Material research with focus of Vattenfalls oxyfuel pilot plant

3rd Oxyfuel Combustion Conference

2013-09-11

Alexander Gerhardt[a], Pamela Henderson[a], Melanie Montgomery[b], Peter Zimmer[c] , Ina Uhlmann[c]

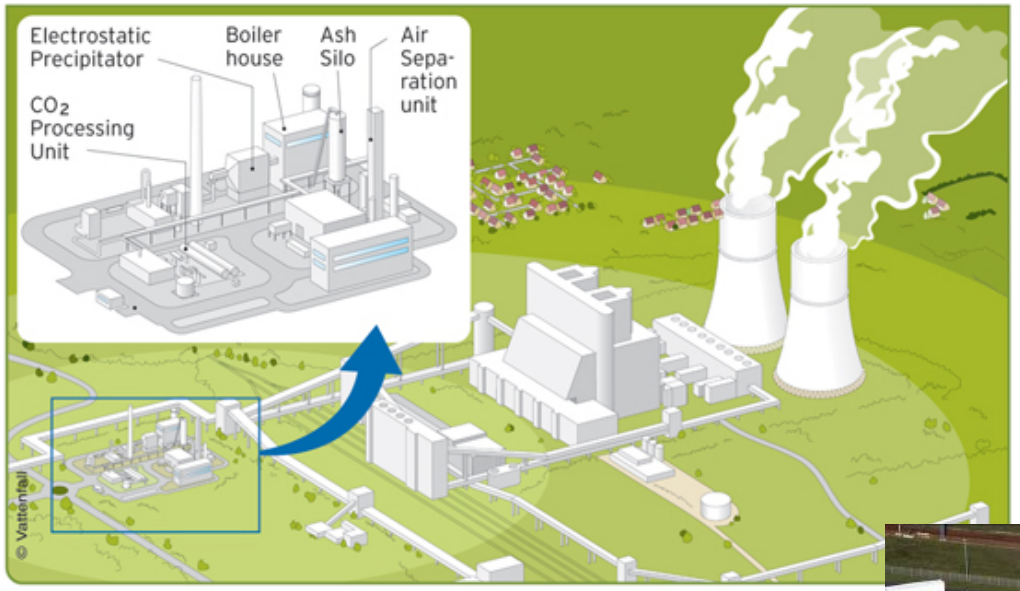
[a]*Vattenfall BU R&D Projects, Otternbuchtstr. 14-16, 13599 Berlin, Germany*
[b]*Vattenfall BU Engineering Chemistry, Kopenhagen, Denmark,*
[c]*Vattenfall BU Engineering Materials, Berlin, Germany*

Overview

VATTENFALL

Introduction

Vattenfalls 30MW Oxyfuel Pilot Plant

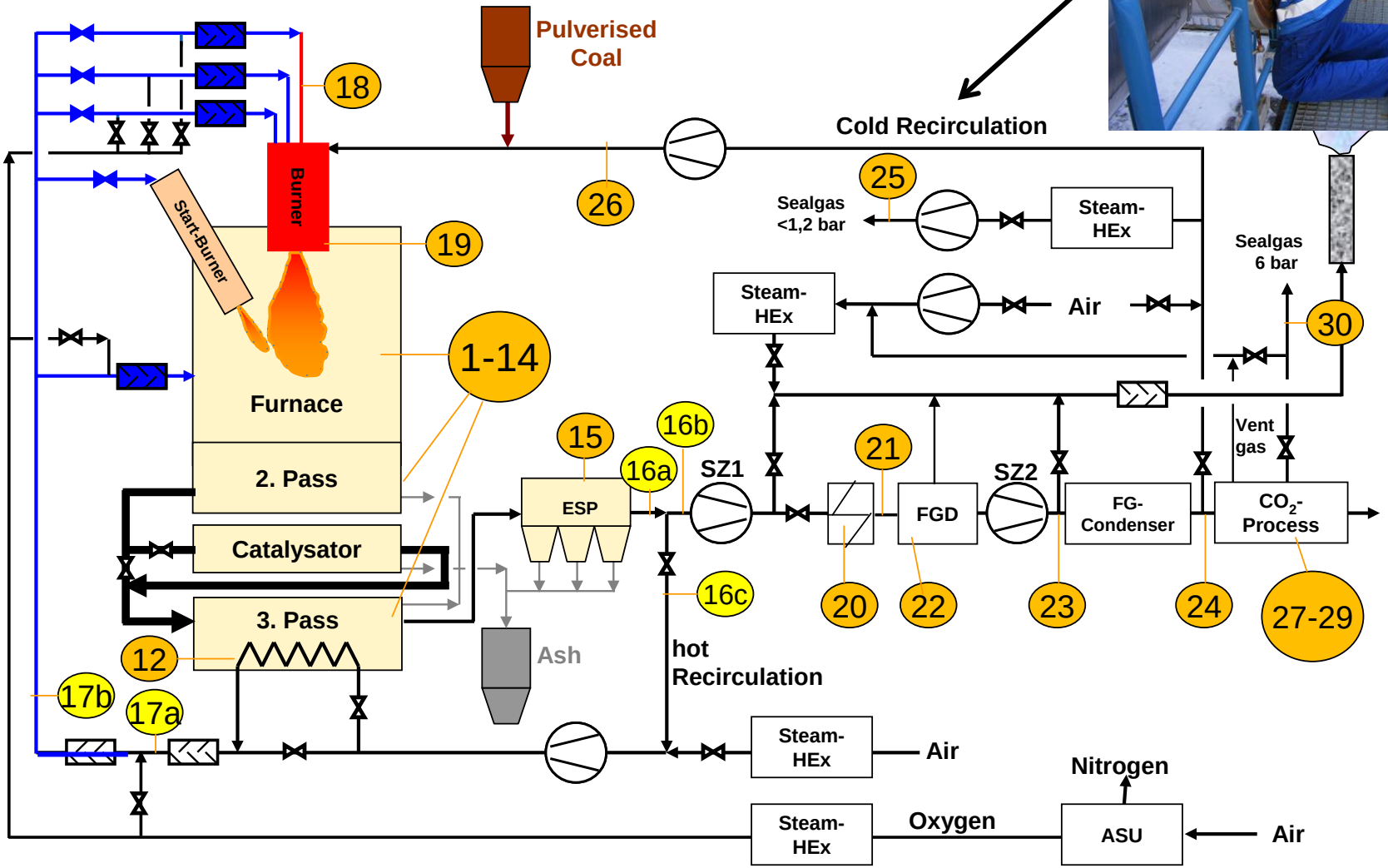


	Measurements in dry gas after ESP					H_2O Vol. % in flue gas	Fly-ash SO_3 mg/kg
	CO_2 Vol %	O_2 Vol%	CO mg/Nm³	SO_2 mg/Nm³	NOx mg/Nm³		
Air-firing	13	6	7	1600	300	8	46 + 9
Oxyfuel	95	6.8	2.5	7000	1600	30	77 + 18

VATTENFALL

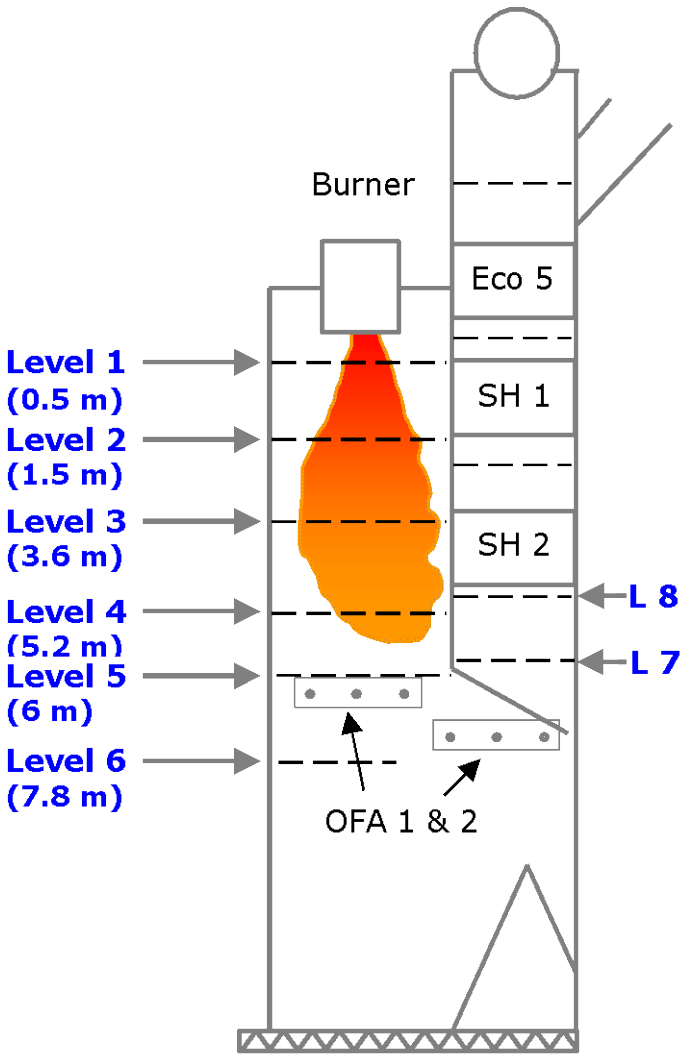
Material tests at Vattenfalls 30MWth Oxyfuel Pilot Plant in Schwarze Pumpe

Material test location



VATTENFALL

Purpose and Questions



- Super heater at 580°C,650 C and 720 C
- Economisers, Water walls
- Low temperature corrosion (70 – 170 C)
- Analysis of deposits formed on super heaters (ash formation)
- ESP, FGD, FGC, recirculation duct, etc
- Identify differences between conventional coal firing and oxyfuel firing

- Different types of probes

- Various burner
- Variation of coal quality (moisture, sulphur content, particle size)

VATTENFALL

Materials, flue gas composition and fly ash

Materials:

Ferritic, Martensitic, Austenitic and

Nickel-base alloys

Examples:

10CrMo910, 13CrMo44, 15Mo3, Super304H,

T23, T92, X20, Inconel625, Alloy617,

Alloy740, KanthalAPMT, 253MA

347HFG, Sanicro25, VM12, HR3C, AC66

… and so on

Flue gas measurements after ESP (wet) for Oxyfuel

- CO2 ~ 65% and O2 < 4 %
- SO_2 ~ 7000mg/m³ (Air ~ 1600mg/m³)
- H_2O ~ 27-29% (Air ~ 8%)
- CO < 200 mg/Nm³, NOx < 500 mg/Nm³

- SO_3 in fly ash
  - Air SO_3 46 $\pm$ 9 (mg/kg)
  - Oxyfuel SO_3 77 $\pm$ 18 (mg/kg)

- Otherwise ash composition is similar
- Corrosive species SO_2 and H_2O approx 4 times greater in oxyfuel.

Low temperature gradient probe

Corrosion probes after exposure in plant

SAF2101 at Level 12 (3rd Draft)

15Mo3 at Level 13 (3rd Draft)

Summary on material tests

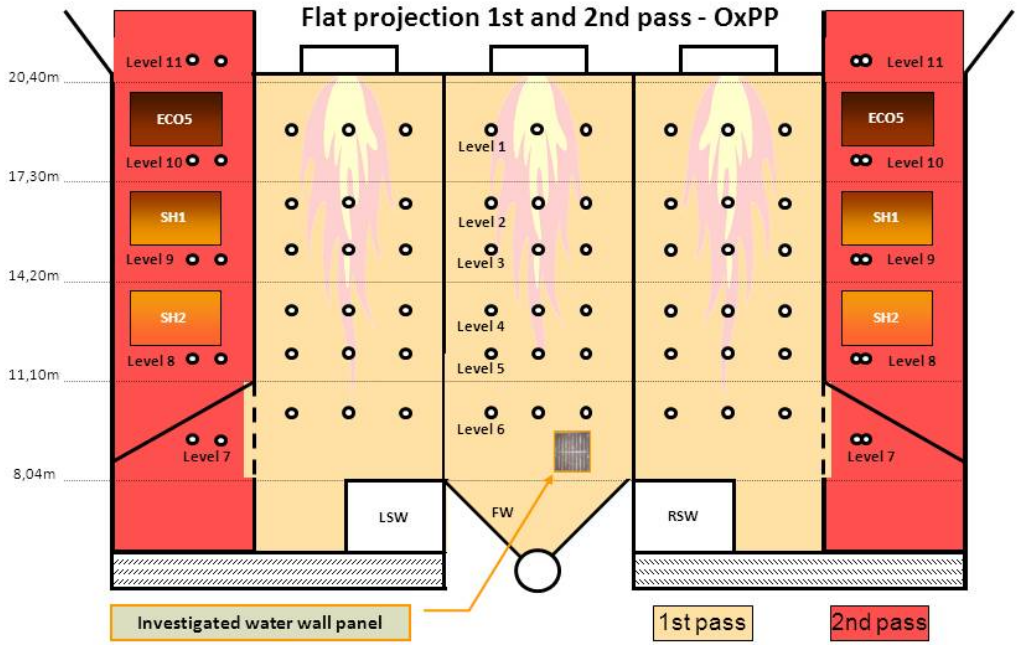
- **Deposit composition and corrosion attack on the high temperature components were similar in both oxyfuel and air firing mode.**
- **Indication of higher material wastage rate in OxyFuel**
- **The temperature range where low temperature components are susceptible to corrosion has increased due to oxyfuel firing probably due to increased susceptibility to SO3 dewpoint corrosion.**
- **There may be more ash deposition in the oxyfuel mode.**

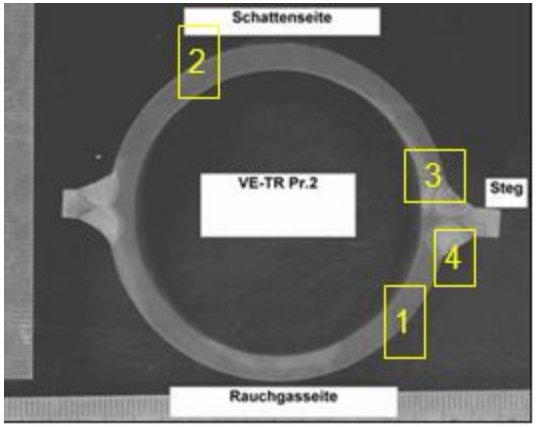
Additional observations with some materials

- Increased S-concentration in corrosion front
- Ni-based alloys may form non-protective NiO
- (Cu – containing alloys may form non-protective Cu-crystallites)
- Al-containing materials may form protective oxide (Al_2O_3) and is not getting carburised
- Super austenitic stainless steels (30%Fe, 30%Ni, 30%Cr) forms protective oxide

Test panel at OxPP

Boiler overview



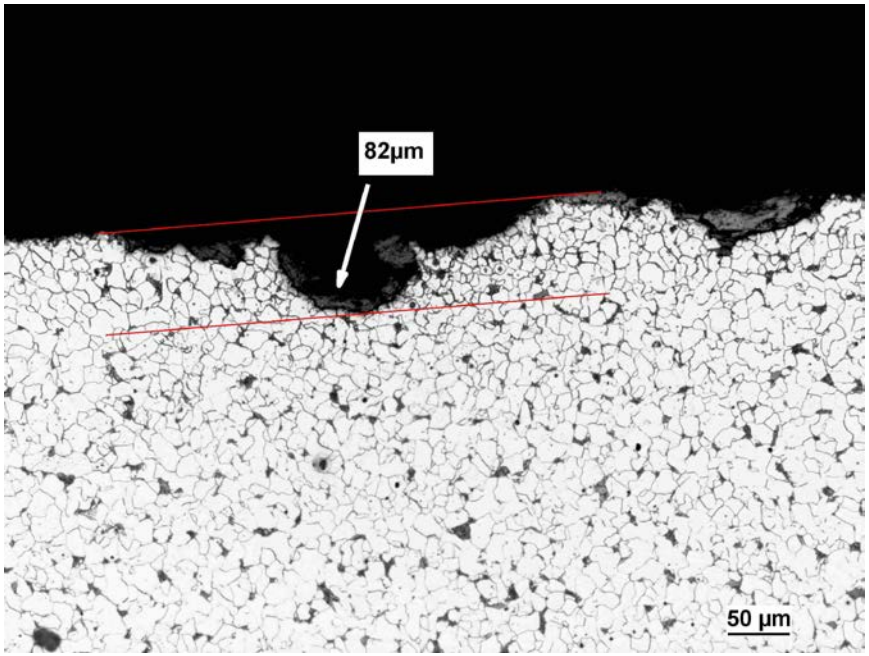


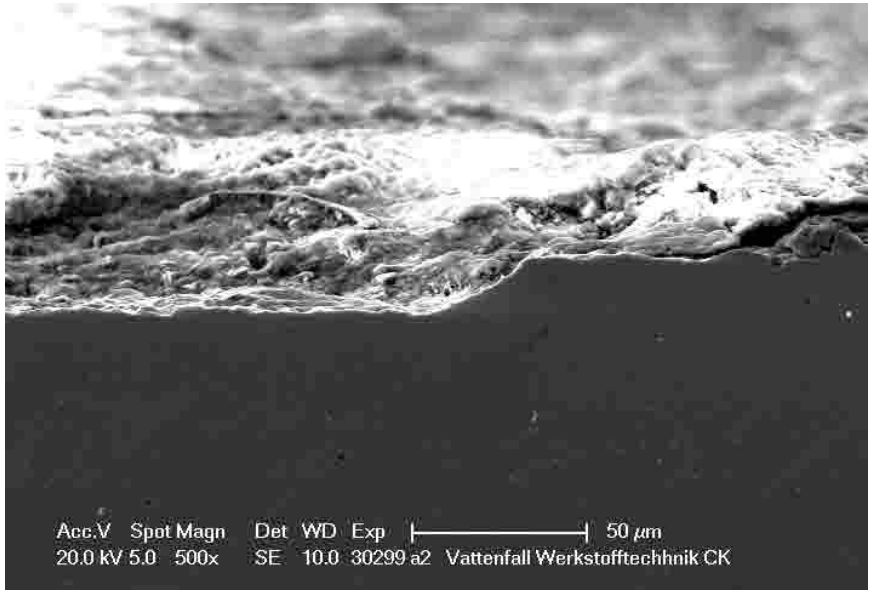
Wall material P235GH (1.0345) with joints made of S235JRG2 (1.0038)
4 part where send to
Alstom, BAM, FZJ and VPC

VATTENFALL

Panel analysis

Air combustion:	3847.5 h
Oxyfuel combustion:	8789.0 h
Steam parameter:	235 C
	30.7 bar





- thin irregular corrosion layer
- some corrosion at HAZ
- isolated corrosion craters at inside and outside

VATTENFALL

OxyCorr - High temperature corrosion test under lignite oxyfuel firing

OxyCorr Project 2009 - 2012

University of Stuttgart, Institute of Combustion and Power Plant Technology (IFK)

Vattenfall Research & Development AB

Swerea KIMAB AB

Alstom Power Systems GmbH, Stuttgart

Outokumpu Stainless AB, Avesta Research Centre

ENEL PRODUZIONE SpA, Area Tecnica Ricera

WP 1: Mechanistic study on material corrosion in an oxy-coal fired flue gas environment:

- Material manufacture
- Long-term hot/cold corrosion tests
- Parametric study on Cl behaviour

IFKs KSVA (500 kWth)

ENELs Fosper (5 MWth)

WP 2: Deposit and material testing in technical scale test facilities:

- Determination of corrosive species
- FA and deposit
- Condensate
- Gas composition in hot and cold zones
- Material exposures in hot and cold zones

WP 3: Impact of oxy-fuel process on the ash characteristics and its usability:

- Role and impact of fly ash on deposit formation, material corrosion and ESP performance
- Characterization of fly ashes according to utilisation requirements

WP 4: Evaluation and assessment of results – implications for full scale plants

VATTENFALL

Lignite used in test campaigns & Flue gas composition

PROXIMATE ANALYSIS				
coal		LaTBK	LaTBK-S	LaTBK-S+
H_2O	% raw	9,8	10,15	8,49
Volatiles	% waf	57,39	56,98	58,05
Ash	% wf	5,57	18,64	12,05
Fixed C	% waf	42,61	43,02	41,95
ULTIMATE ANALYSIS				
coal		LaTBK	LaTBK-S	LaTBK-S+
C	% waf	66,45	67,99	65,76
H_F	% waf	4,75	5,33	4,98
N	% waf	0,66	0,73	0,59
S	% waf	0,56	2,31	2,62
O	% waf	27,58	23,65	26,05
Cl	% waf	---	< 0,02	0,016
MAIN ELEMENTS				
coal		LaTBK	LaTBK-S	LaTBK-S+
Al_2O_3	% wf	3,71	5,95	9,45
CaO	% wf	26,6	8,43	10,9
Fe_2O_3	% wf	24,1	8,1	16,4
K_2O	% wf	0,63	0,98	0,931
MgO	% wf	8,65	2,4	3,97
Na_2O	% wf	0,13	0,19	0,101
P_2O_5	% wf	0,01	0,08	0,064
SiO_2	% wf	12,5	48,7	43,6
TiO_2	% wf	0,15	0,44	0,51
SO_3	% wf	18,3	9,34	12,3
HEATING VALUE				
coal		LaTBK	LaTBK-S	LaTBK-S+
HHV	J/g, raw	22.279	19.424	21.548
LHV	J/g, raw	21.163	18.078	20.473

LaTBK-S and LaTBK-SS lignite were used for material tests:

- Rich in sulfur and alumino-silicatic character.
- Higher volatile content at *"waf"* basis.
- different ash content

FG composition, combustion chamber:

0,3 MW with approx.60 % recirculation rate

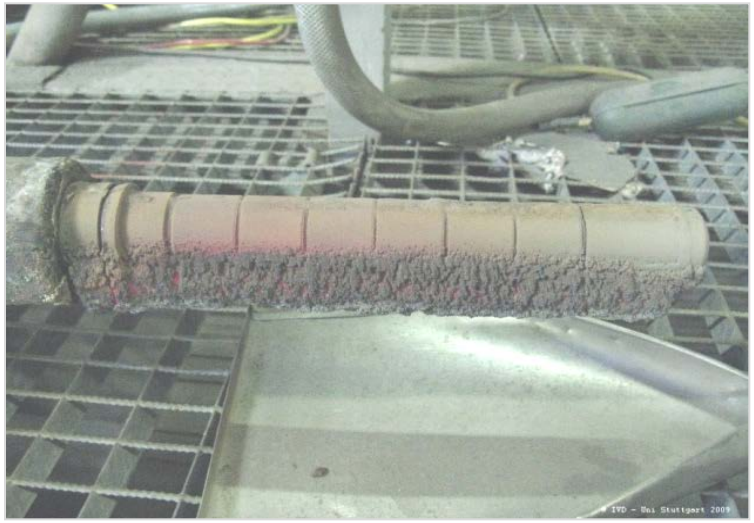
FG composition		LaTBK		LaTBK-S		LaTBK-S+	
		Air	Oxy I	Air	Oxy	Air Staged	Oxy Staged
O_2	%-vol., dry	3,8	6,8	3,3	4,8	3,3	3,9
CO_2	%-vol., dry	15,9	89,6	16,3	89,8	15,9	91,2
CO	ppm, dry	< 10	< 10	37	44	22	11
SO_2	ppm, dry	413	1067	1718	5368	2530	7480
H_2O (in front of ESP)	%-vol.	11,5	28,6	9	26	8	25

LaTBK-S lignite_ Corrosive species in the FG ducts:

HCl = 60 mg/m_N^3 ; SO_3 = 100 mg/m_N^3

VATTENFALL

Test campaign conditions for material tests



<< Probe with material rings and deposits (wind side)

	Grade	C	Ni	Cr	Co	Mo	Si	Mn	P	S
T92	1.4901	0,100	0,220	8,790	-	0,440	0,240	0,380	0,015	0,003
310S	1.4845 / 1.4951	0,046	19,050	25,270	0,073	-	0,059	0,086	0,020	0,001
304L	1.4307	0,022	8,200	18,200	-	-	0,400	1,580	0,034	0,001
Alloy 617	2.4663	0,006	54,700	22,000	11,600	8,700	0,090	0,080	0,003	0,002

	Grade	Cu	V	B	N	W	Nb	Al	Pb	Fe
T92	1.4901	-	0,190	0,003	0,004	1,89	0,006	0	-	-
310S	1.4845 / 1.4951	0,170		-	0,031	-	0,003	-	-	-
304L	1.4307	-	-	-	0,043	-	-	-	-	-
Alloy 617	2.4663	-	-	-	-	-	-	1,1	0,0002	1,1

Test 1 – Nov 2010: 72h exposure time

one probe 580 C material temperature exposed at 750 C flue gas temperature

one probe 650 C material temperature exposed at 1050 C flue gas temperature

one set of pre-exposed samples were further tested in a lab furnace at their respective material temperature

Test 2 – Nov 2011: 38h exposure time

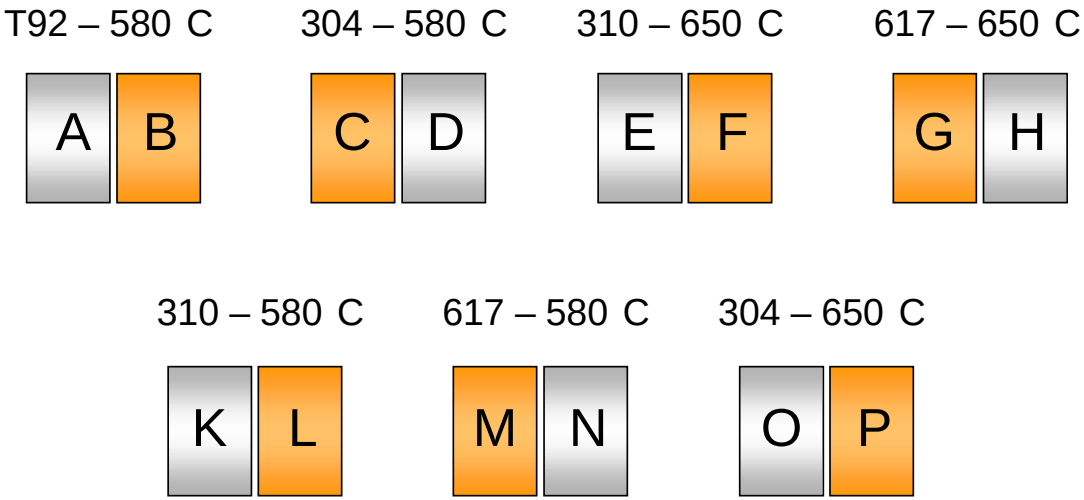
two probes at 480 C material temperature exposed at 1200 C flue gas

VATTENFALL

HTC – Probe samples from Test 1

Direct analysis after Test 1 (72h exposure)	-F (310 650 C) -P (304 650 C) -C (304 580 C) -B (T92 580 C) -G (617 650 C) -L (310 580 C) -M (617 580 C)

Analysis after Test 1 (72h) and lab exposure (928h)	-A (T92 580 C) -D (304 580 C) -E (310 650 C) -H (617 650 C) -K (310 580 C) -N (617 580 C) -O (304 650 C)

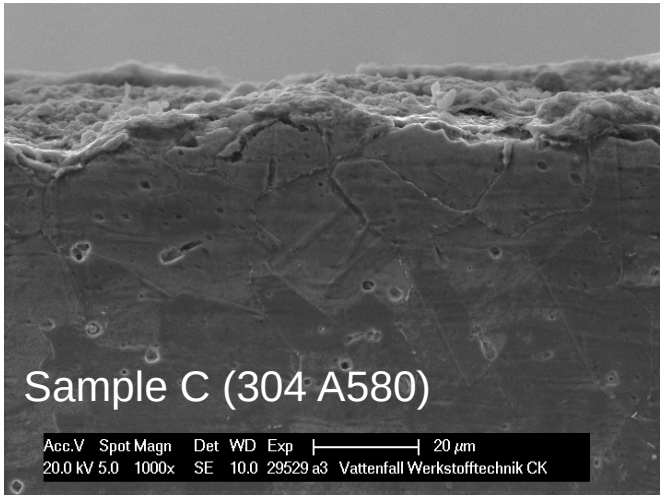


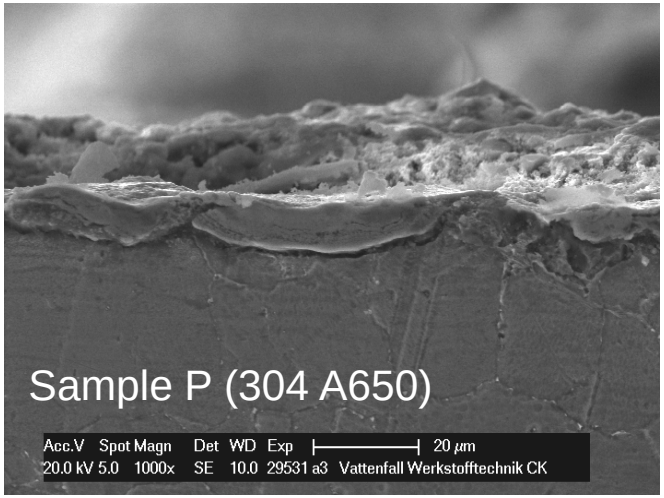
(Alloys - planned temperature)

VATTENFALL

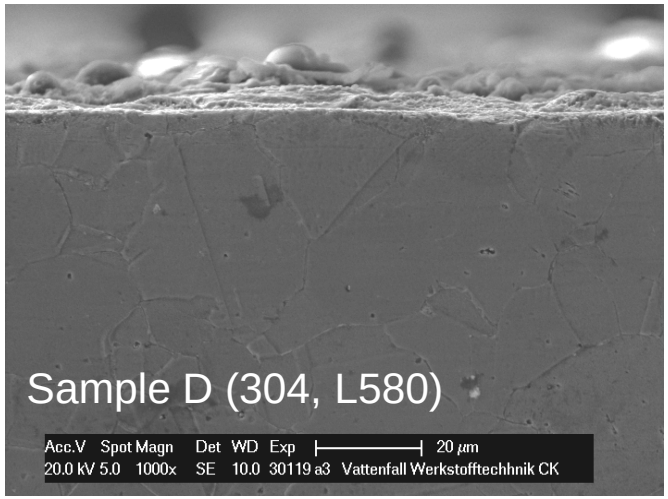
304 at 580°C and 650°C

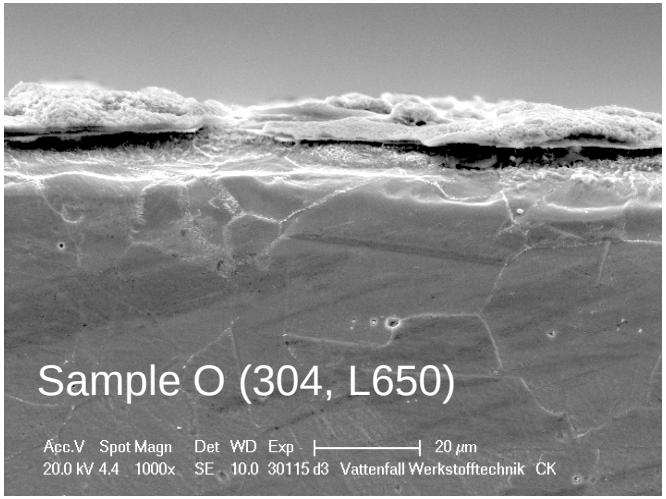
Test 1





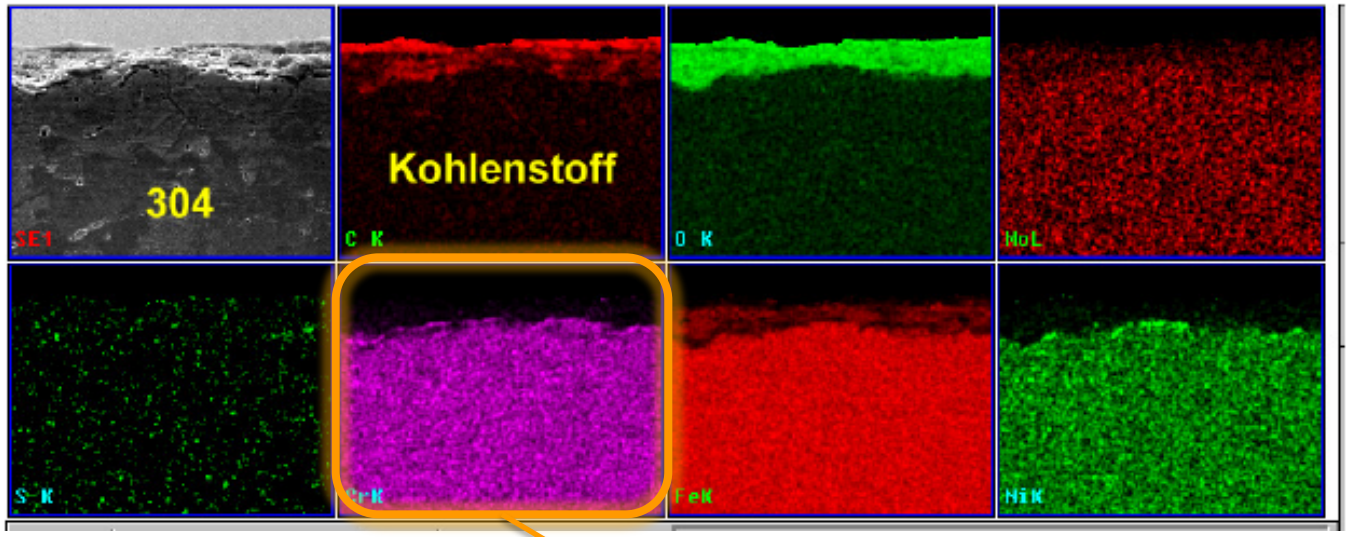
Test 1 + Lab





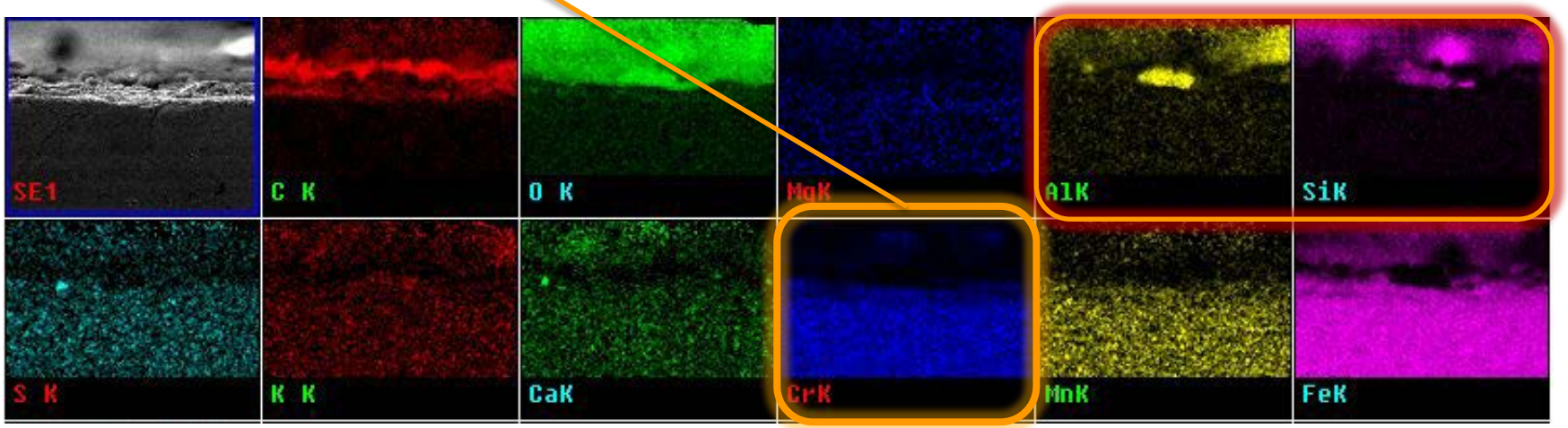
VATTENFALL

304 – 580C (Sample C and D)



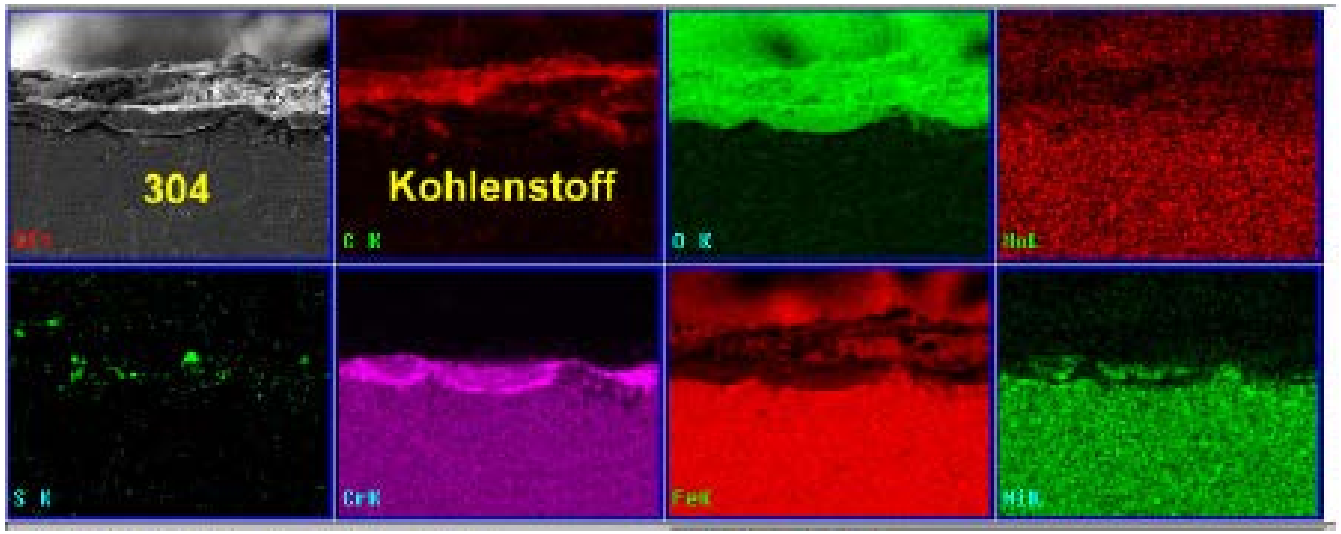
Sample C – A580

Sample D – L580

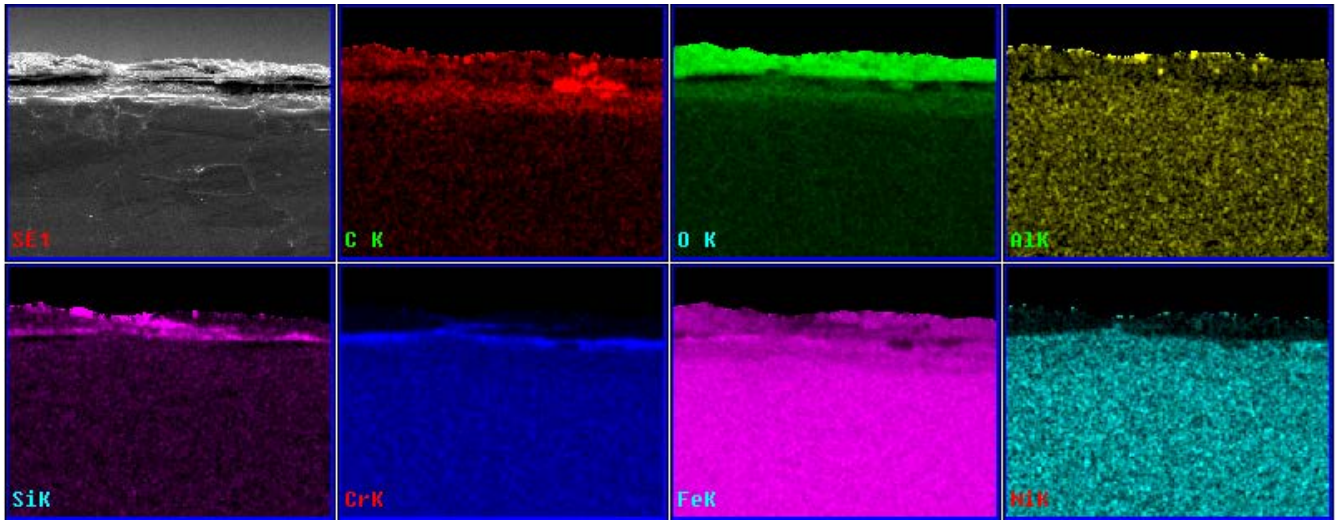


VATTENFALL

304 – 650C (Sample P and O)



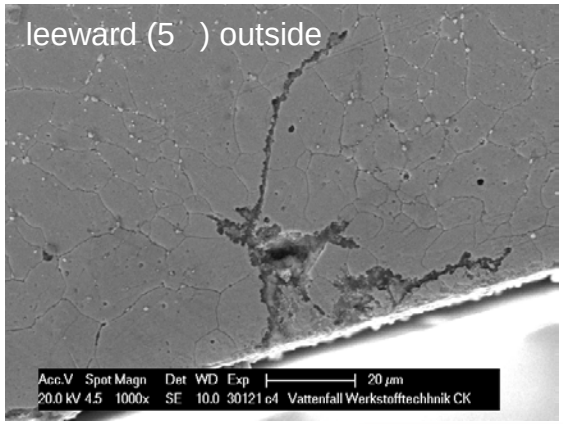
Sample P – A650

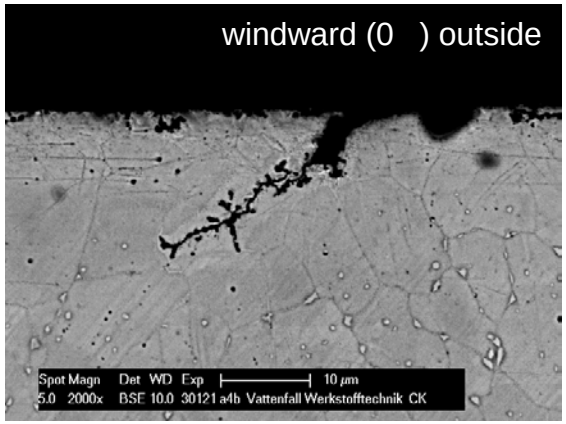


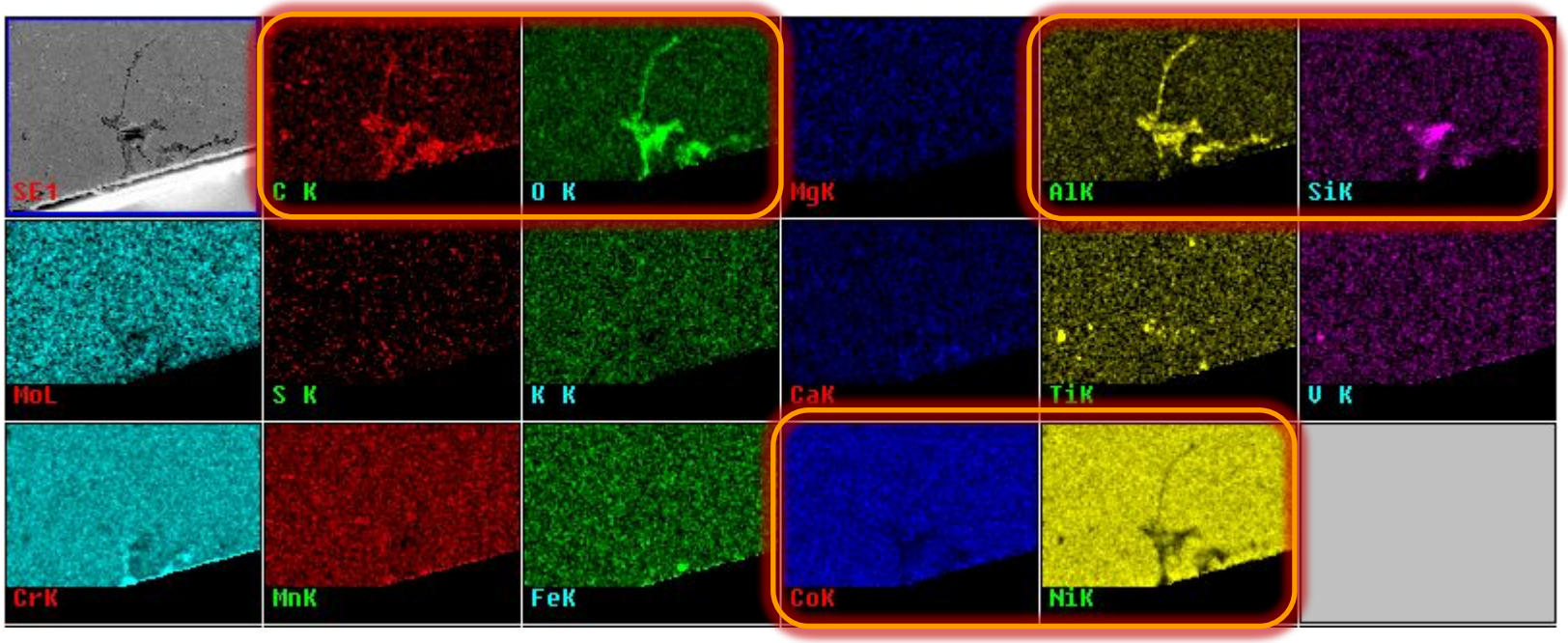
Sample O – L650

VATTENFALL

617 – 580C (Sample N)

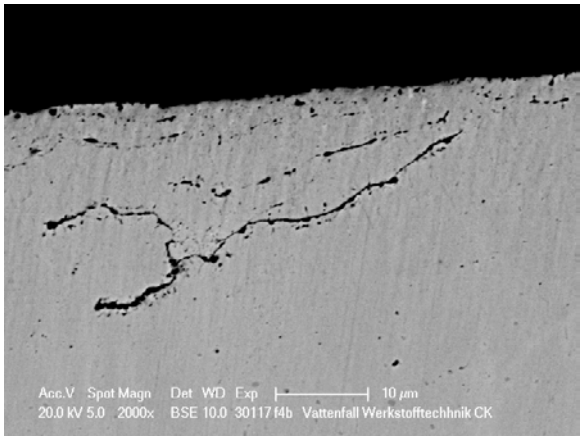


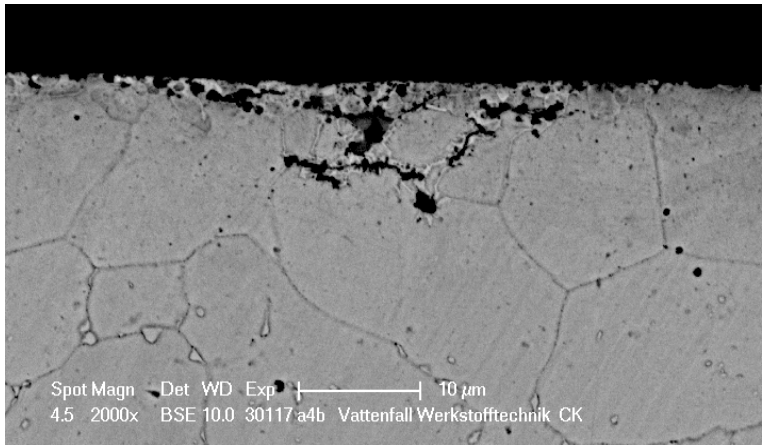


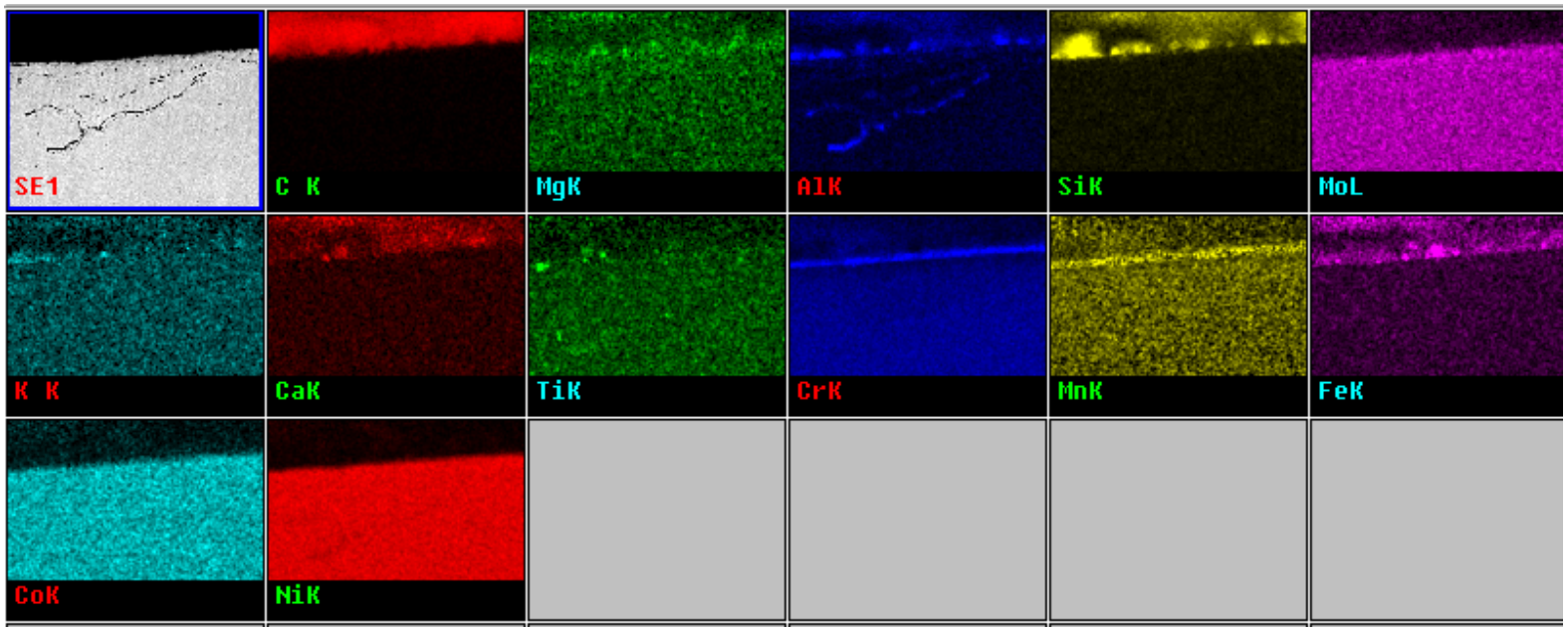


VATTENFALL

617 – 650C (Sample H)







VATTENFALL

Conclusion OxyCorr

- Corrosion as expected more for low alloyed steel T92 and less for high alloyed austenitics
- However it seems that alloy 617 could be susceptible to more attack.
- Steel with higher Cr content for 580C
- Stainless steels form protective oxide layer at 650 which appears to be affected by prolonged exposure
- Stainless steels more effective at 650 than 580

The work performed in the frame of the OxyCorr Project was partly funded by the **RFCS Research Program of the European Commission** (**RFCR-CT-2009-00005**). The authors are very grateful to the European Commission for the support.


alexander.gerhardt@vattenfall.de