok CS E-site 4-interface tube 2-Map Sum Spectrum

	Wt%	σ
C	59.2	0.0
O	20.8	0.0
K	5.9	0.0
Ca	5.6	0.0
S	4.0	0.0
Zn	1.2	0.0
P	0.9	0.0
Na	0.6	0.0
Mg	0.6	0.0
Cl	0.5	0.0
Si	0.4	0.0
Fe	0.2	0.0
Al	0.1	0.0
Mn	0.1	0.0

Boiler inspection 14/04/2016:

whole deposit cross-section – stalactite surface (outer side)



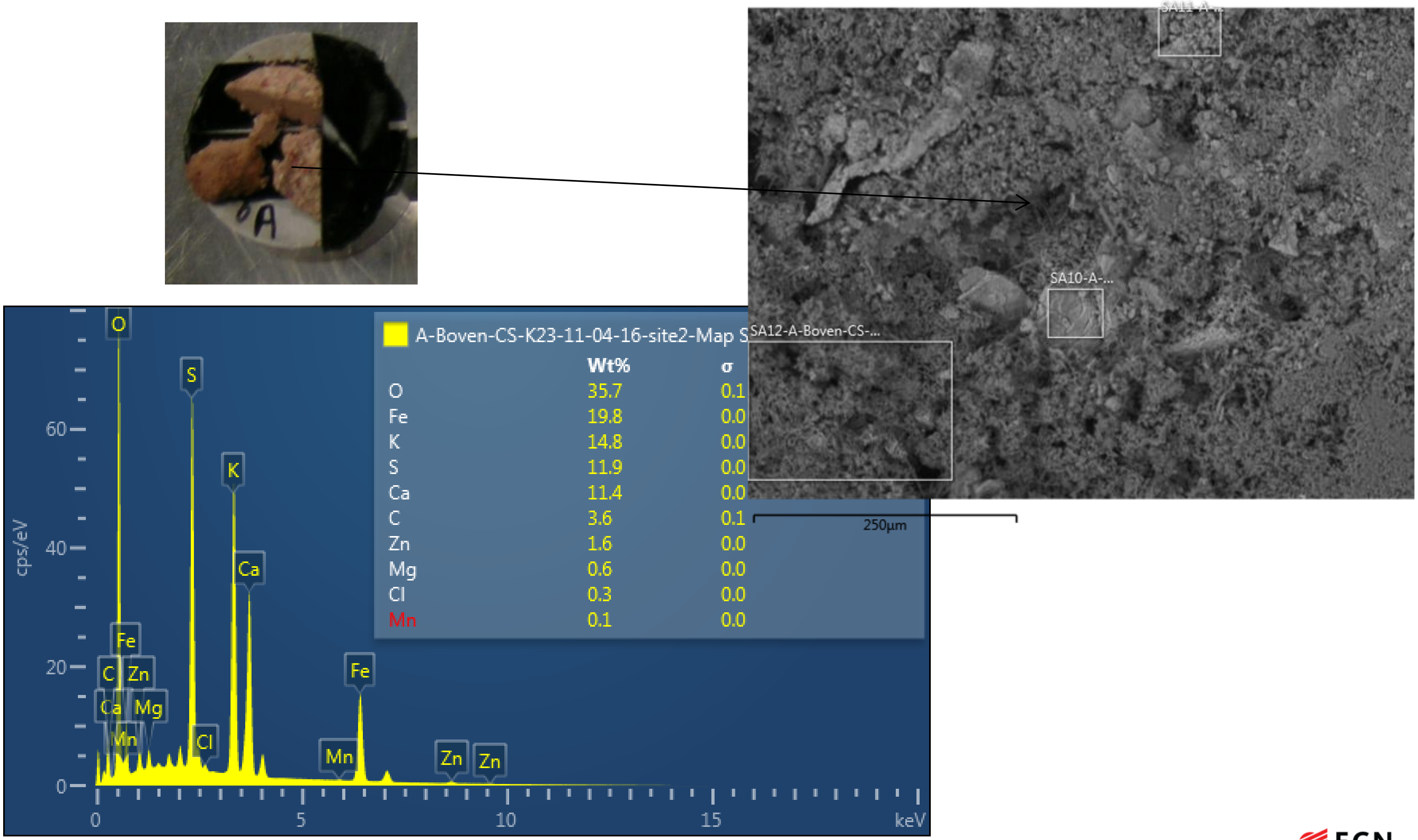


SA-1-sessie2-Rode tong verstopping-Site 1

	Wt%	σ
C	29.5	0.3
O	27.0	0.2
K	11.2	0.1
Ca	11.0	0.1
Fe	9.6	0.1
S	6.5	0.1
Na	1.1	0.0
P	1.0	0.0
Zn	1.0	0.1
Mg	0.7	0.0
Cl	0.7	0.0
Si	0.6	0.0
Al	0.1	0.0

Boiler inspection 14/04/2016:

loose/wet deposit k23 – “bulk” deposit

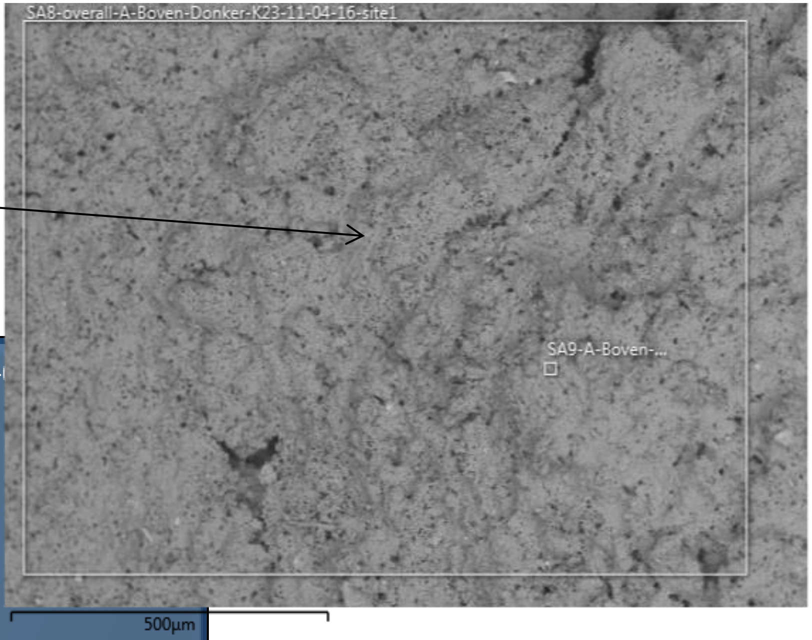


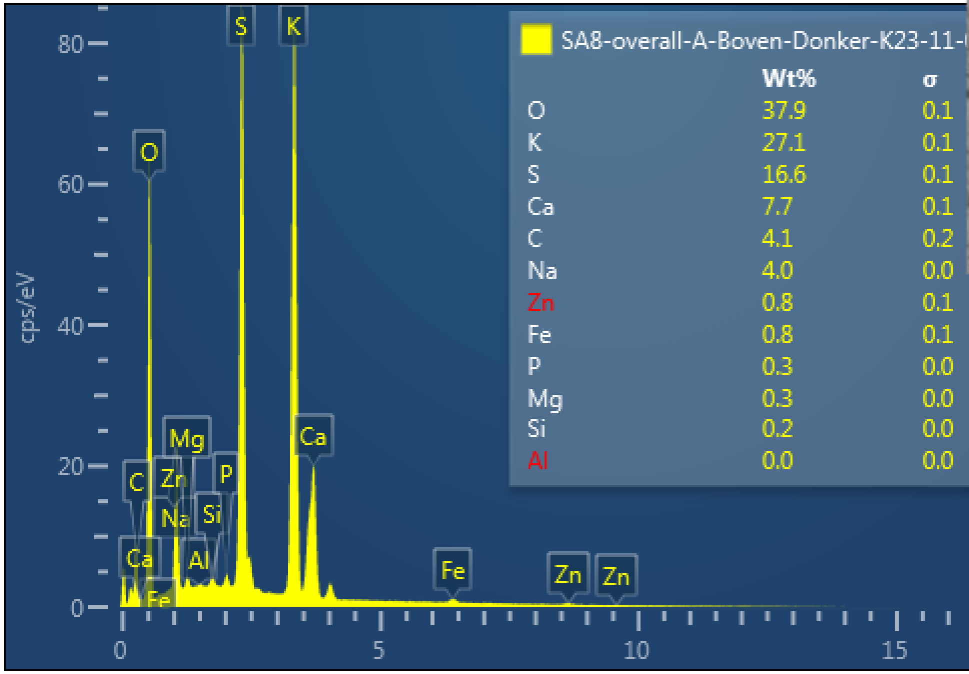
A-Boven-CS-K23-11-04-16-site2-Map S

	Wt%	σ
O	35.7	0.1
Fe	19.8	0.0
K	14.8	0.0
S	11.9	0.0
Ca	11.4	0.0
C	3.6	0.1
Zn	1.6	0.0
Mg	0.6	0.0
Cl	0.3	0.0
Mn	0.1	0.0

Boiler inspection 14/04/2016:

loose/wet deposit k23 – “fine, dark, rusty” deposit





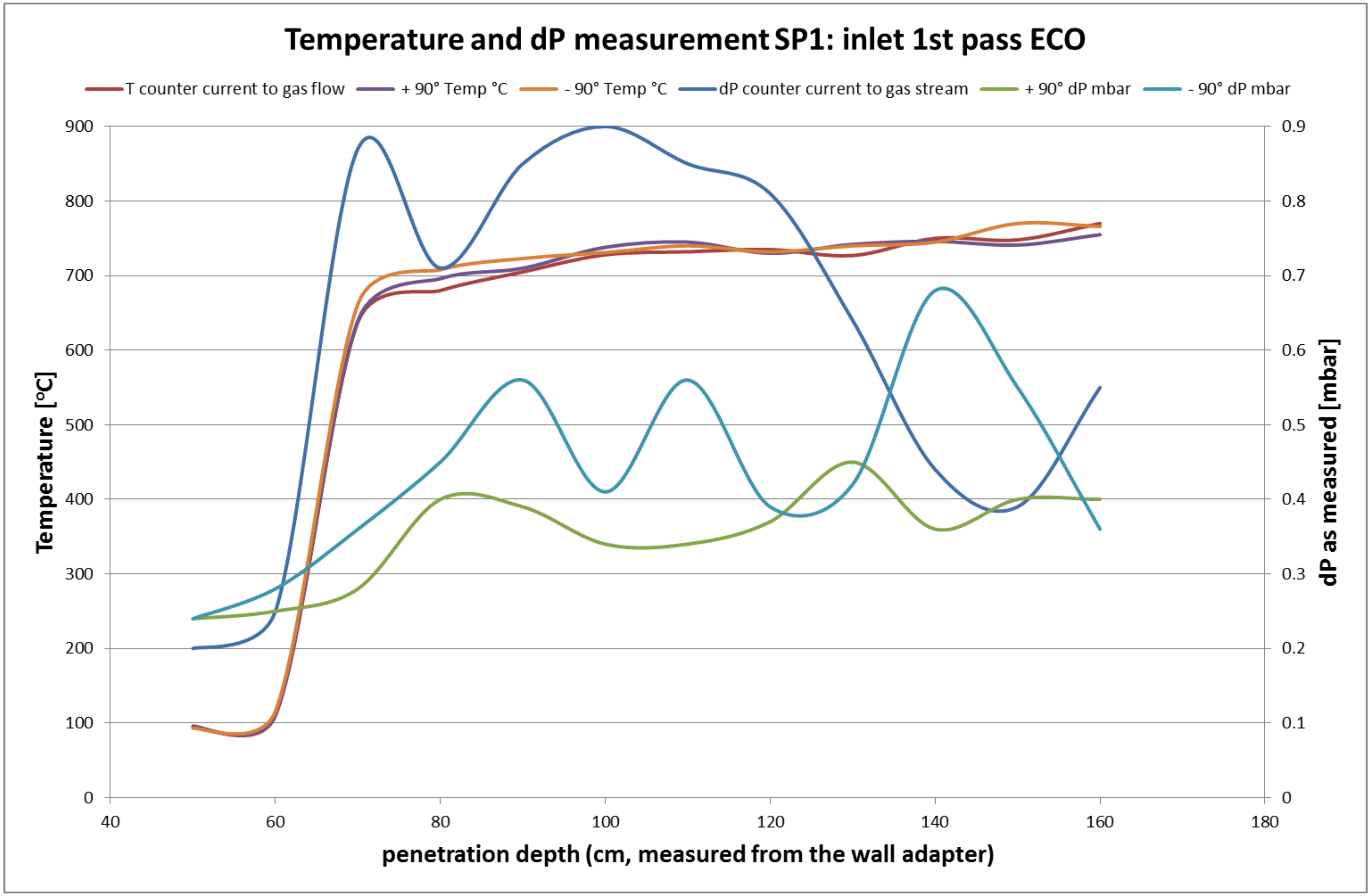
🟨 SA8-overall-A-Boven-Donker-K23-11-

	Wt%	σ
O	37.9	0.1
K	27.1	0.1
S	16.6	0.1
Ca	7.7	0.1
C	4.1	0.2
Na	4.0	0.0
Zn	0.8	0.1
Fe	0.8	0.1
P	0.3	0.0
Mg	0.3	0.0
Si	0.2	0.0
Al	0.0	0.0

2nd measurement campaign

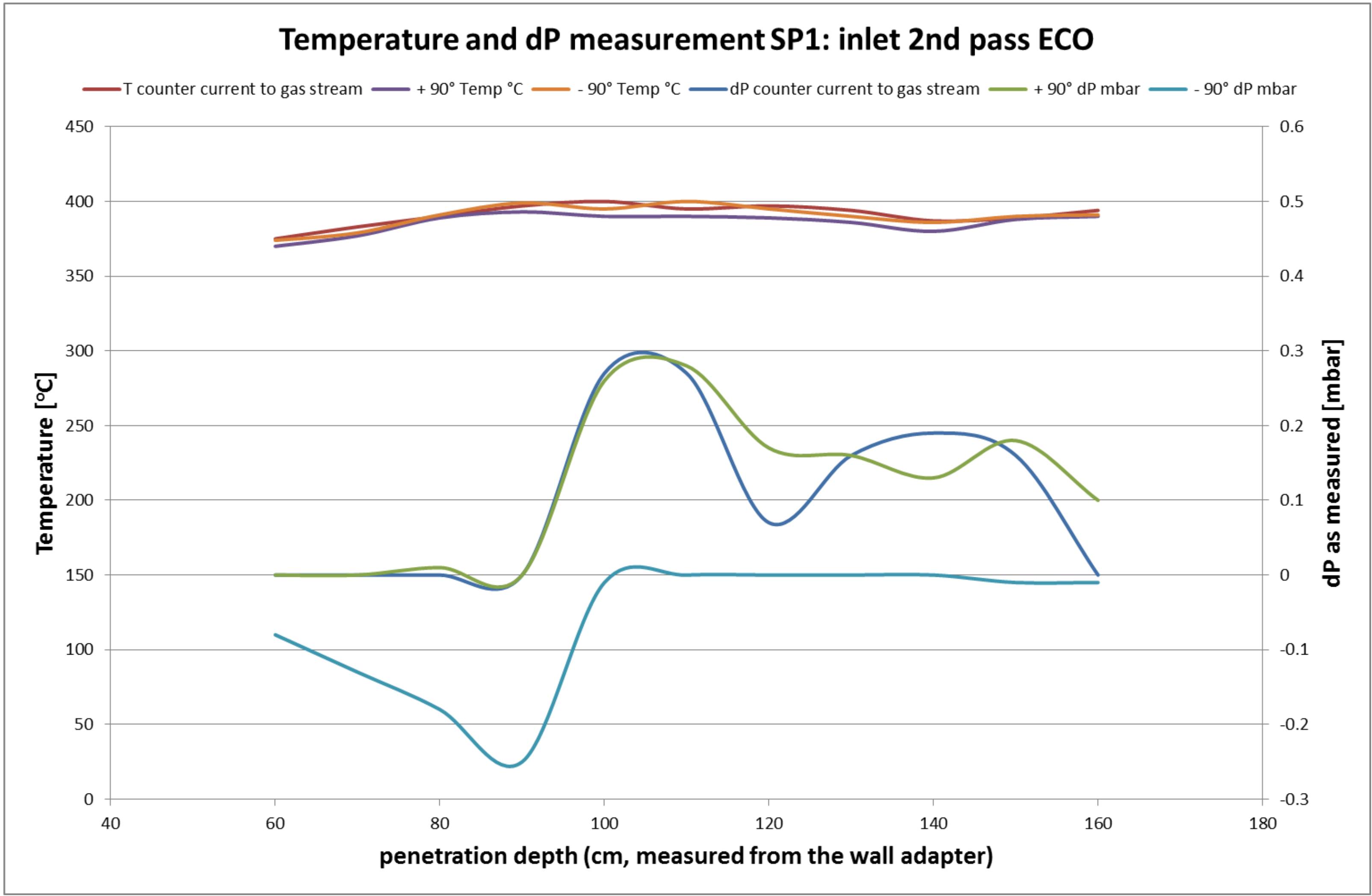
2^{nd} measurement campaign May 2016:

T/dP profiles ECO, SP1 (inlet ECO)



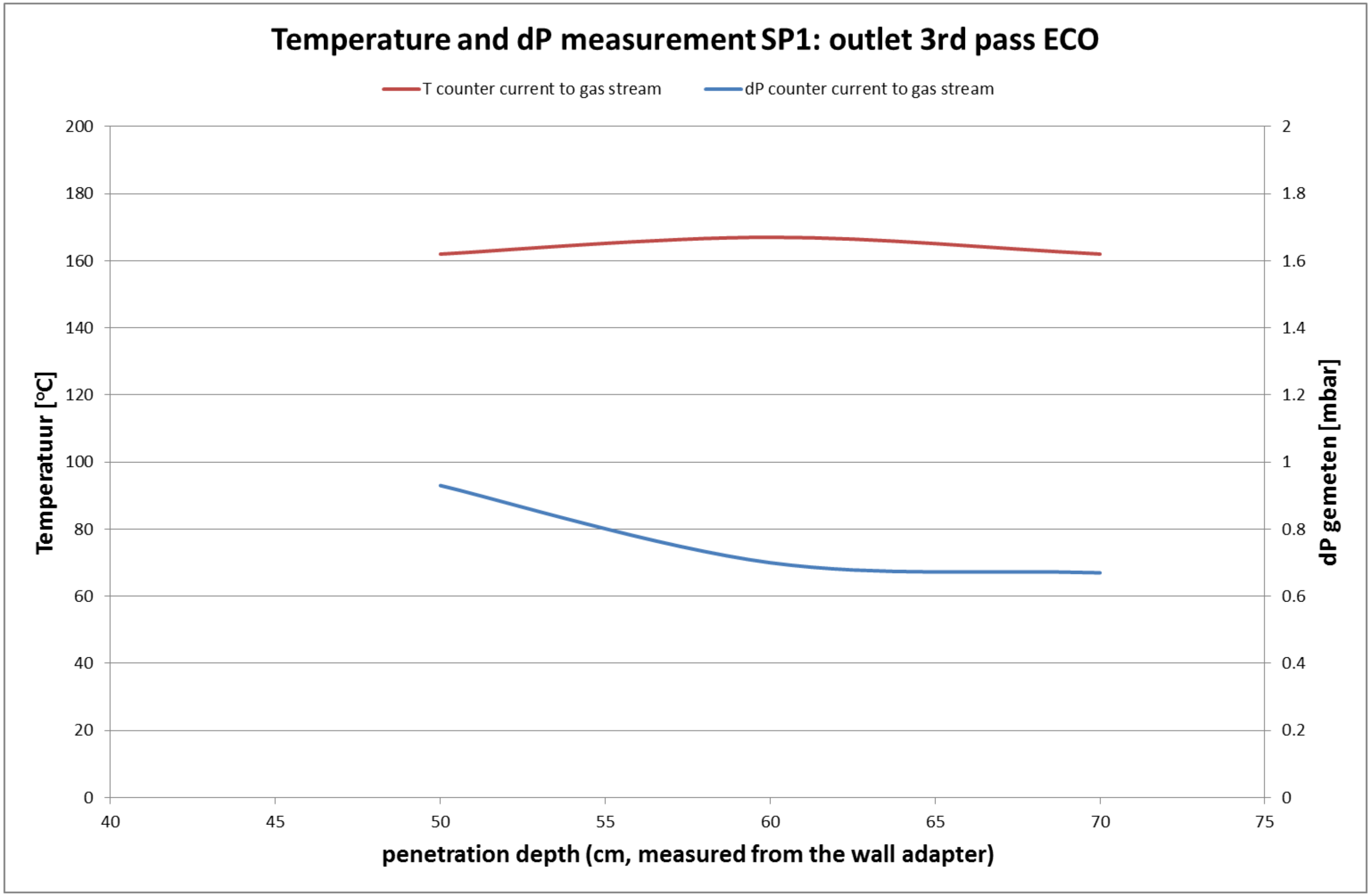
2nd measurement campaign May 2016:

T/dP profiles ECO, SP2 (inlet 2nd pass)



2nd measurement campaign May 2016:

T/dP profiles ECO, SP3 (outlet 3rd pass)



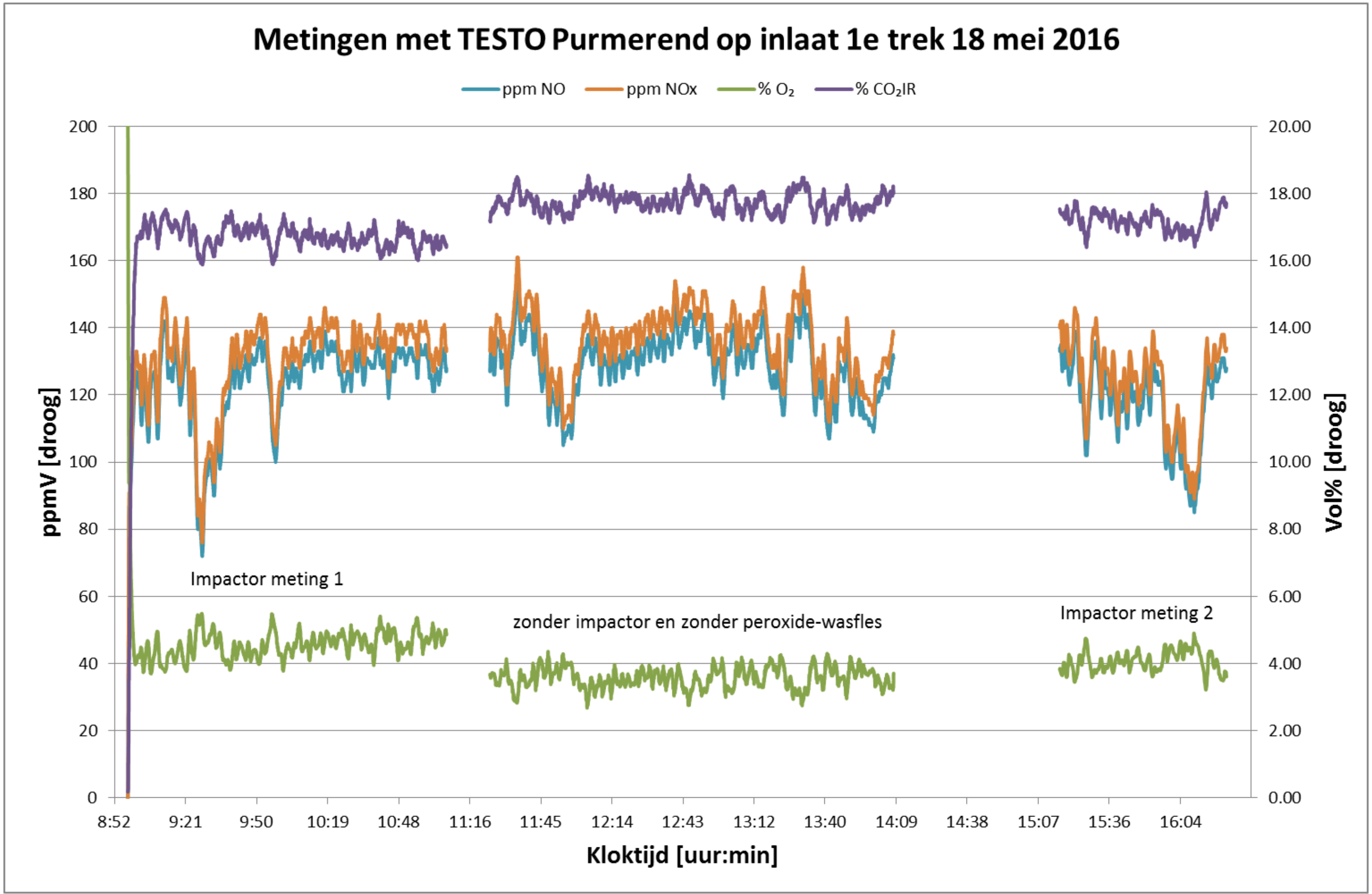
2nd measurement campaign May 2016:

temperature and pressure measurements: discussion

- Temperature profiles fairly uniform
    - T SP1 = 700-780 °C T SP2 = 370-400 °C T SP3 = 160-168 °C
- Pressure flow profiles
    - Changing cyclically at SP1, in both vertical (upwards) and horizontal (rather towards the boiler than away from it)
    - Vertical and horizontal vectors clearly separated (dominant flow vertical)
    - Changing cyclically at SP2, indicating a more tilted flow (roughly 45° tilt downwards and away from the boiler)
    - Fairly uniform at SP3
    - All points characterised by relatively low velocities, hence sampling slightly overisokinetic (at minimum cascade impactor flow)
- Are the sampling points SP1 and SP2 representative for the whole section?
    - SP1 (too close to boiler side) and SP2 (too big flow profile changes) probably not
    - Particularly regarding the coarse ash flow field that might have impact on the sampling
    - SP3 must be representative

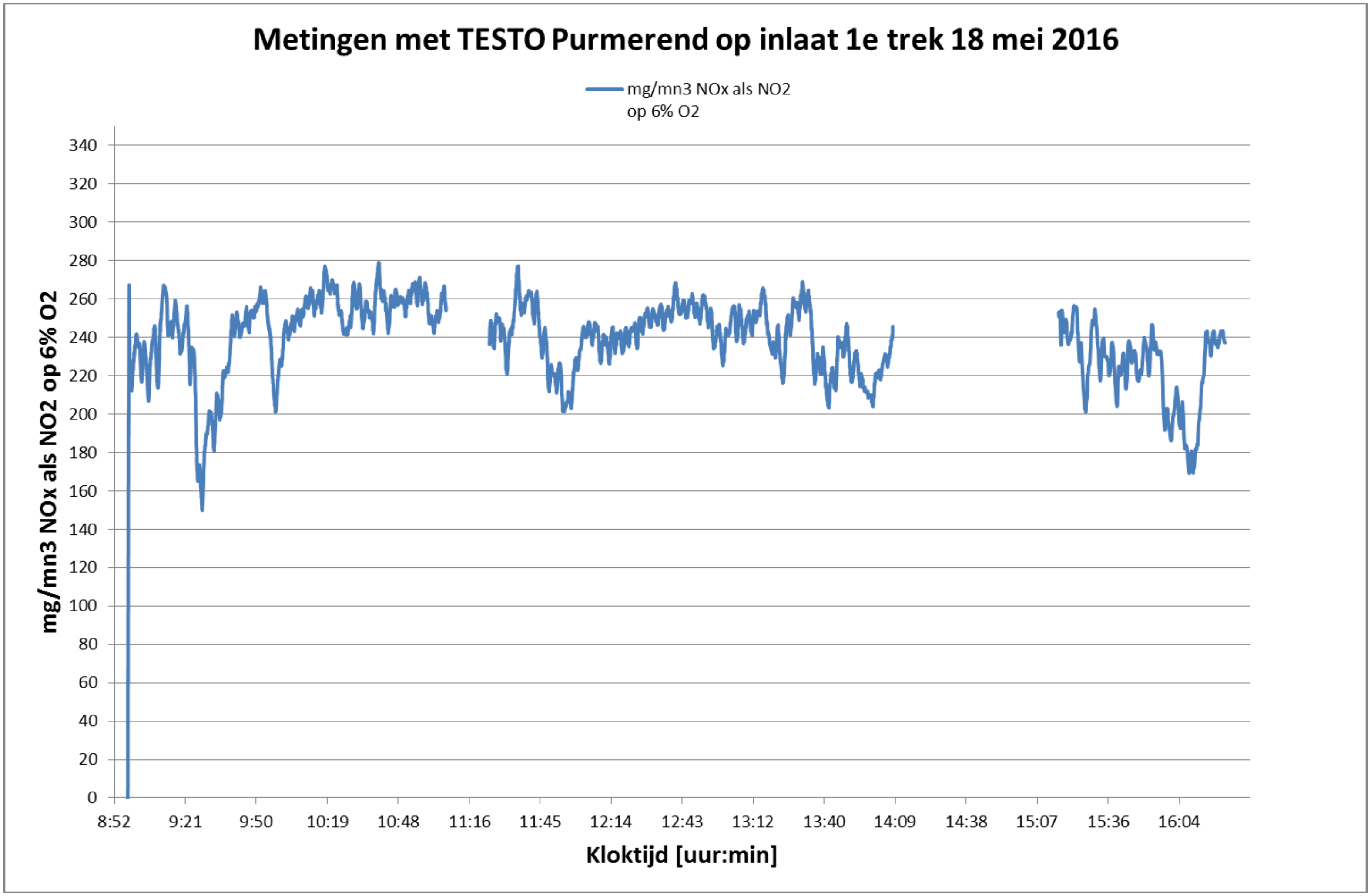
2^{nd} measurement campaign May 2016:

on-line flue gas measurement, May 18



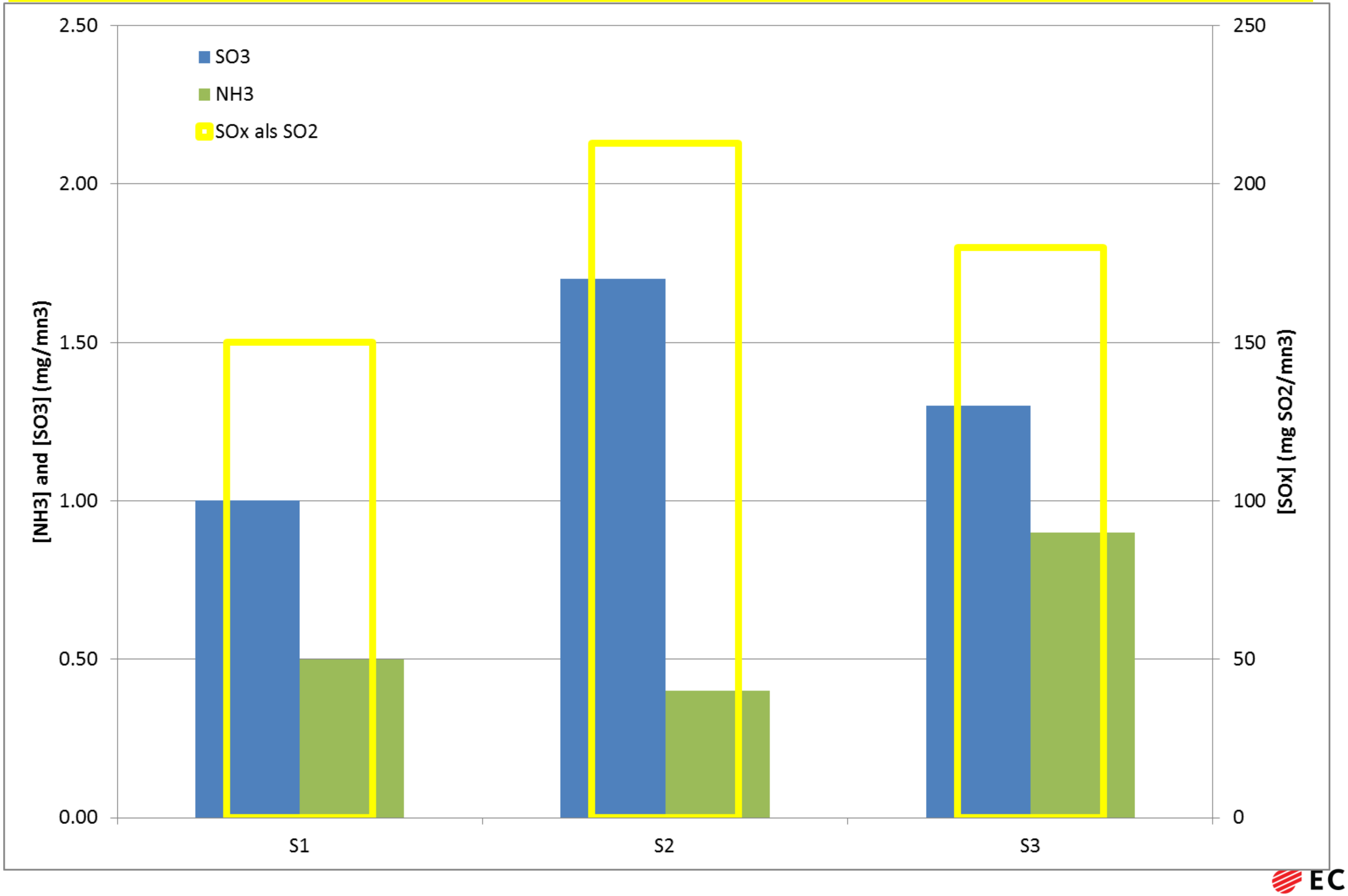
2^{nd} measurement campaign May 2016:

on-line NOx, normalised as NO2 at 6% [O2], May 18



2nd measurement campaign May 2016:

on-line SOx May 18



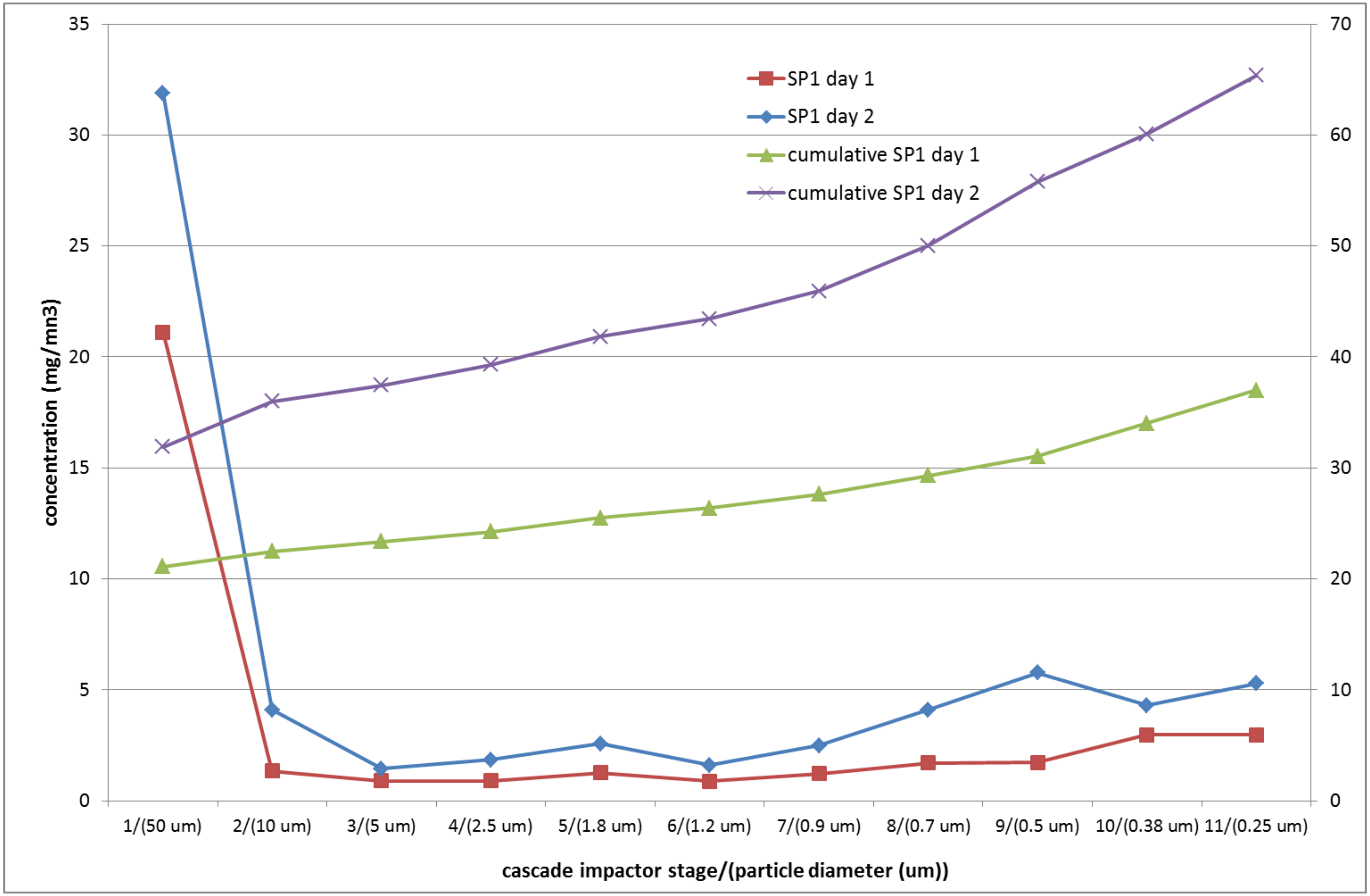
2nd measurement campaign May 2016:

flue gas composition: discussion

- Overall high NOx emissions, at ca 250 mg/m_n^3 NO_2 at 6% [O_2], both days, swinging slightly (+/- 10%) and cyclically at ca. 30 min interval
- Almost no ammonia slip, at ca. 1 mg/m_n^3
- High levels of free (so non-dust-bonded) SOx, at ca. 130 mg/m_n^3 as SO_2 almost 2.5x higher as compared with December 2015 campaign at the same boiler (despite lower humidifier duty)
- Despite high SOx concentration, only very low levels of SO_3 at ca 1% of the total SOx load (so no/very little peroxidation and low chance for direct sulphuric acid condensation from the flowing gas)

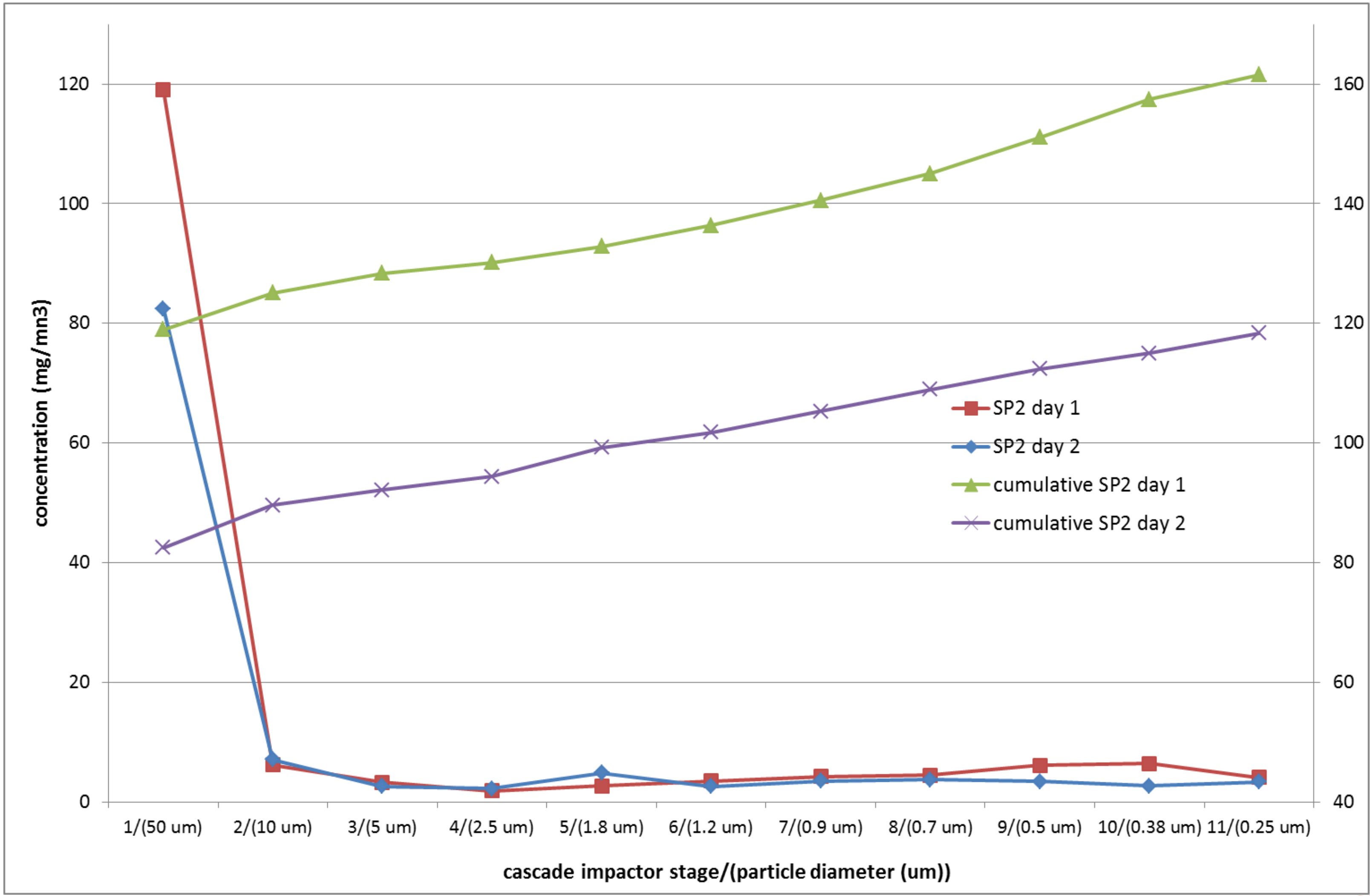
2nd measurement campaign May 2016:

Cascade Impactor derived dust load, SP1



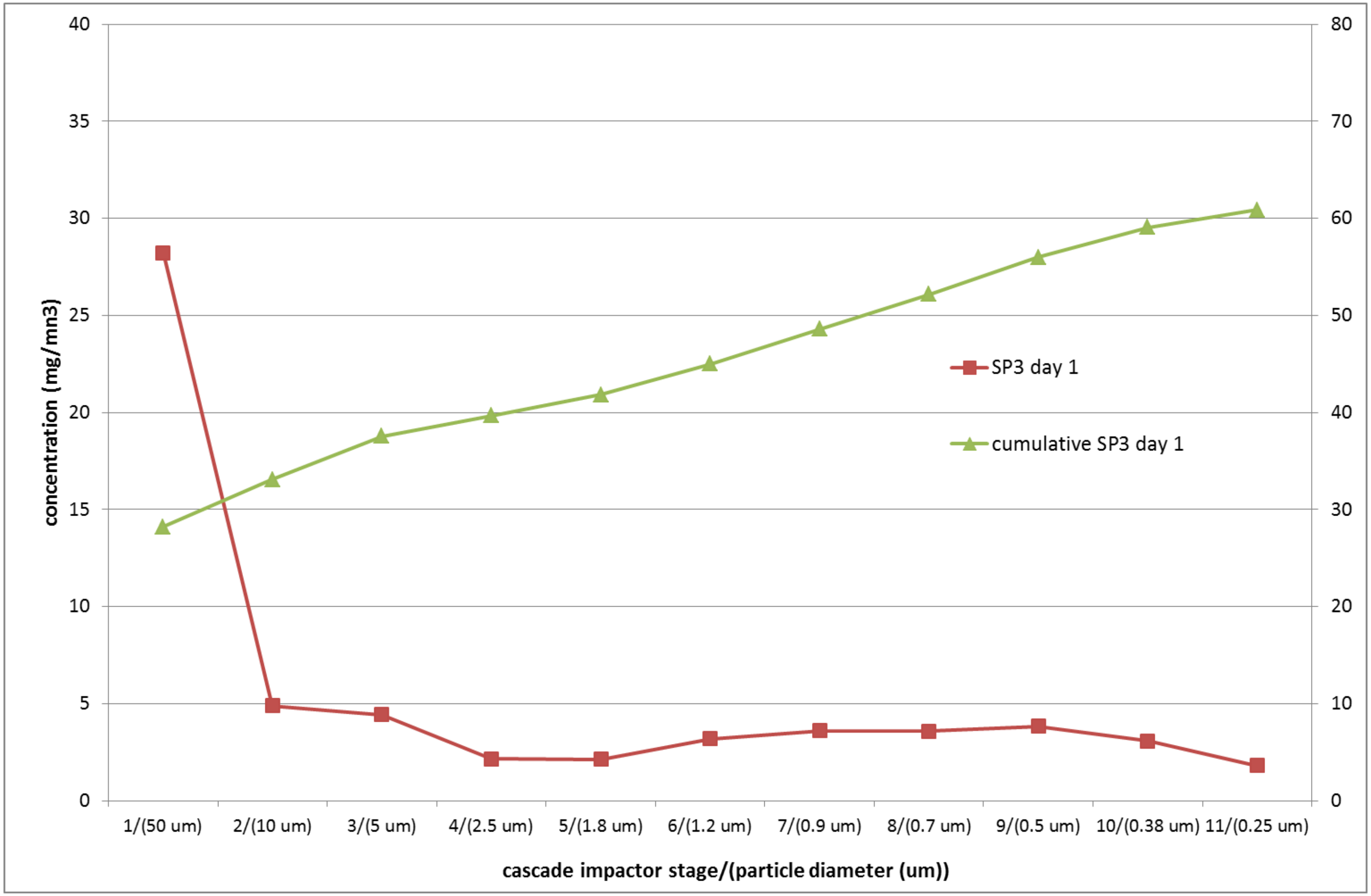
2nd measurement campaign May 2016:

Cascade Impactor derived dust load, SP2



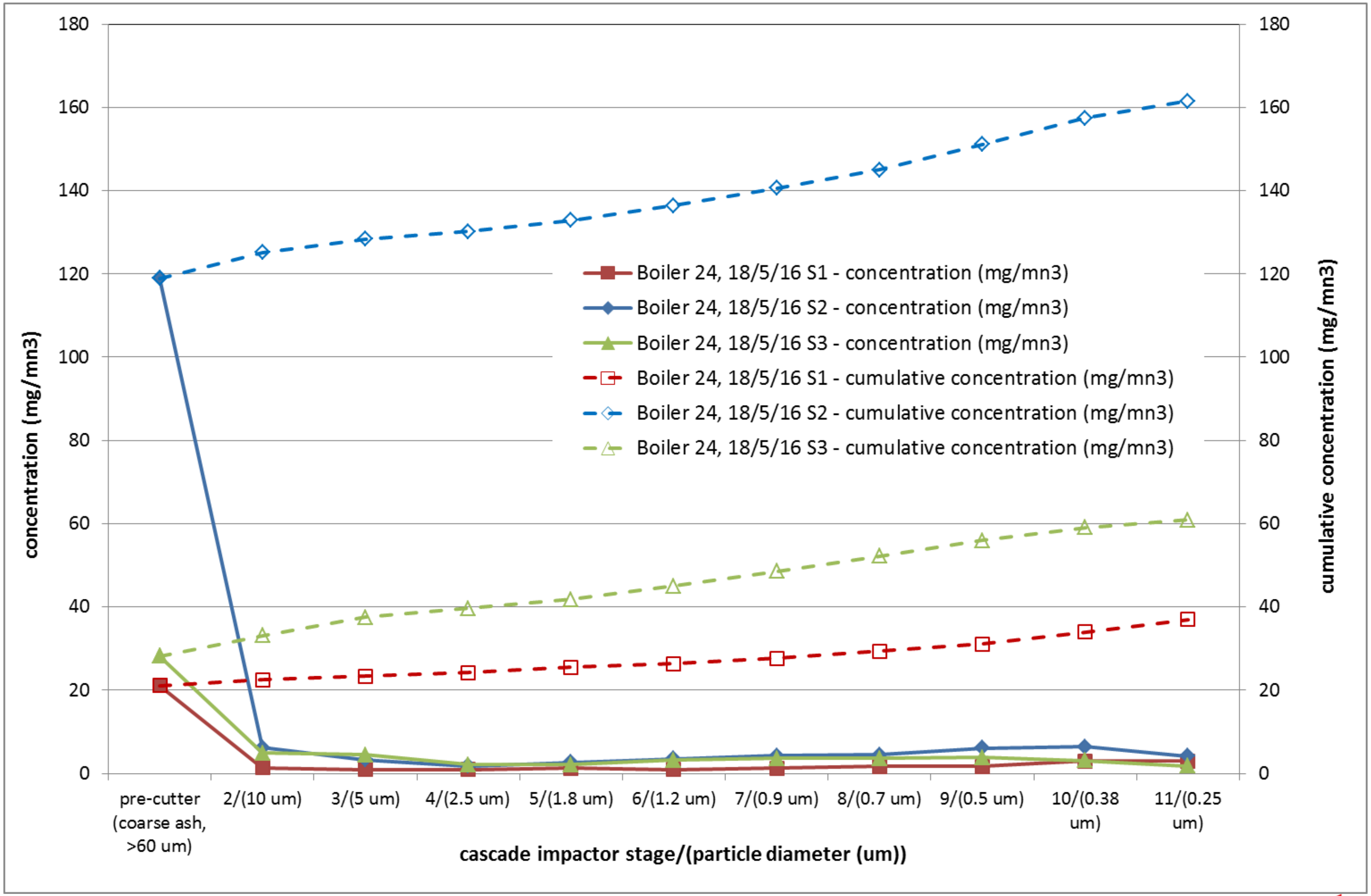
2nd measurement campaign May 2016:

Cascade Impactor derived dust load, SP3



2nd measurement campaign May 2016:

Cascade Impactor derived dust loads, SP1-3 May 18 compared



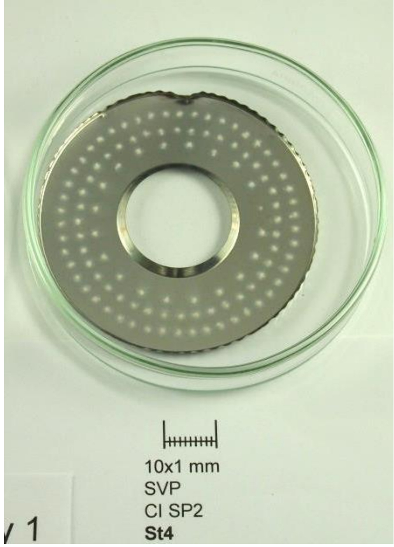
2nd measurement campaign May 2016:

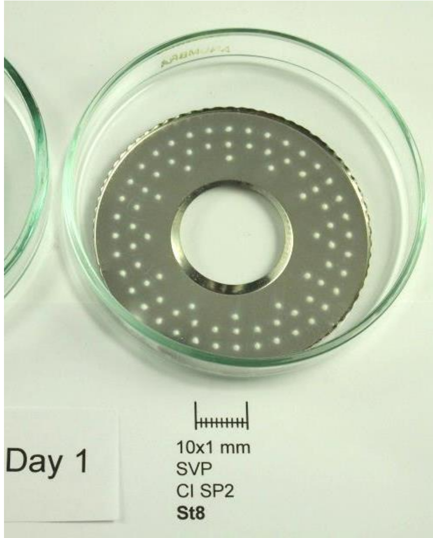
dust loads: discussion

- Overall dust loads 50-100% higher than in December, yet that effect primarily ascribable to coarse ash (> 60 mg/mn3) at all three positions (logic trend, as now counter current sampling was applied)
- Stage 2-11 only limited variation throughout the ports, compared to total load
- SP3 roughly comparable with SP1 (so good basis for comparison Fe load in/out ECO)

2nd measurement campaign May 2016:

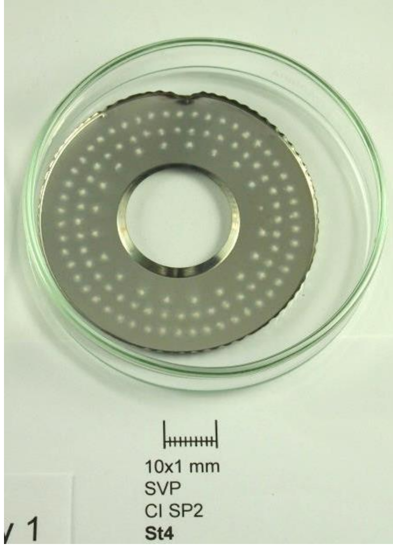
Cascade Impactor photographic record

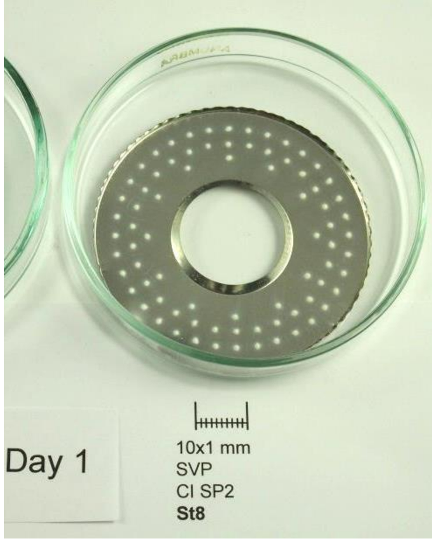


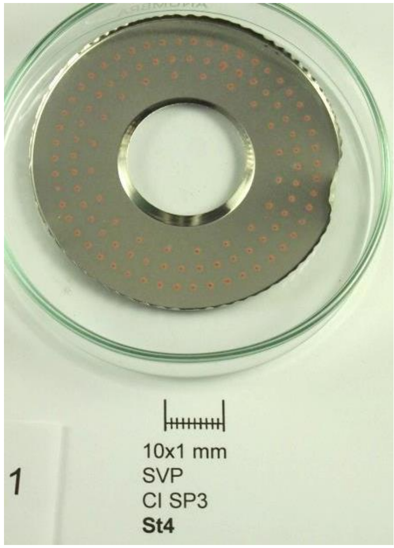


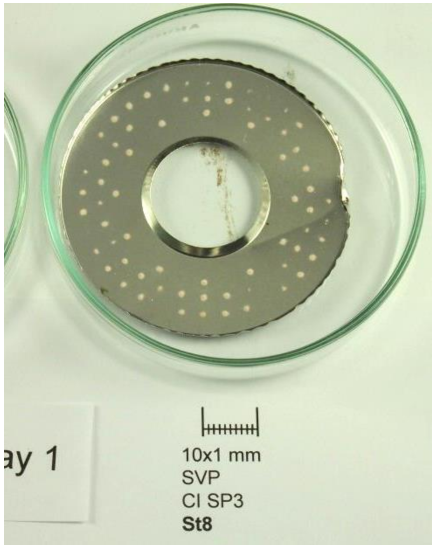
2^{nd} measurement campaign May 2016:

Cascade Impactor photographic record









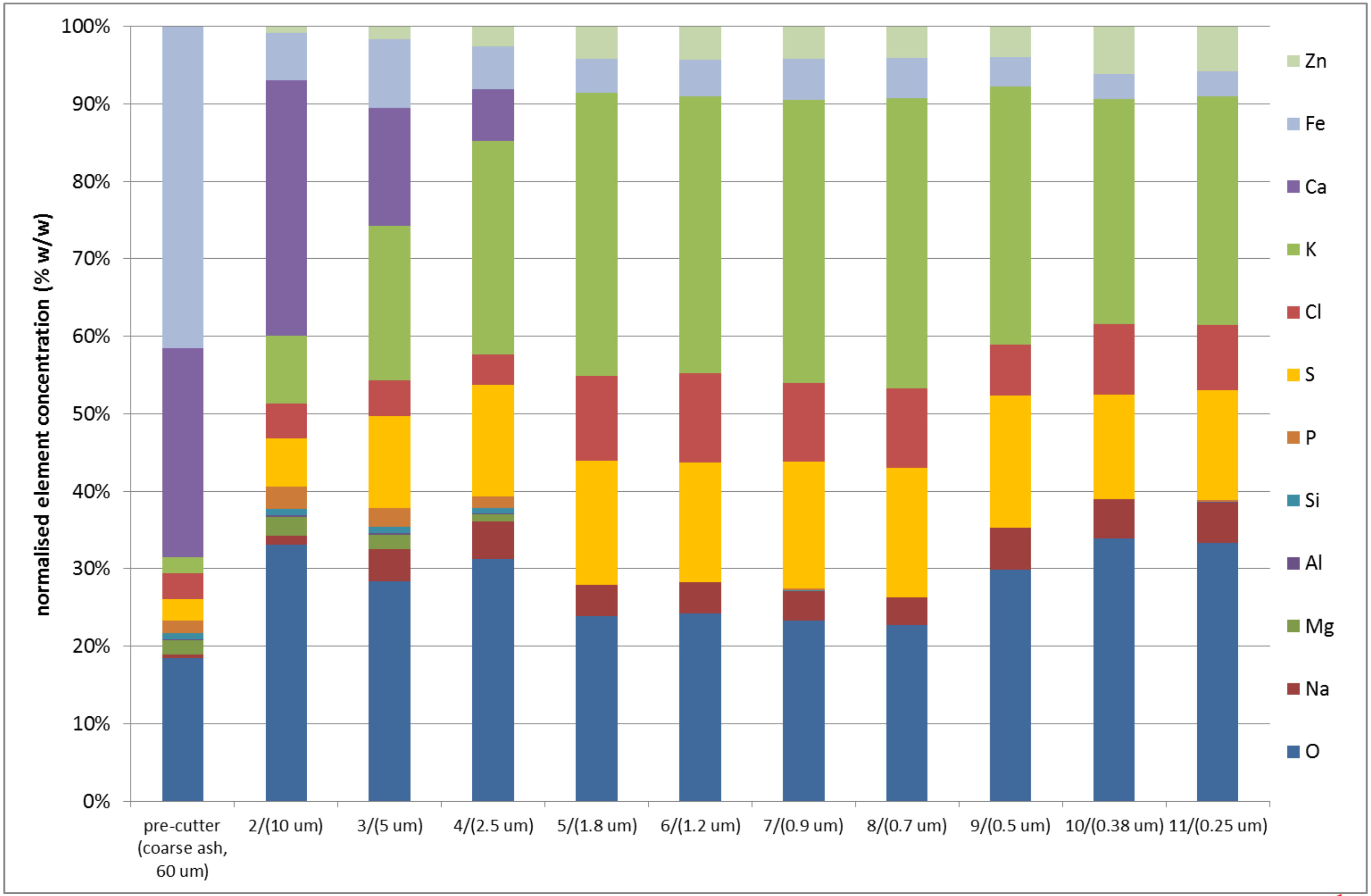
2^{nd} measurement campaign May 2016:

dust colour: discussion

- At the inlet, only coarse ash brown-coloured, while at SP2 brown and SP3 red colour progressively appearing in fine ash
- At all points, the fines stages are still bright white (so no evaporation of volatile Fe salts

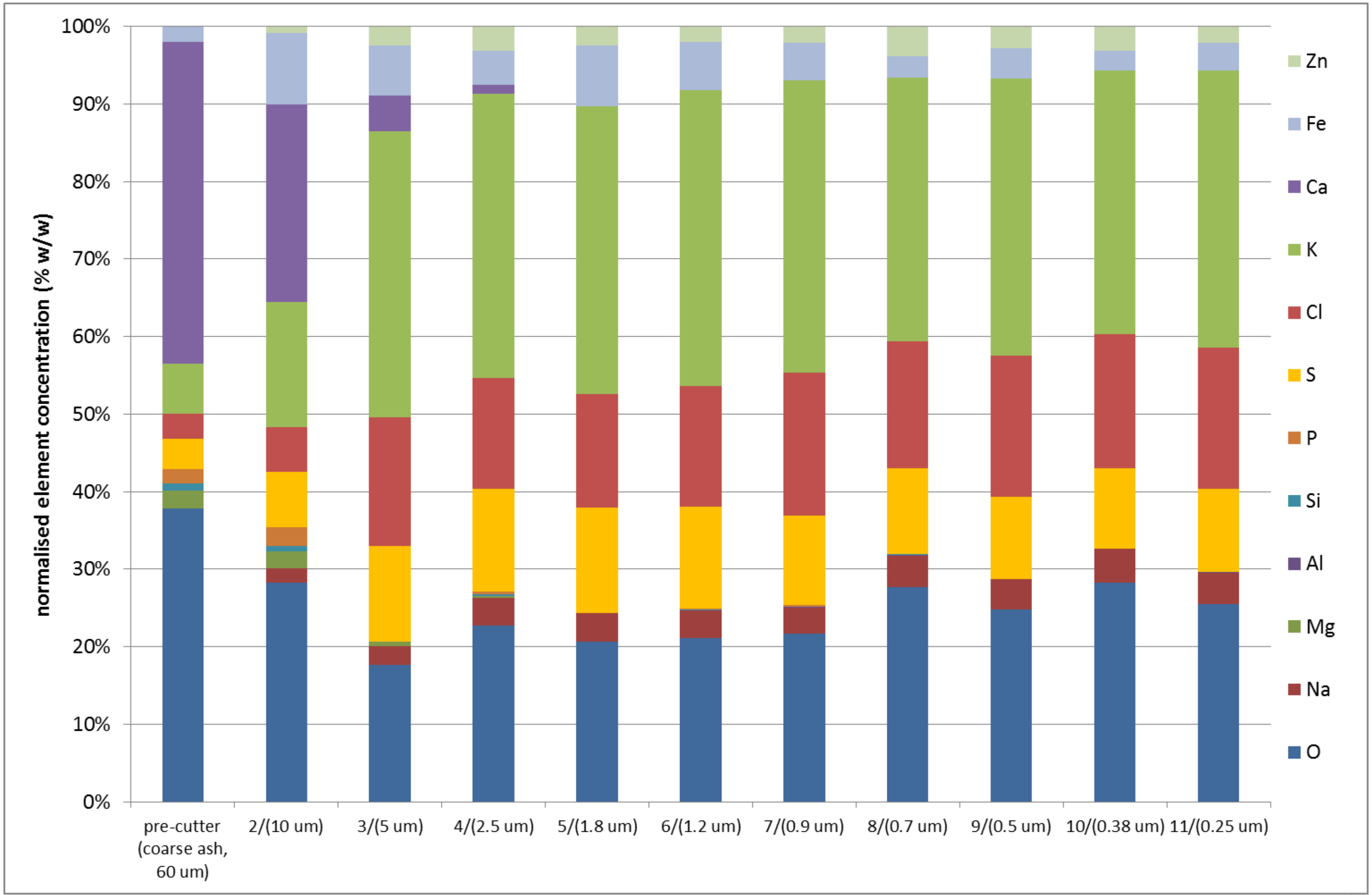
2^{nd} measurement campaign May 2016:

Cascade Impactor derived dust compositions, SP1 18 May



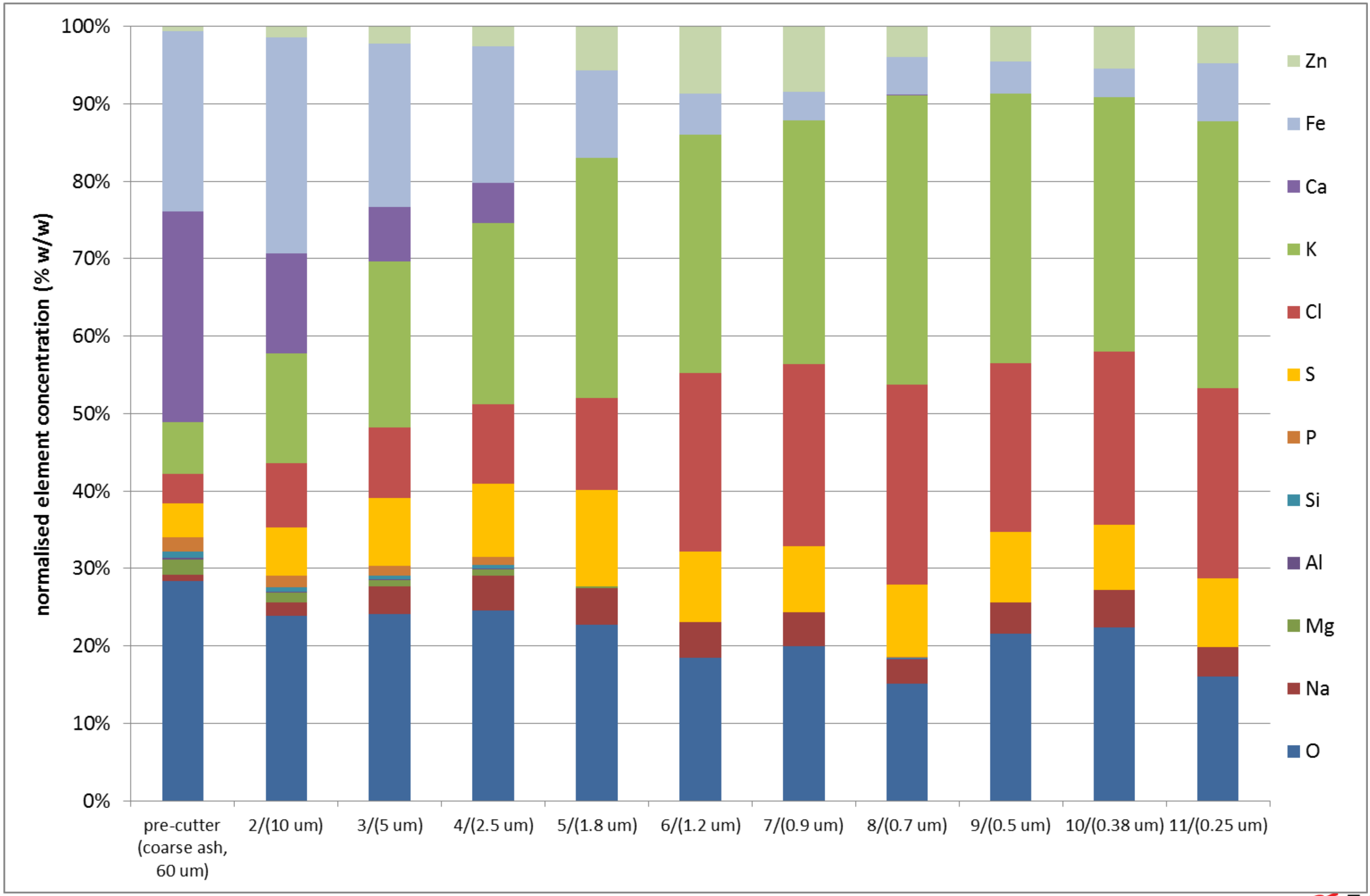
2nd measurement campaign May 2016:

Cascade Impactor derived dust compositions, SP2 18 May



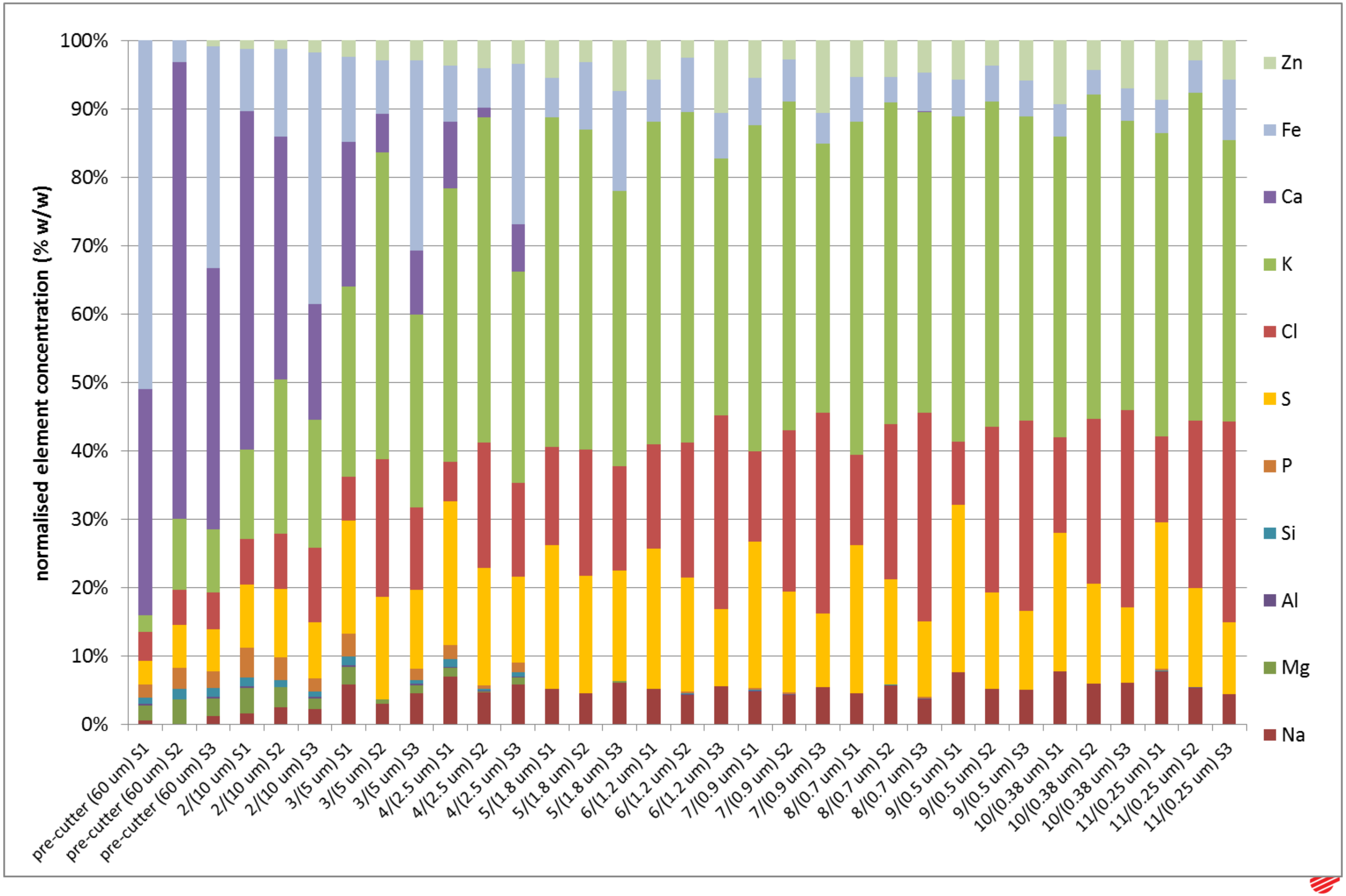
2nd measurement campaign May 2016:

Cascade Impactor derived dust compositions, SP3 18 May



2nd measurement campaign May 2016:

Cascade Impactor derived dust compositions, all points 18 May



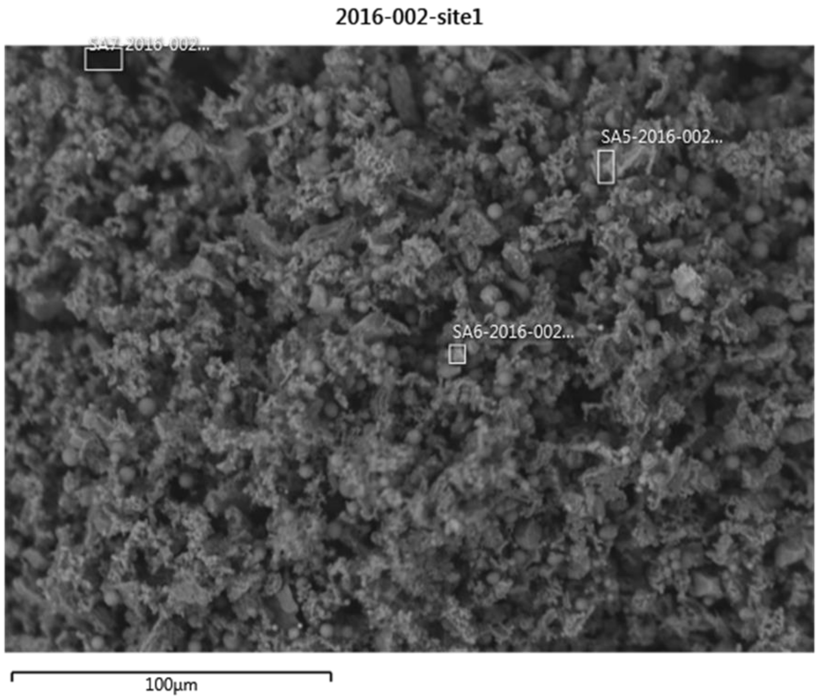
2nd measurement campaign May 2016:

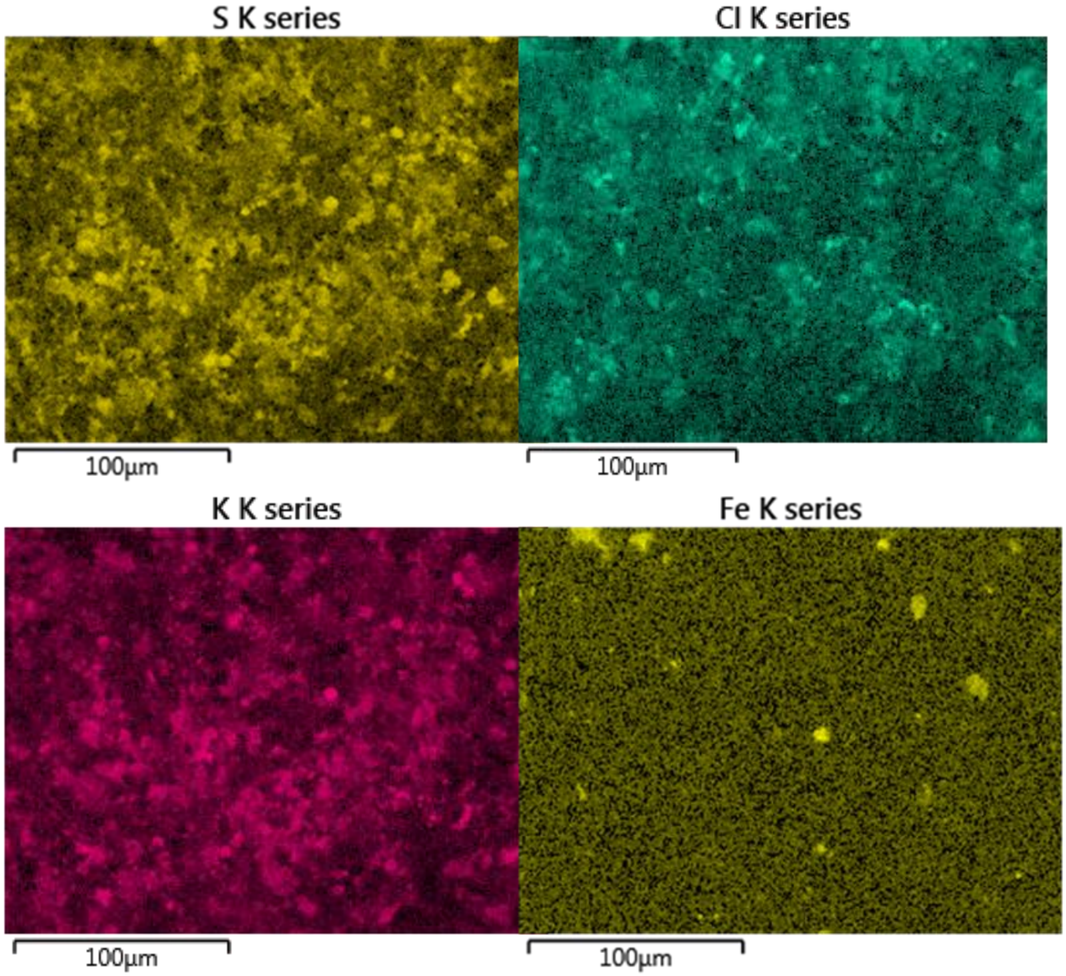
SEM/EDX *dust compositions: discussion*

- SP1: coarse ash clearly higher in Fe and lower in other elements when compared with similar samples from SP2 and SP3, but could be misleading due to large differences in concentration of that fraction
- Fine ash progressively enriched in Fe and Cl, while constant in alkalies and lower in S, when moving from SP1 to SP3
- Clearly the Fe gets redistributed in ECO, though there are lumps of iron-rich material already at SP1
- ? Is it iron chunks being ground to fine material or is it corossion and/or erosion of ECO?

2nd measurement campaign May 2016:

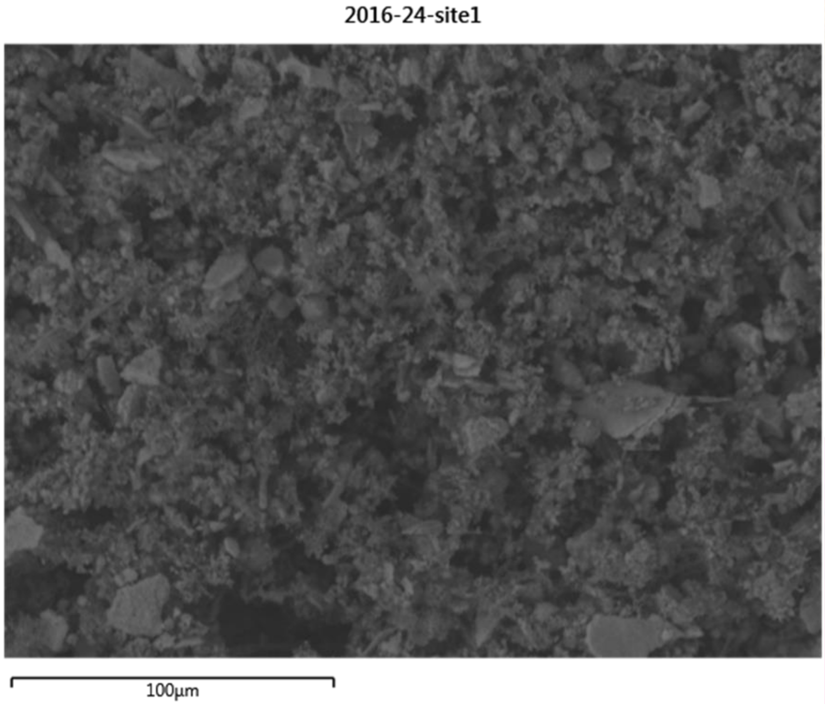
SEM/EDX record, example SP1 stage 2

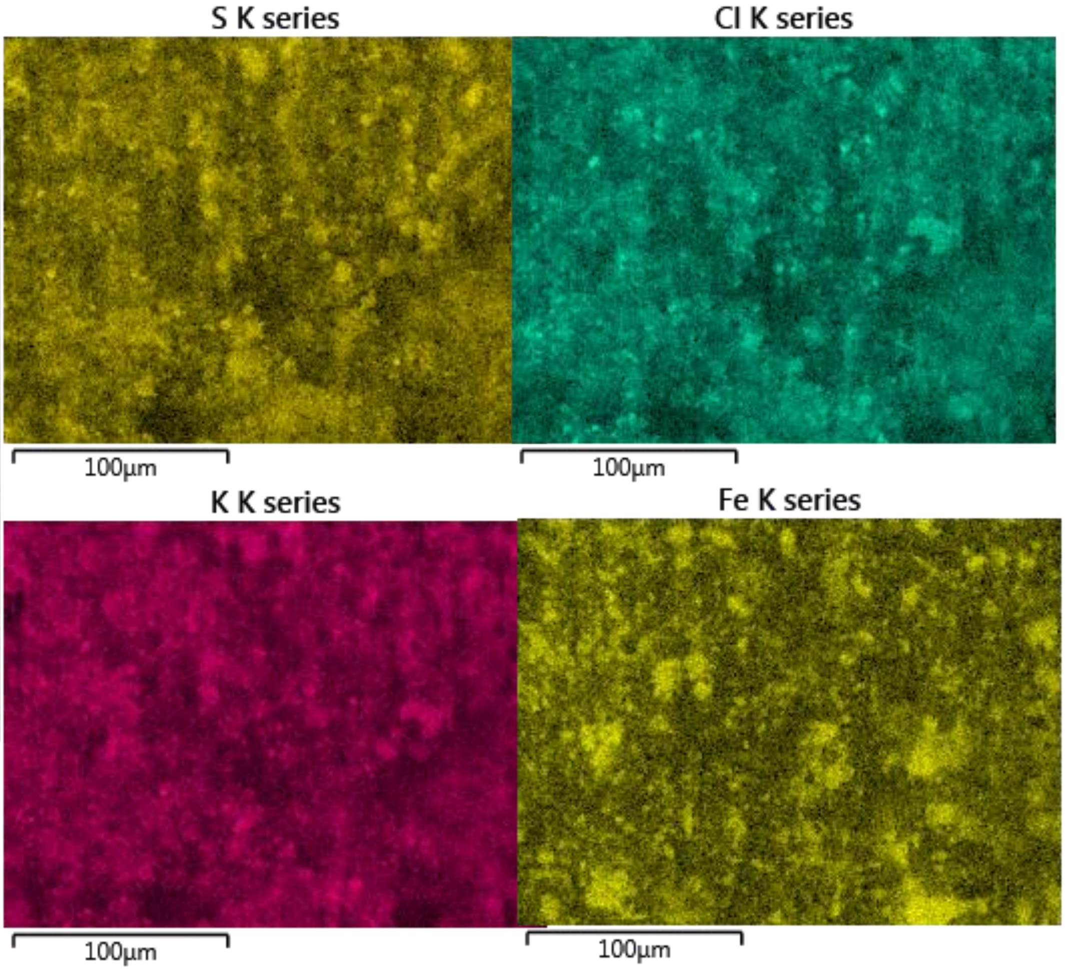




2nd measurement campaign May 2016:

SEM/EDX record, example SP3 stage 2

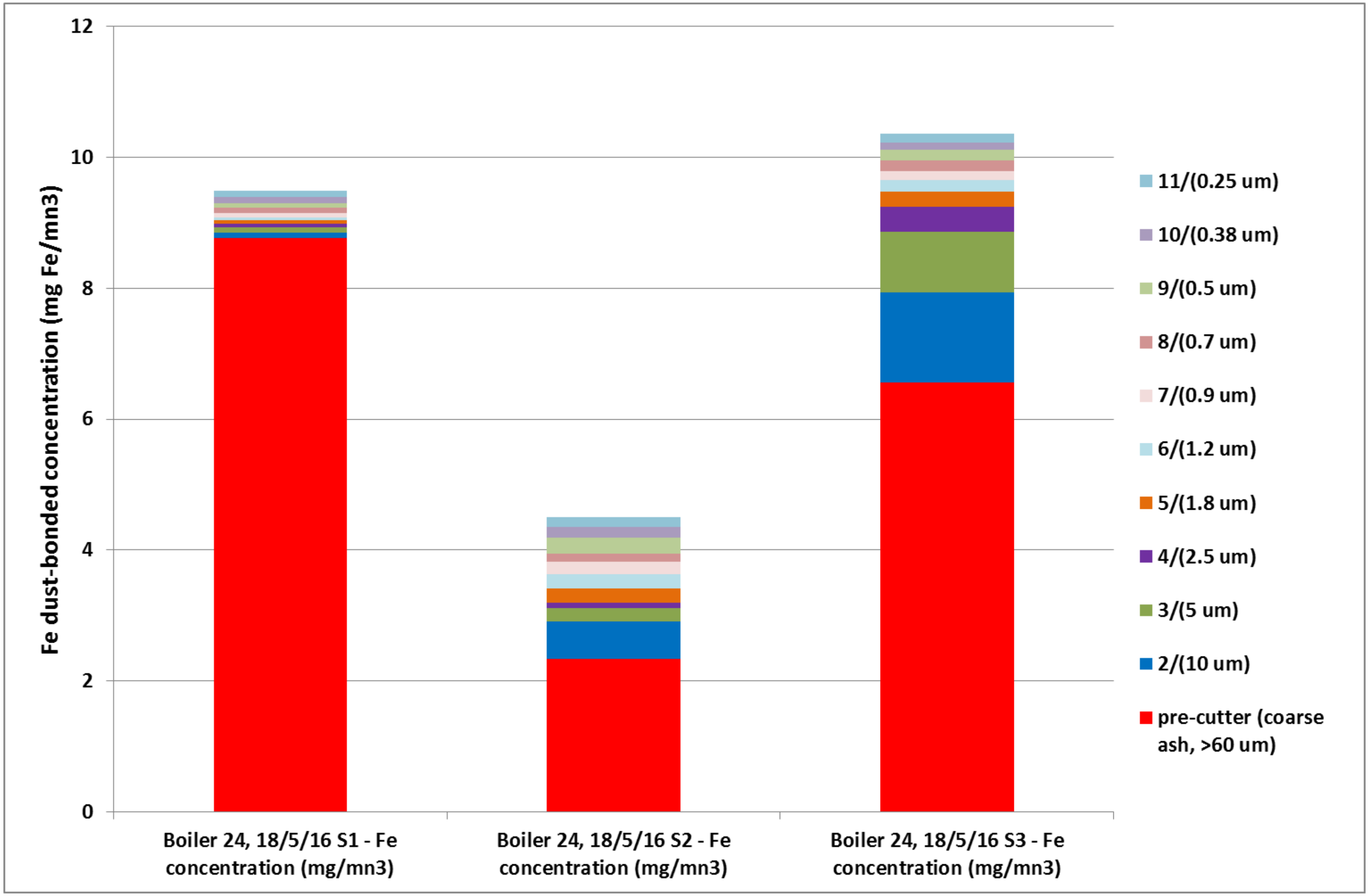




- Definitely enriched in Fe, but not in Cl compared with SP1!

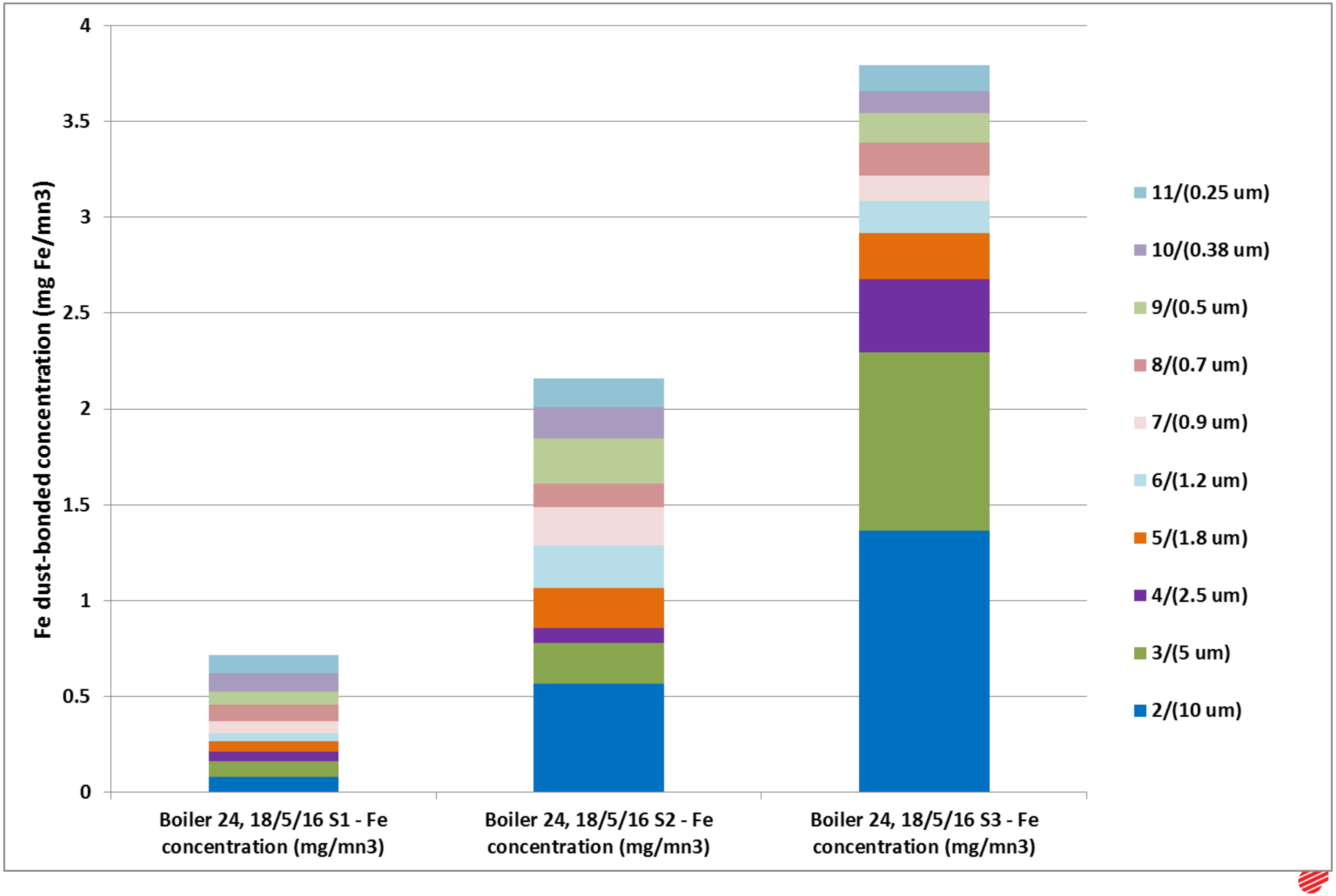
2nd measurement campaign May 2016:

Cascade Impactor derived Fe fluxes, all points 18 May



2nd measurement campaign May 2016:

Cascade Impactor derived Fe fluxes, all points 18 May



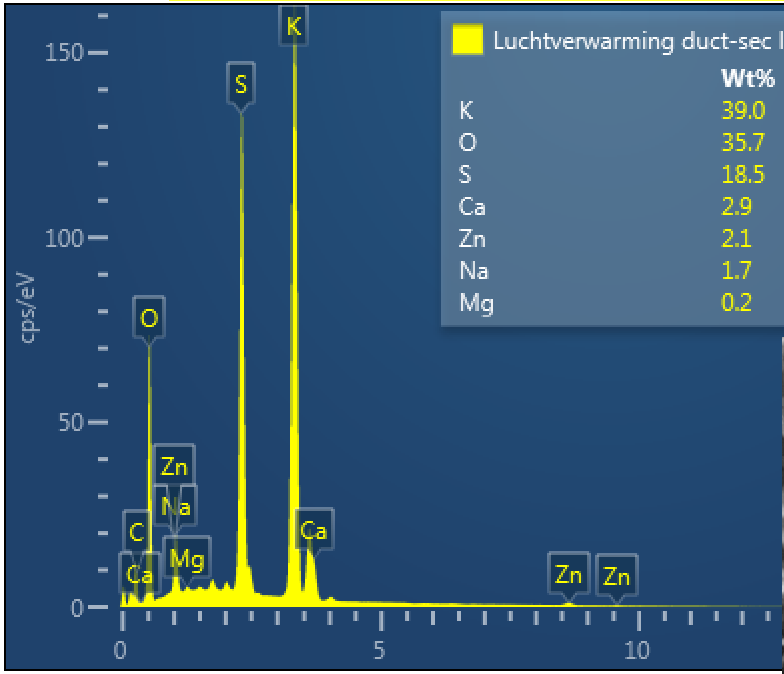
2^{nd} measurement campaign May 2016:

SEM/EDX *dust compositions: discussion of Fe enrichment*

- With Fe from coarse ash, the overall load barely increasing
- However, when subtracting this unreliable ash fraction (due to sampling issues) the Fe load does progressively increase
- The increase is primarily in supermicron fraction (roughly 10-fold increase), which rather indicates erosion mechanism of fragile FexOy layer in the ECO and progressive grinding of iron-rich material carried into ECO from the boiler
- Submicron-fraction also getting richer, accompanied by distintive increase in Cl, which could be ascribed to corossion and mobilisation/volatilisation of FexCly (which can volatilise already at ~180°C under oxygen-depleted conditions)
- Either way: ECO does get eaten away… (over to Erik)

Additional inspection boiler 12:

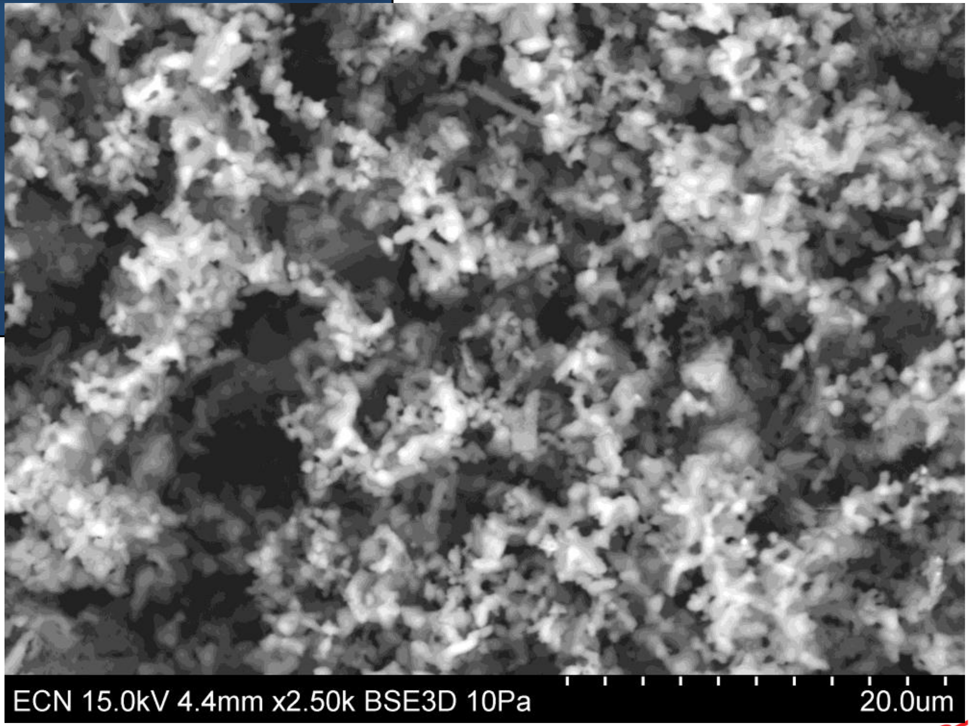
solids from OFA duct



Luchtverwarming duct-sec lucht-12-Map Sum Spectrum

	Wt%	σ
K	39.0	0.0
O	35.7	0.0
S	18.5	0.0
Ca	2.9	0.0
Zn	2.1	0.0
Na	1.7	0.0
Mg	0.2	0.0

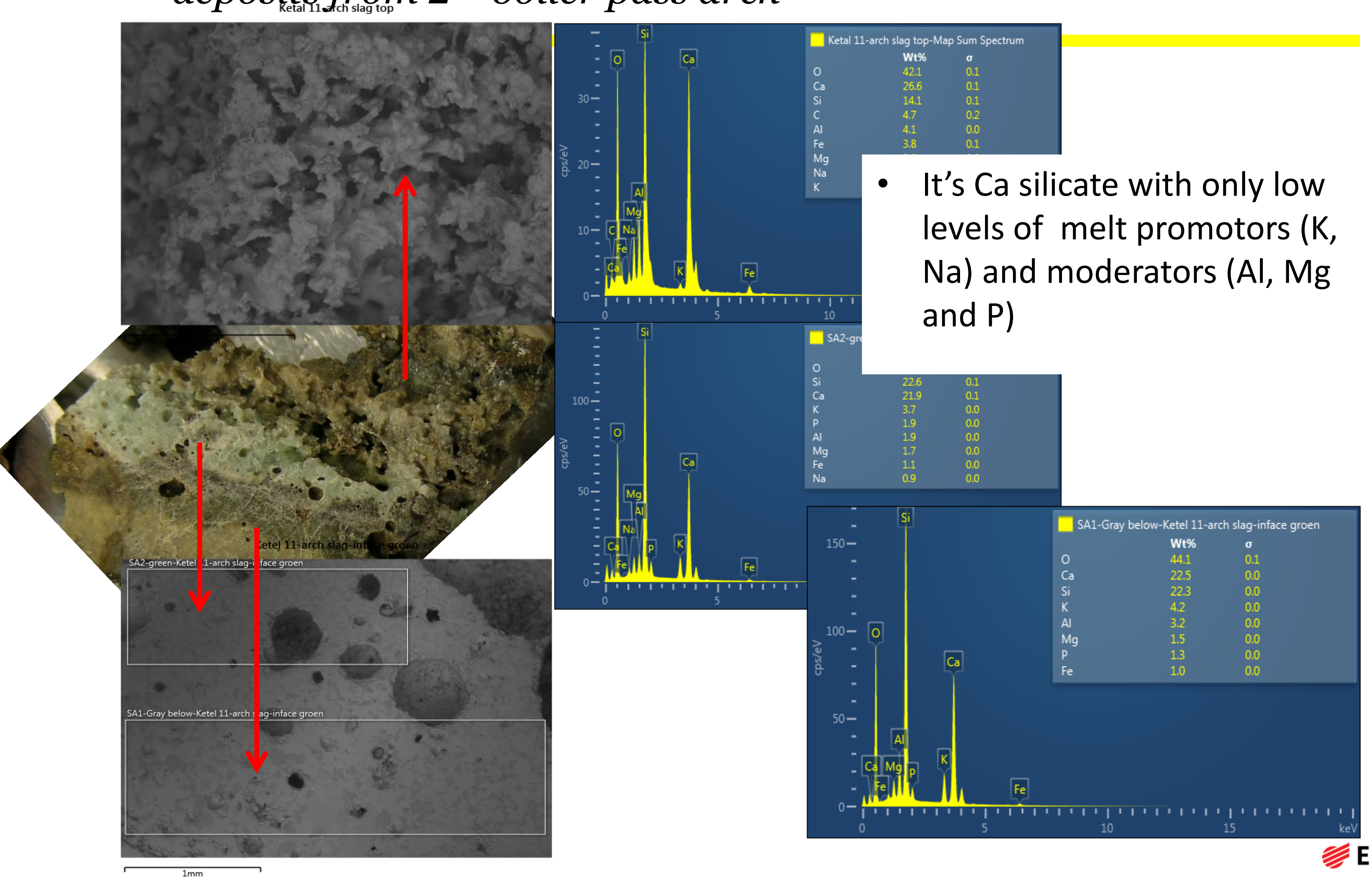
- This proves beyond doubt K and S are recycled through OFA (likely through the humidifier)



ECN

Additional inspection boiler 11:

deposits from 2nd boiler pass arch



Ketal 11-arch slag top-Map Sum Spectrum

	Wt%	σ
O	42.1	0.1
Ca	26.6	0.1
Si	14.1	0.1
C	4.7	0.2
Al	4.1	0.0
Fe	3.8	0.1
Mg		
Na		
K		

SA2-gre

O		
Si	22.6	0.1
Ca	21.9	0.1
K	3.7	0.0
P	1.9	0.0
Al	1.9	0.0
Mg	1.7	0.0
Fe	1.1	0.0
Na	0.9	0.0

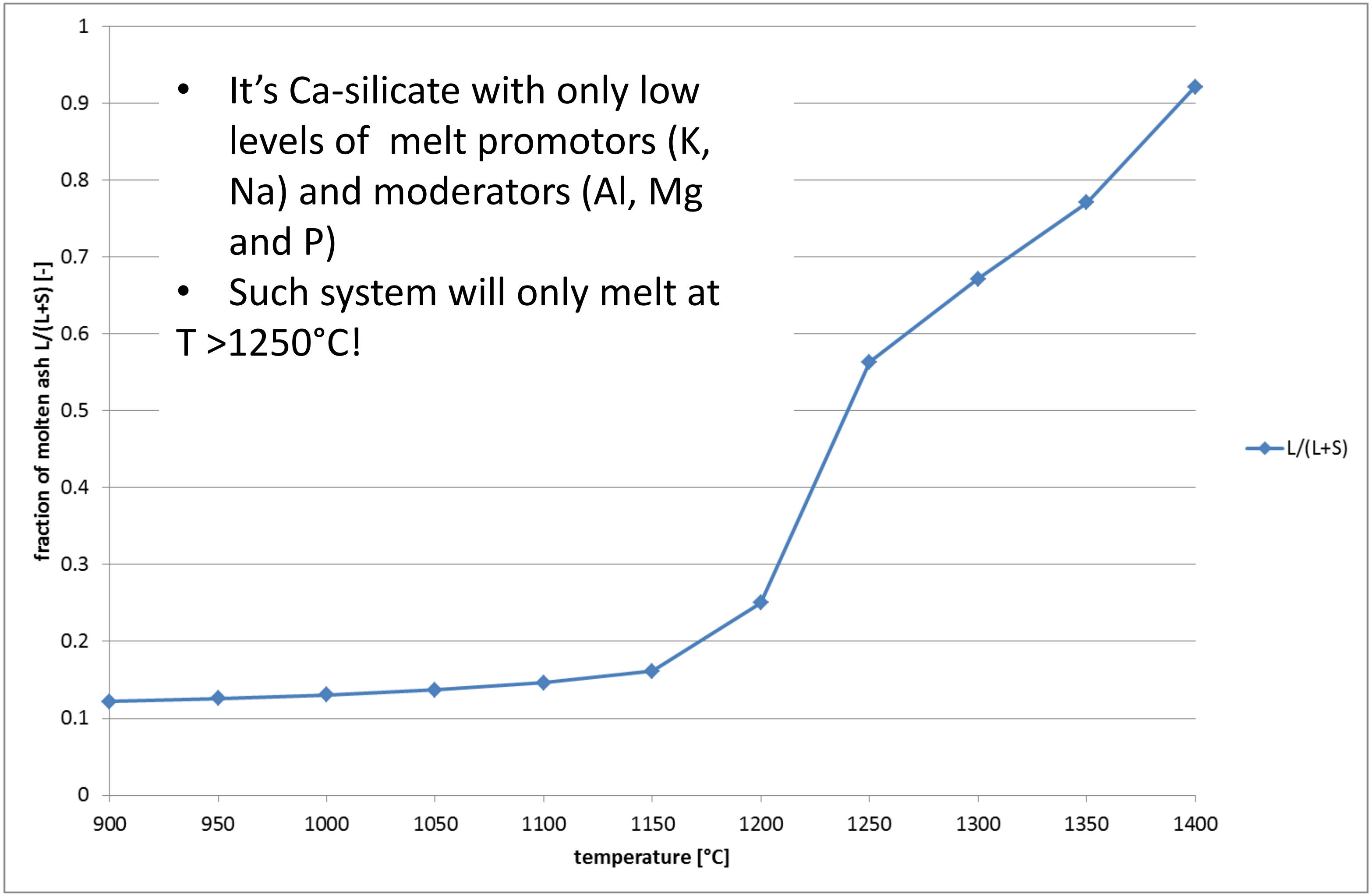
SA1-Gray below-Ketel 11-arch slag-inface groen

	Wt%	σ
O	44.1	0.1
Ca	22.5	0.0
Si	22.3	0.0
K	4.2	0.0
Al	3.2	0.0
Mg	1.5	0.0
P	1.3	0.0
Fe	1.0	0.0

- It’s Ca silicate with only low levels of melt promotors (K, Na) and moderators (Al, Mg and P)

Additional inspection boiler 11:

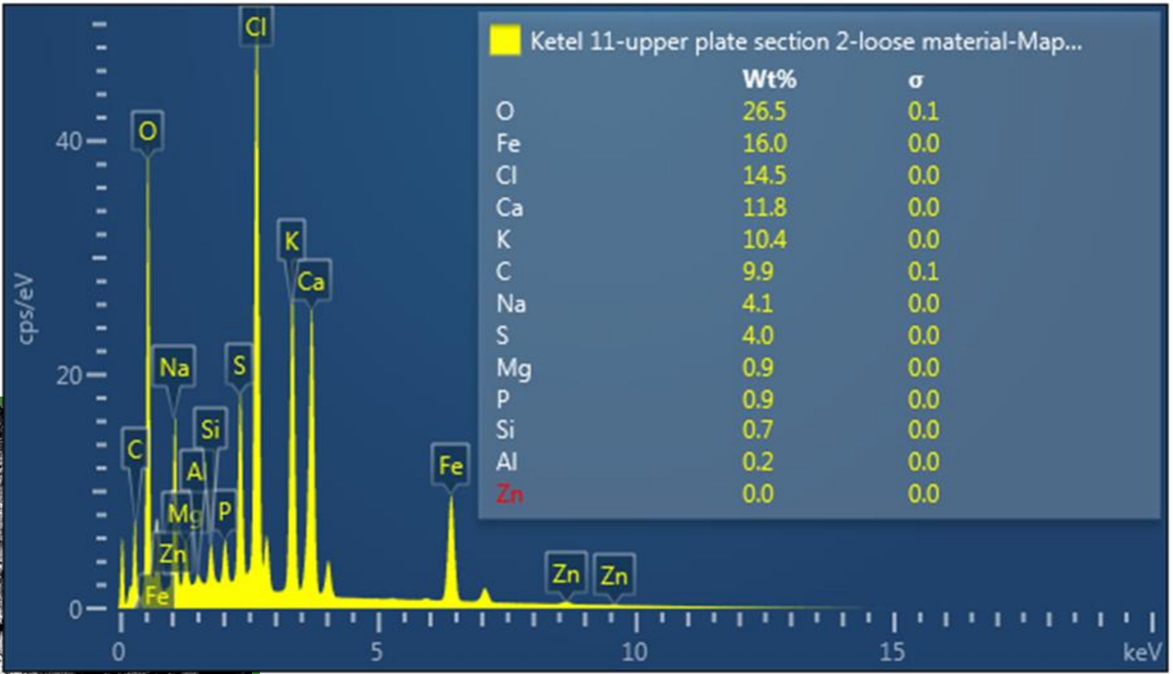
deposits from 2nd boiler pass arch, melting point calculation



- It's Ca-silicate with only low levels of melt promotors (K, Na) and moderators (Al, Mg and P)
- Such system will only melt at T >1250°C!

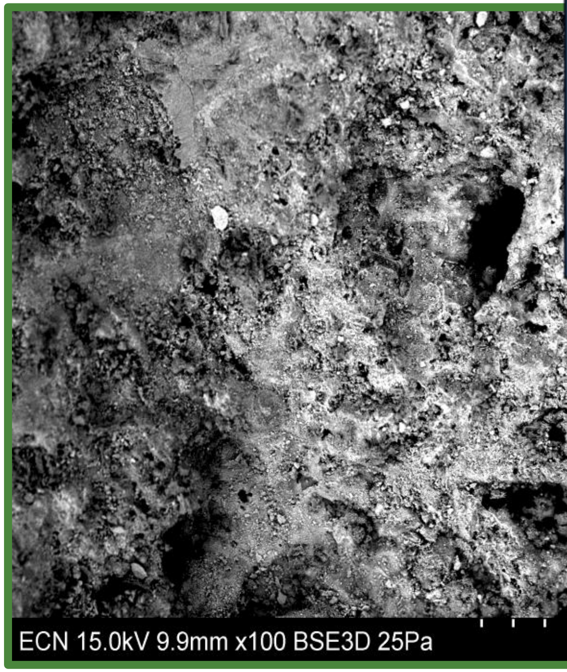
Additional inspection boiler 12:

deposits top part ECO: red, loose stuff from 1st pass tube



Ketel 11-upper plate section 2-loose material-Map...

	Wt%	σ
O	26.5	0.1
Fe	16.0	0.0
Cl	14.5	0.0
Ca	11.8	0.0
K	10.4	0.0
C	9.9	0.1
Na	4.1	0.0
S	4.0	0.0
Mg	0.9	0.0
P	0.9	0.0
Si	0.7	0.0
Al	0.2	0.0
Zn	0.0	0.0

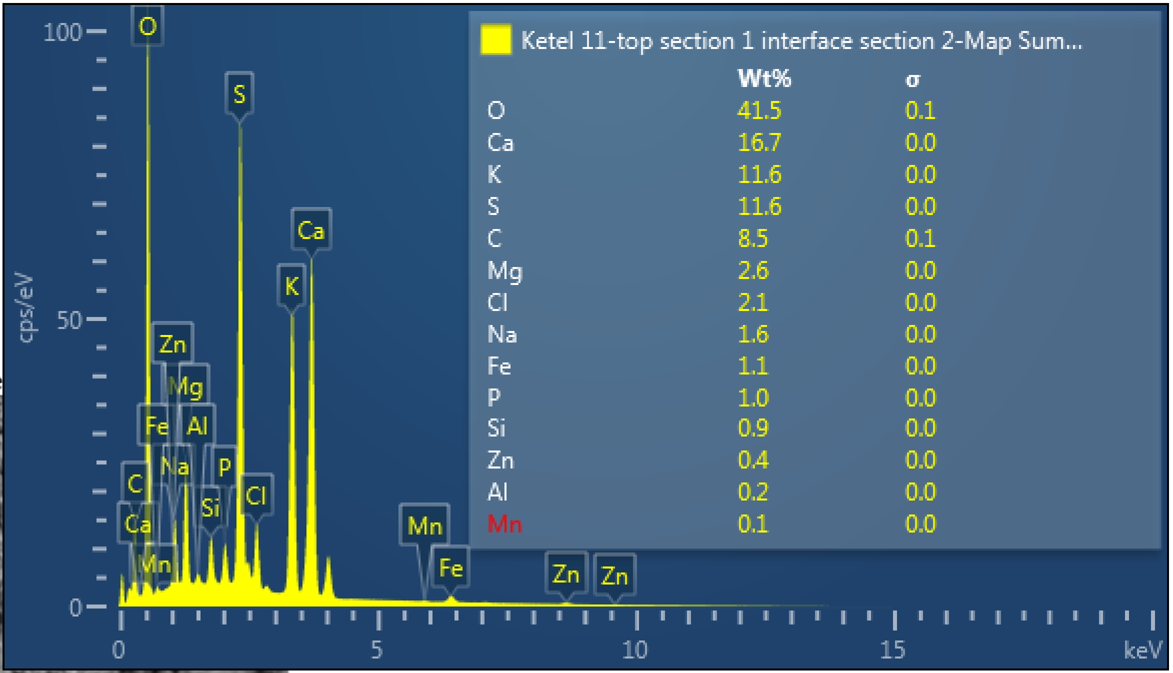


- Please note the Fe and Cl enrichment!
- So this is likely the fine material stripped off the wall and ending up in the fine fraction?!

Additional inspection boiler 12:

deposits top part ECO: white, loose stuff from 1st pass tube/plate

Ketel 11-top section 1 interface se



🟨 Ketel 11-top section 1 interface section 2-Map Sum...

	Wt%	σ
O	41.5	0.1
Ca	16.7	0.0
K	11.6	0.0
S	11.6	0.0
C	8.5	0.1
Mg	2.6	0.0
Cl	2.1	0.0
Na	1.6	0.0
Fe	1.1	0.0
P	1.0	0.0
Si	0.9	0.0
Zn	0.4	0.0
Al	0.2	0.0
Mn	0.1	0.0

- That’s just benign ash…

Conclusions and outlook

Conclusions:

the campaign

- The observed corrosion issues are unlikely to be related to the fluid (either water vapour or ionic solutions) condensation issues in the heat exchangers of the installation.
- Dew points were 65-67 °C without and 70-71 °C with the humidifier .
- A part-load humidifier operation still increases the dew point by a couple of degrees.
- SNCR injection system only a minor impact on the dew point, increasing it only to approx. 72 °C
- SNCR did not lead to the formation of the potentially highly corrosive and highly volatile ammonium salts.
- Condensates contain increased inorganic constituents like sulphur and chlorine, associated primarily with sodium retained in the condensate at relatively high concentrations. These inorganics are re-injected into the system when using the humidifier.

Conclusions:

the campaign

- CI fine dust (aerosol) sampling shows high concentration (approx. 50 mg/m_n^3) of near- and sub-micron particulate in the flue gas.
- This particulate is for over 80 % w/w composed from potassium chloride and sulphate, and hence should be considered a major corrosion risk factor.
- The obtained data also suggest that using the humidifier at full load does lead to higher dust-bonded sulphur concentrations. This may enhance the chloride-induced corrosion.
- At constant humidifier load free SO2 gas-bonded concentration increases significantly.
- Nonetheless running with humidifier at constant load may possibly lead to a stable and safe operation, when maintaining controlled SO2 levels and avoiding KCl deposition (particularly at start ups)

Conclusions:

ASPEN modelling

- ASPEN modelling indicates:
  - **NH3 slip from even under optimised SNCR conditions results in significant increase of SOx uptake in the condensate and the flue gas concentration through the humidifier loop, while it does not affect the HCl behaviour**
  - This is likely an important reason for the increase in corrosion while using (non-optimised) SNCR
  - Controlling the slip does lead to lower SOx uptake and recycle
  - Under acceptable/expected slip (5-20 mg/m_n^3) the SOx concentrations in the condensate should remain < 300 mg/kg
  - Variations in flue gas flow (due to fuel quality/moisture changes) have significant impact on the SOx uptake
  - The SOx from the condensate re-injected through the humidifier increases significantly (~2x) the flue gas SOx levels
  - Increase in condensate purge/bleed with water decreases the SOx proportionally in the condensate and in the flue gas
  - Lowering flue gas inlet temperature to 150°C from the regular 180°C decreases affects SOx and HCl only in a minor way

Conclusions:

ash and condensate samples

- Condensate samples:
  - Clearly measurable levels of NH3 (up to > 200 mg/kg) proving that ammonia slip is readily scrubbed in the condensor
  - High ammonium ion levels coinciding with the highest levels of $SO4^{2-}$ (up to 700 mg/kg)
  - Cl^- levels much lower (<< 100 mg/kg) and varying only slightly
  - Overall the compositions very similar to the compositions predicted by ASPEN
- Fly ash samples:
  - Large variation in Fe levels,
  - High Fe levels appear to coincide with high C levels and lower S levels
  - Also measurable concentrations of Zn, when increased levels of Cl present

Conclusions:

ECO inspection

- ECO inspection (K11)
  - Some, yet limited corrosion in 1st pass, while 2nd/3rd pass basically intact, except for ruptured welds and ripped off/spalling off oxide layers due to mechanical removal of the ash deposits
  - Chunks of C-rich and partly molten material at the bottom of the ECO inlet
  - Granular, char/carbon an calcium rich deposits in (the bottom part of) the 1st pass
  - Top-side 1st pass and 2nd/3rd pass only very fine crystalline material, very similar to the earlier sampled fine-ash fraction from the boiler (K and S-dominated, with small proportions of Cl and Zn)
  - Metal/tube-side deposits enriched in Fe (simply flakes of the oxide layer detached from the tube wall)
  - No indications of Fe penetration into the bulk of the deposits
  - Brown/reddish colour (except for the wall-side deposits) associated with high C levels and not with Fe levels.

Outlook:

open actions and curative measures

- ~~Flue gas acidic components concentrations should be verified.~~
- ~~Fuel quality consistency should be verified.~~
- ~~Condensate hold up system and use should be re-routed in a way excluding (excessive) inorganics/sulphur build up - ASPEN modelling ready for this part~~
- **Running additional ASPEN cases may shed light on fuel quality impact on S/Cl behaviour and the possible impact on corrosion**
- **Mineral additives can possibly be deployed for in-boiler capture of free alkalis. Even at the same Cl/S load this should further diminish the corrosion.**
- These additives (clays, typically kaolinites, halloysites etc.) should be either pre-mixed with the fuel or injected above grate.
- The efficiency of any of the proposed curative actions ~~can be tested at ECN grate-fired test facility and~~ verified by on-site measurements (cascade impactor~~/deposition probe/~~prescribed standard flue gas sampling etc.)

Thank you for your attention

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