

PROCESS CHEMISTRY CENTRE



Skyrec

December 16th 2009



SUOMEN SOODAKATTILAYHDISTYS
FINNISH RECOVERY BOILER COMMITTEE

Skyrec - project

1. High temperature behavior of steels under alkali sulfates and chlorides containing synthetic ashes in reducing atmosphere

Temperatures: 450°C, 500°C, 550°C, 600°C

Salts:

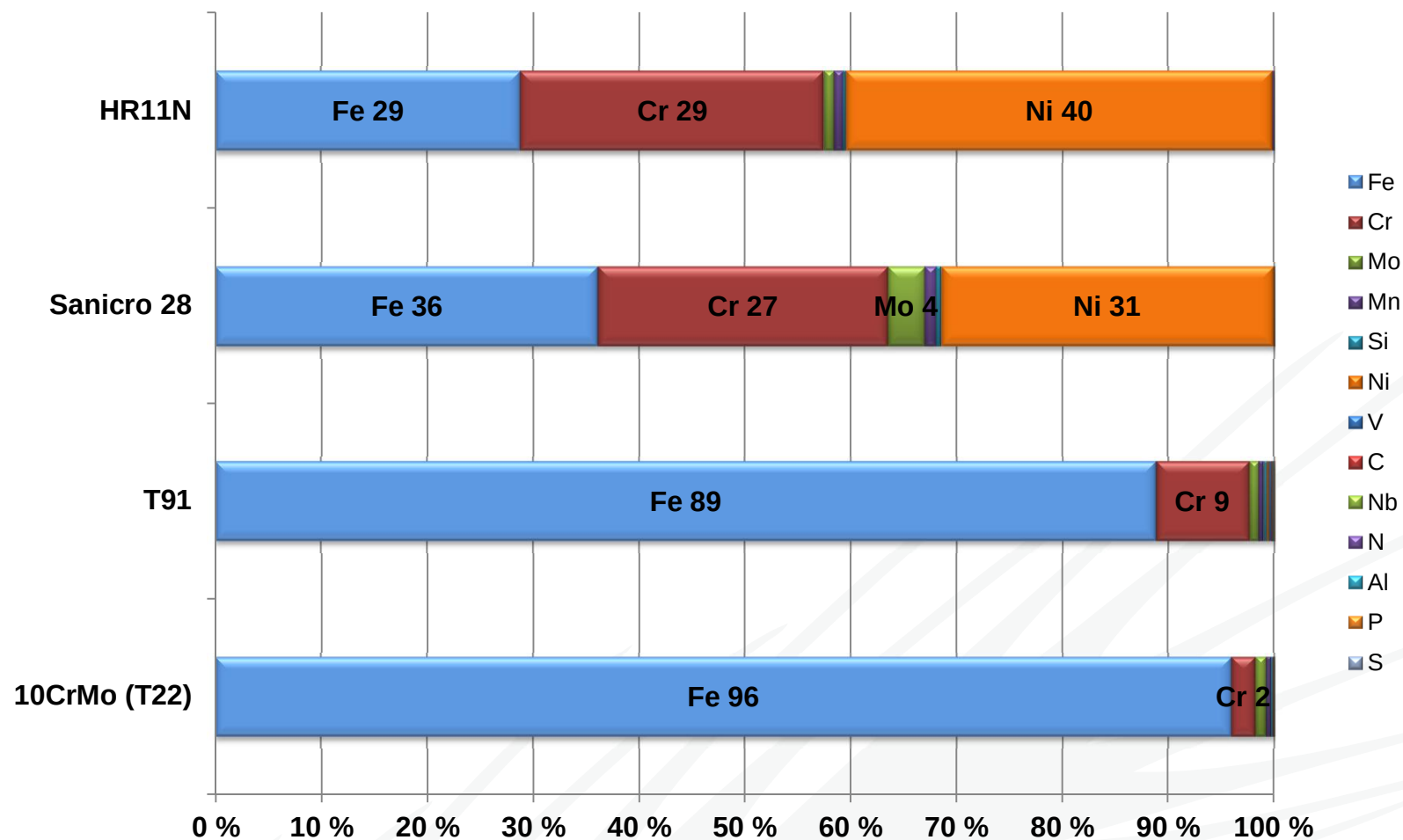
- Salt 5 - Na_2SO_4
- Salt 8 - $\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{NaCl} + \text{KCl}$
- Salt 9 - $\text{Na}_2\text{SO}_4 + \text{NaCl}$
- Salt 10 - $\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{KCl}$

Steels:

10CrMo9-10
T91
S28
HR11N

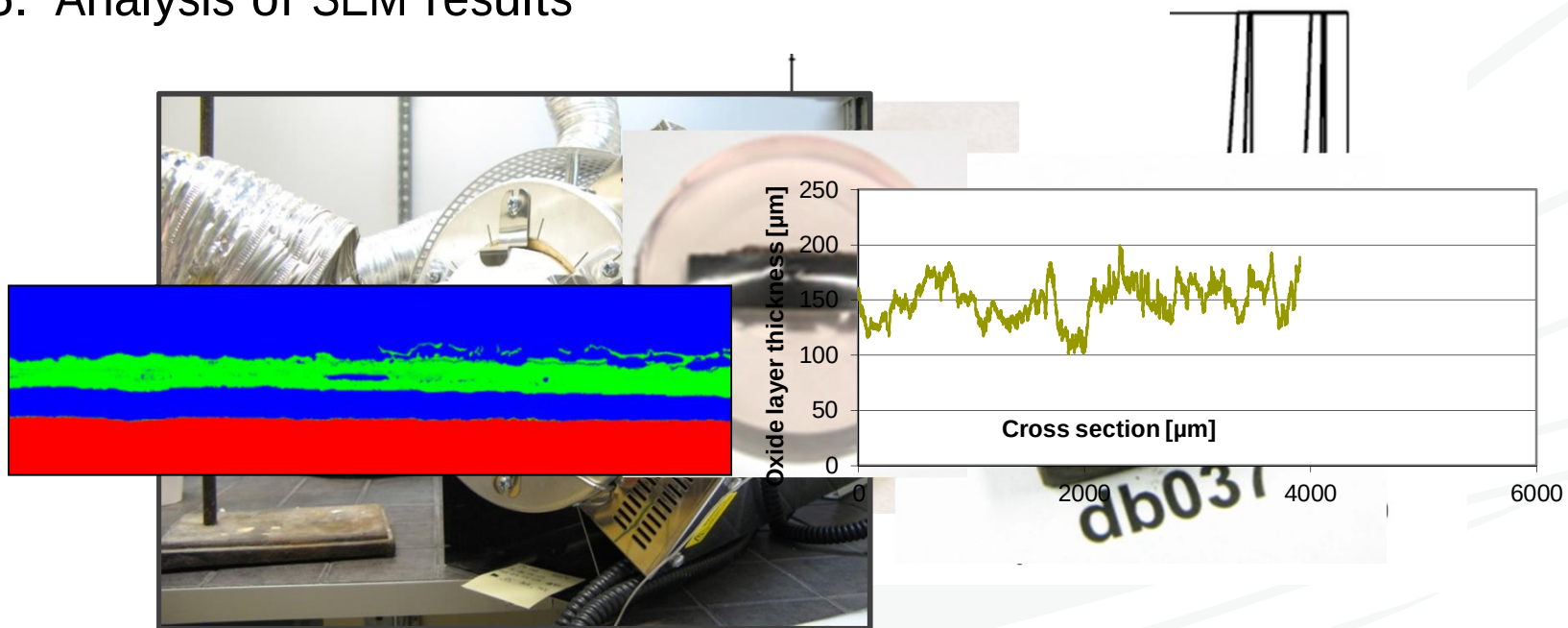
Atmosphere: reducing (5% CO + 95% N₂ – 2 l/min)

Skyrec - tested steels composition

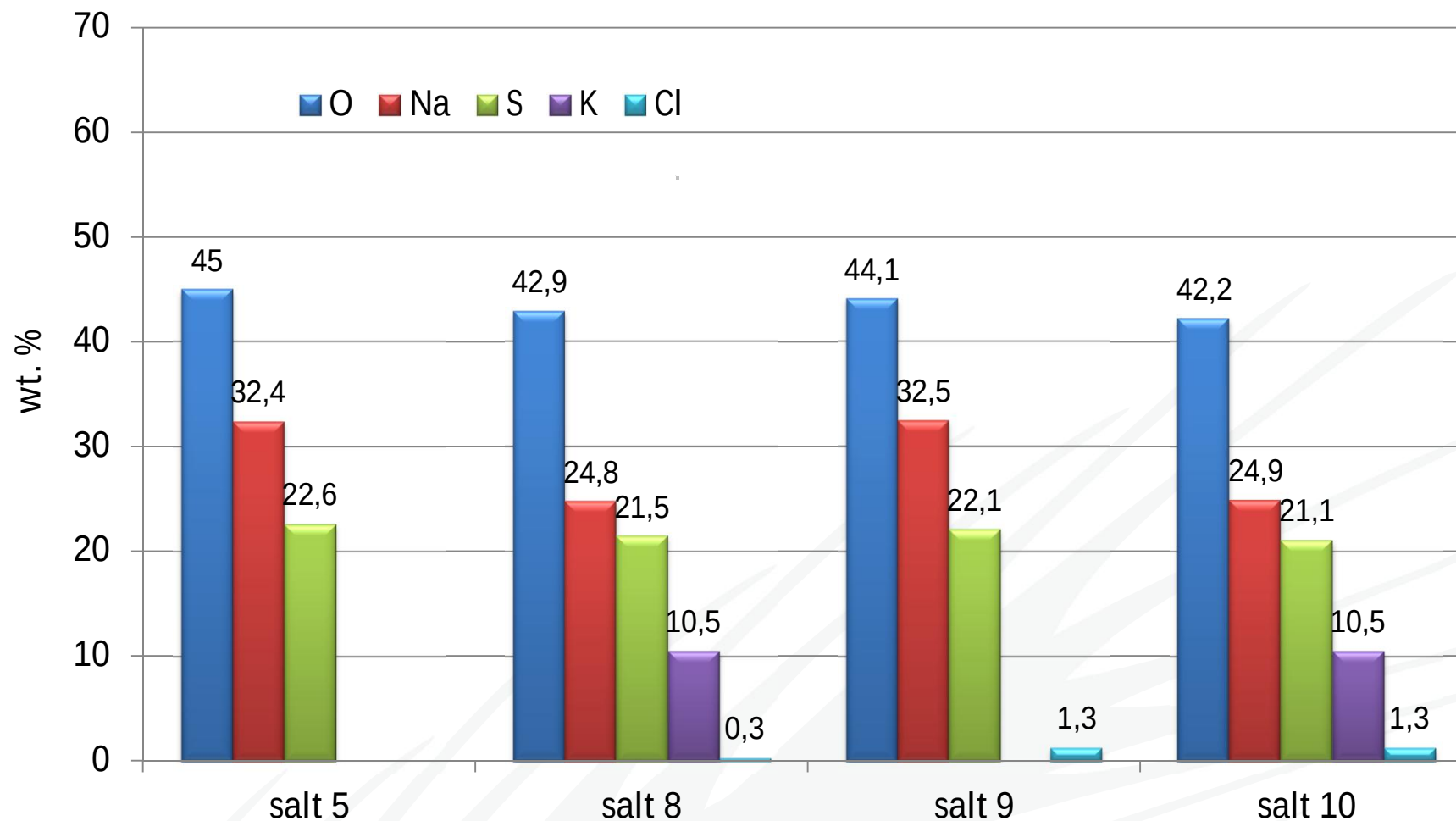


Laboratory method for HT corrosion tests

1. Preparation of salts
2. Preparation of steel samples for the experiment
3. Tube furnace tests
4. Preparation of samples for SEM/EDXA
5. Analysis of SEM results



Skyrec – synthetic ashes composition



Skyrec - corrosion test matrix - Na₂SO₄

	Salt	Steel	Temp	Corrosion products thickness
1	Na ₂ SO ₄	10CrMo	450	
2	Na ₂ SO ₄	T91	450	
3	Na ₂ SO ₄	Sanicro 28	450	
4	Na ₂ SO ₄	HR11N	450	
5	Na ₂ SO ₄	10CrMo	450	
6	Na ₂ SO ₄	10CrMo	500	
7	Na ₂ SO ₄	T91	500	
8	Na ₂ SO ₄	Sanicro 28	500	
9	Na ₂ SO ₄	HR11N	500	
10	Na ₂ SO ₄	T91	500	
11	Na ₂ SO ₄	10CrMo	550	
12	Na ₂ SO ₄	T91	550	
13	Na ₂ SO ₄	Sanicro 28	550	
14	Na ₂ SO ₄	HR11N	550	
15	Na ₂ SO ₄	Sanicro 28	550	
16	Na ₂ SO ₄	10CrMo	600	24
17	Na ₂ SO ₄	T91	600	6
18	Na ₂ SO ₄	Sanicro 28	600	
19	Na ₂ SO ₄	HR11N	600	2
20	Na ₂ SO ₄	HR11N	600	

Salt 5 characteristic:

T₀ = 884°C

No Cl⁻

No K⁺

Skyrec - corrosion test matrix - Na₂SO₄+NaCl

	Salt	Steel	Temp	Corr prod. thickness
41	Na ₂ SO ₄ +NaCl	10CrMo	450	1
42	Na ₂ SO ₄ +NaCl	T91	450	
43	Na ₂ SO ₄ +NaCl	Sanicro 28	450	
44	Na ₂ SO ₄ +NaCl	HR11N	450	
45	Na ₂ SO ₄ +NaCl	10CrMo	450	
46	Na ₂ SO ₄ +NaCl	10CrMo	500	2
47	Na ₂ SO ₄ +NaCl	T91	500	
48	Na ₂ SO ₄ +NaCl	Sanicro 28	500	
49	Na ₂ SO ₄ +NaCl	HR11N	500	
50	Na ₂ SO ₄ +NaCl	T91	500	
51	Na ₂ SO ₄ +NaCl	10CrMo	550	13
52	Na ₂ SO ₄ +NaCl	T91	550	
53	Na ₂ SO ₄ +NaCl	Sanicro 28	550	
54	Na ₂ SO ₄ +NaCl	HR11N	550	
55	Na ₂ SO ₄ +NaCl	Sanicro 28	550	
56	Na ₂ SO ₄ +NaCl	10CrMo	600	62
57	Na ₂ SO ₄ +NaCl	T91	600	
58	Na ₂ SO ₄ +NaCl	Sanicro 28	600	
59	Na ₂ SO ₄ +NaCl	HR11N	600	
60	Na ₂ SO ₄ +NaCl	HR11N	600	

Salt 9 characteristic:

T₀ = 621°C

1.3 wt% of Cl⁻

No K⁺

Skyrec - corrosion test matrix - $\text{Na}_2\text{SO}_4 + \text{NaCl} + \text{K}_2\text{SO}_4 + \text{KCl}$

	Salt	Steel	Temp	Corr prod. thickness
21	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{NaCl} + \text{KCl}$	10CrMo	450	11
22	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{NaCl} + \text{KCl}$	T91	450	9
23	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{NaCl} + \text{KCl}$	Sanicro 28	450	
24	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{NaCl} + \text{KCl}$	HR11N	450	
25	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{NaCl} + \text{KCl}$	10CrMo	450	3
26	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{NaCl} + \text{KCl}$	10CrMo	500	3
27	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{NaCl} + \text{KCl}$	T91	500	
28	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{NaCl} + \text{KCl}$	Sanicro 28	500	
29	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{NaCl} + \text{KCl}$	HR11N	500	
30	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{NaCl} + \text{KCl}$	T91	500	
31	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{NaCl} + \text{KCl}$	10CrMo	550	
32	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{NaCl} + \text{KCl}$	T91	550	
33	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{NaCl} + \text{KCl}$	Sanicro 28	550	
34	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{NaCl} + \text{KCl}$	HR11N	550	
35	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{NaCl} + \text{KCl}$	Sanicro 28	550	
36	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{NaCl} + \text{KCl}$	10CrMo	600	334
37	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{NaCl} + \text{KCl}$	T91	600	
38	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{NaCl} + \text{KCl}$	Sanicro 28	600	
39	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{NaCl} + \text{KCl}$	HR11N	600	
40	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{NaCl} + \text{KCl}$	HR11N	600	

Salt 8 characteristic:

$T_0 = 526^\circ\text{C}$

0.3 wt% of Cl^-

10.5 wt% of K^+

Skyrec - corrosion test matrix - $\text{Na}_2\text{SO}_4 + \text{KCl} + \text{K}_2\text{SO}_4$

	Salt	Steel	Temp	Corr prod. thickness
61	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{KCl}$	10CrMo	450	
62	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{KCl}$	T91	450	
63	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{KCl}$	Sanicro 28	450	
64	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{KCl}$	HR11N	450	
65	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{KCl}$	10CrMo	450	
66	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{KCl}$	10CrMo	500	
67	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{KCl}$	T91	500	
68	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{KCl}$	Sanicro 28	500	
69	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{KCl}$	HR11N	500	
70	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{KCl}$	T91	500	
71	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{KCl}$	10CrMo	550	2
72	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{KCl}$	T91	550	2
73	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{KCl}$	Sanicro 28	550	2
74	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{KCl}$	HR11N	550	2
75	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{KCl}$	Sanicro 28	550	2
76	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{KCl}$	10CrMo	600	306
77	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{KCl}$	T91	600	54
78	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{KCl}$	Sanicro 28	600	53
79	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{KCl}$	HR11N	600	76
80	$\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{KCl}$	HR11N	600	24

Salt 10 characteristic:

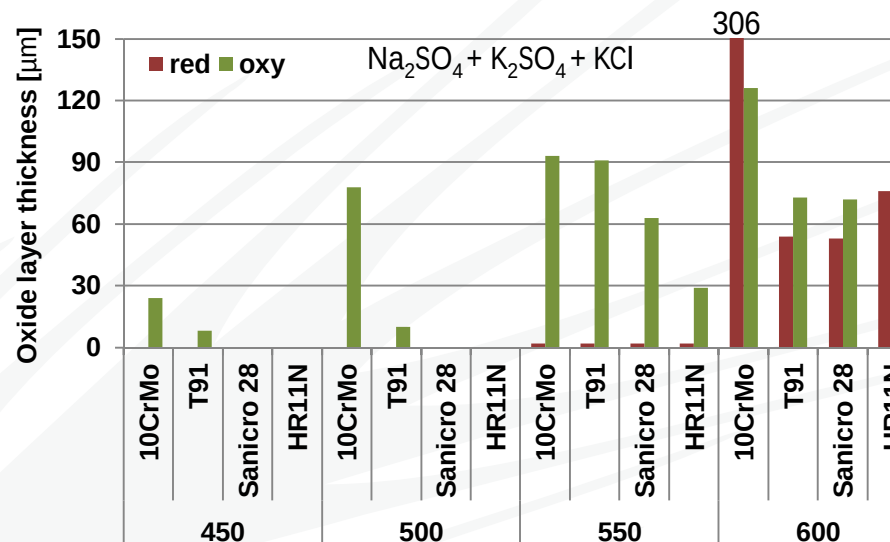
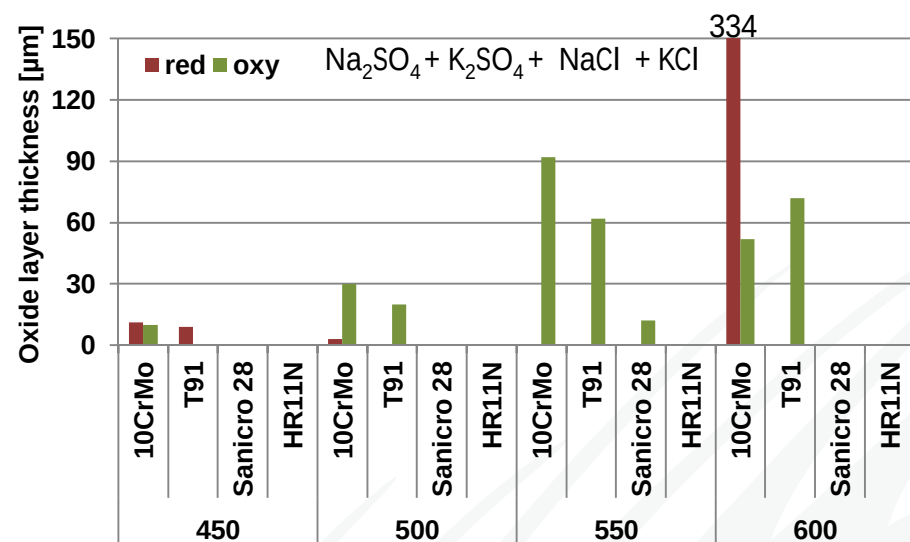
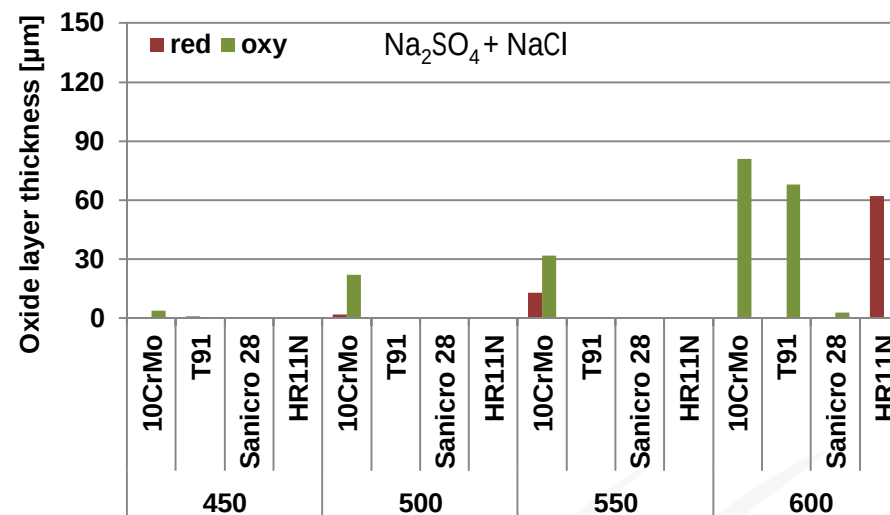
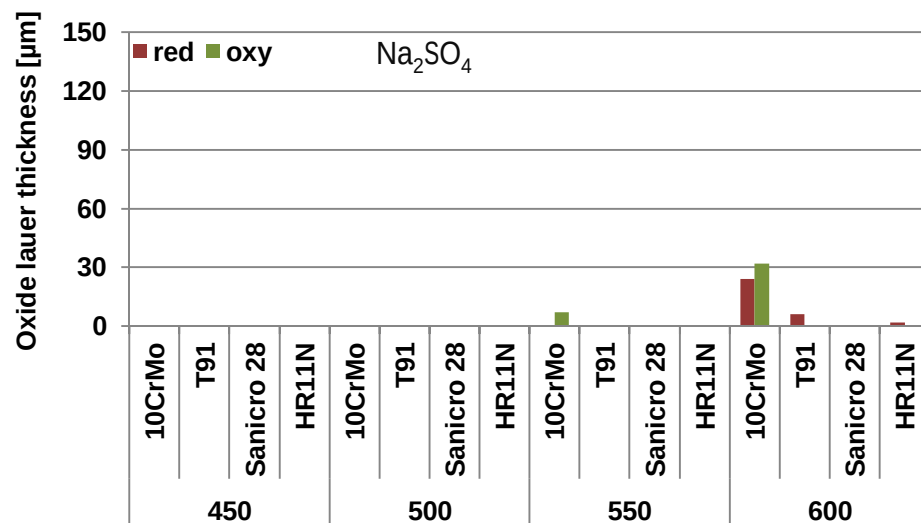
$T_0 = 522^\circ\text{C}$

1.3 wt% of Cl^-

10.5 wt% of K^+

←← {Oxide layer + internal attack} thickness

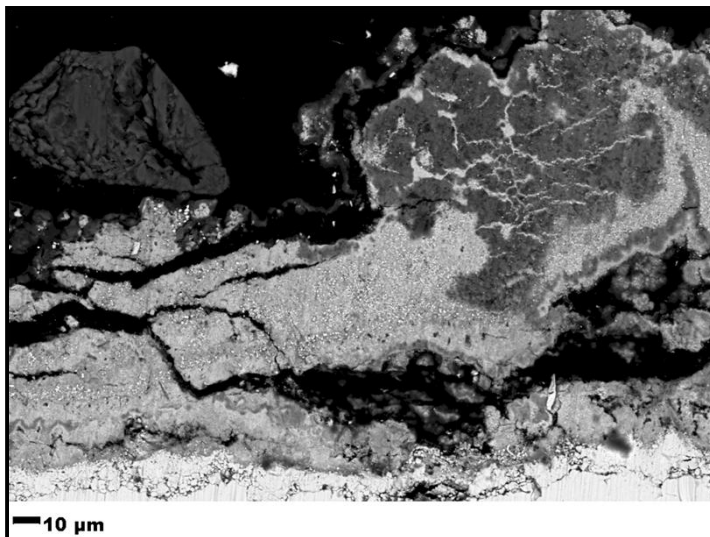
Skyrec – reducing vs ambient atmosphere



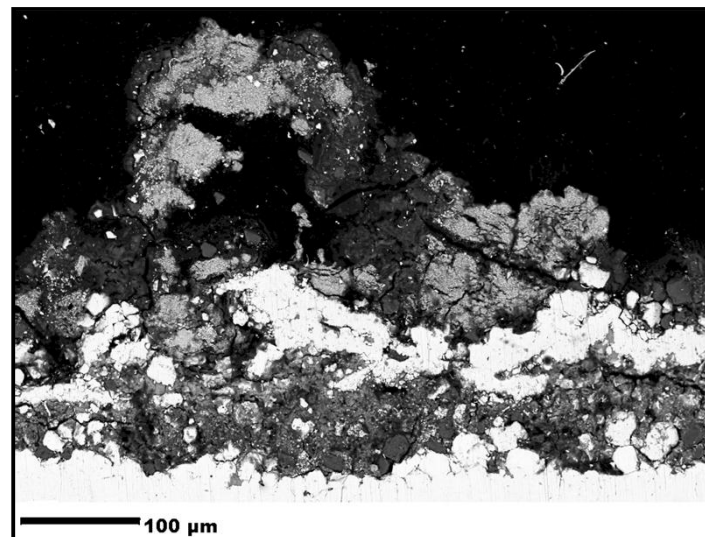
Skyrec – results

10CrMo, 600°C

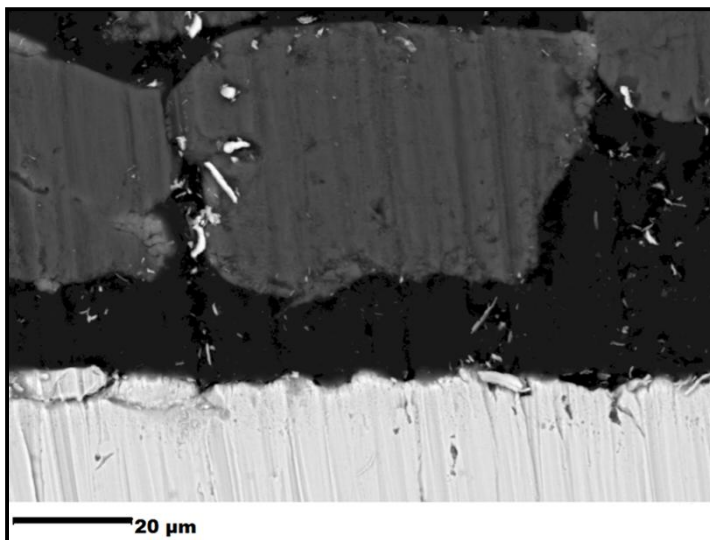
$T_0 = 884^\circ\text{C}$
No Cl
No K
Salt 5
24 μm



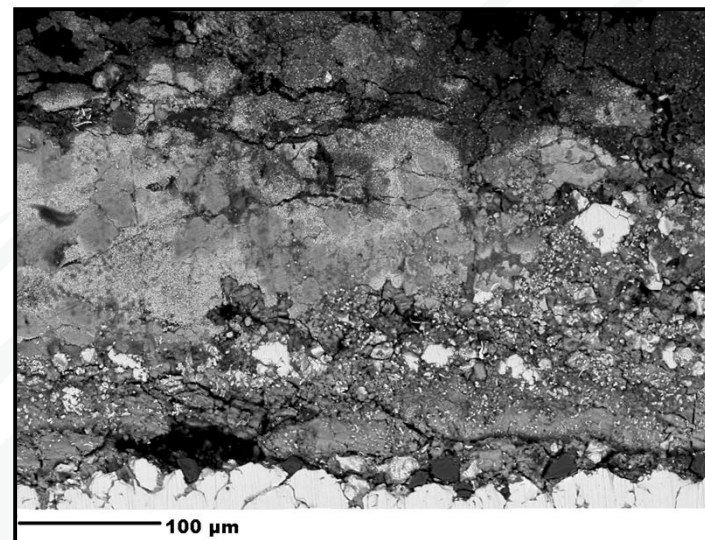
$T_0 = 526^\circ\text{C}$
0.3 mol% of Cl
13 mol% of K
Salt 8
334 μm



$T_0 = 621^\circ\text{C}$
1.7 mol% of Cl
No K
Salt 9
0 μm

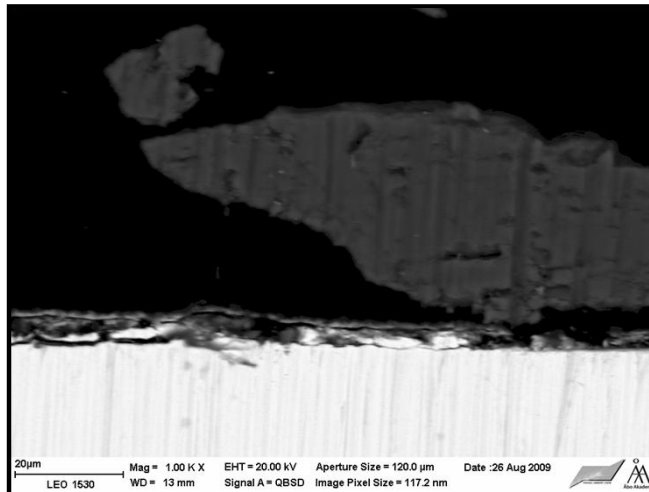


$T_0 = 522^\circ\text{C}$
1.7 mol% of Cl
13 mol% of K
Salt 10
306 μm

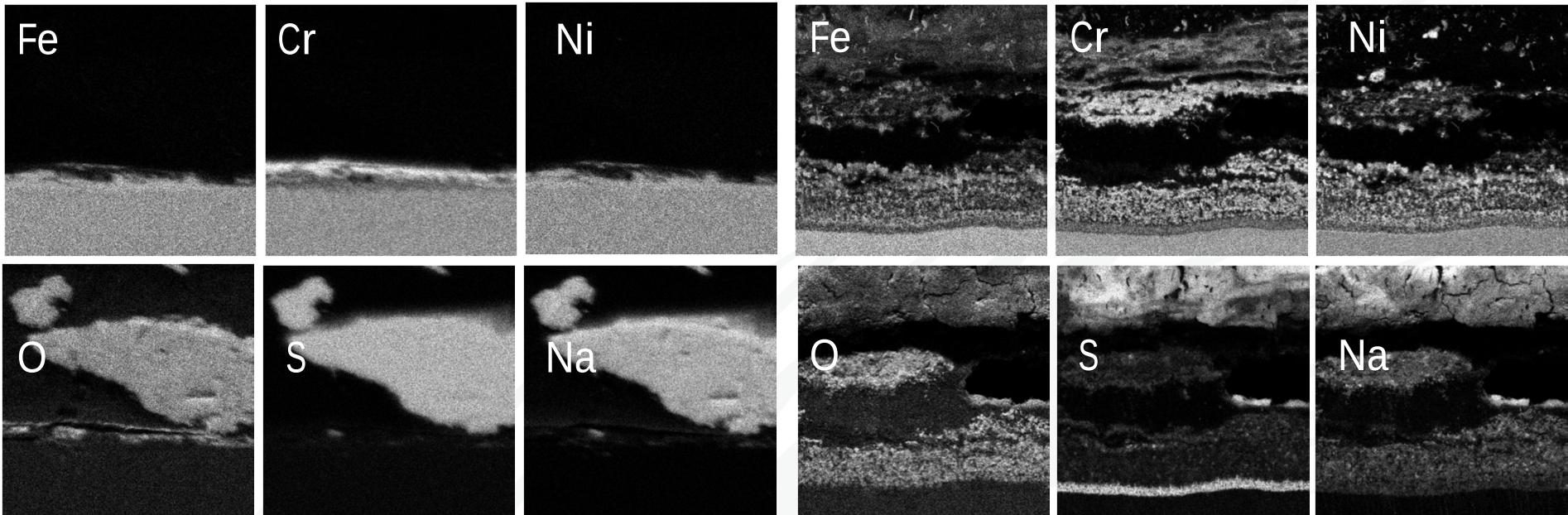
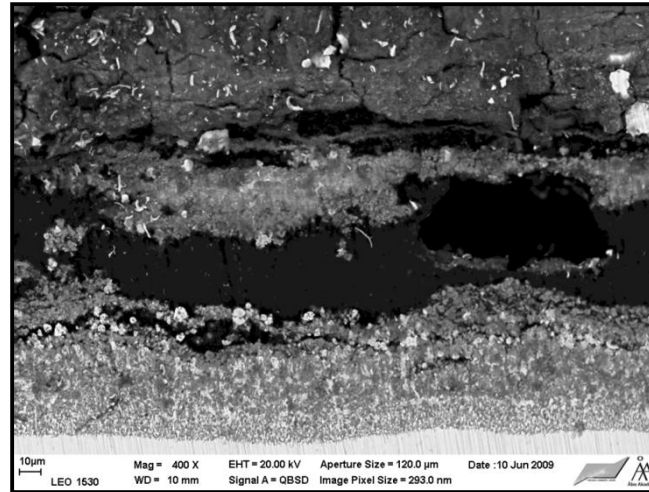


Skyrec – results, 600°C

HR11N, red
 Na_2SO_4
Salt 5
2 μm

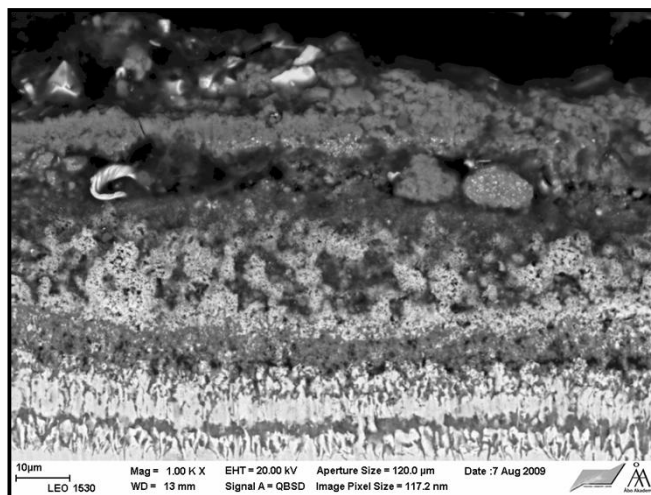


HR11N, red
 Na_2SO_4 + NaCl
Salt 9
62 μm

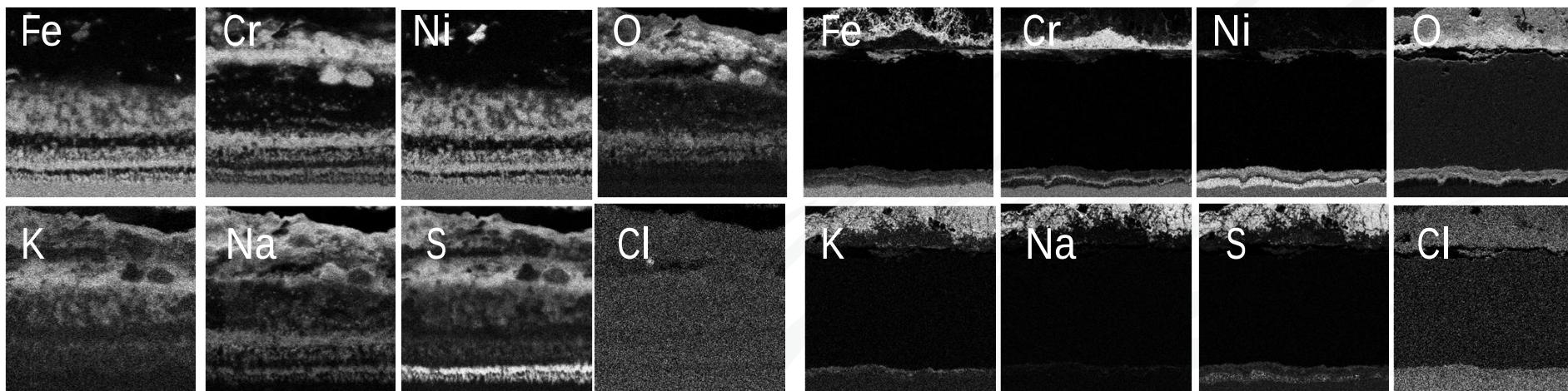
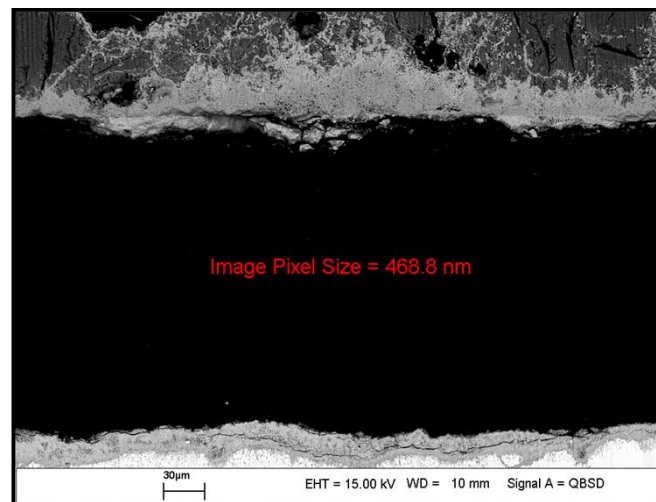


Skyrec – results, 600°C

S28, red
 Na_2SO_4 +
 K_2SO_4 + KCl
 Salt 10
 53 μm



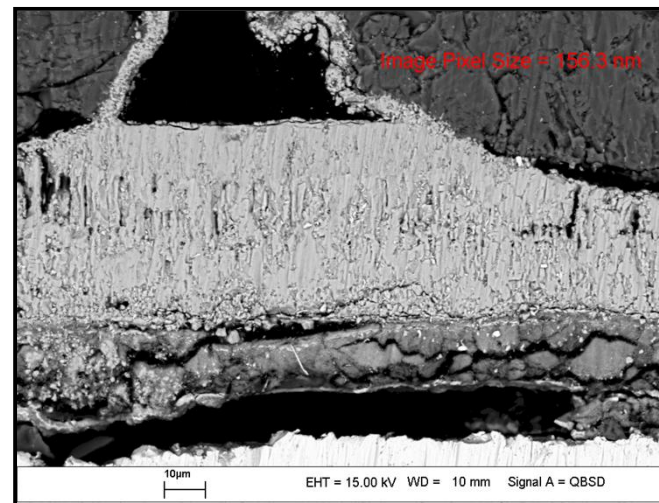
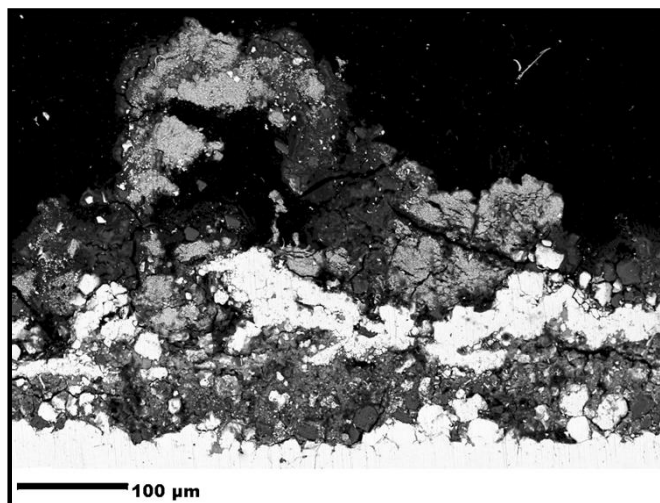
S28, ambient
 Na_2SO_4 +
 K_2SO_4 + KCl
 Salt 10
 72 μm



Skyrec – results, 600°C

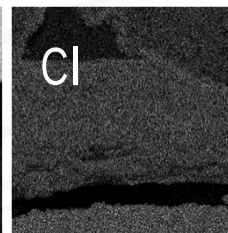
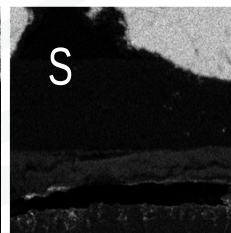
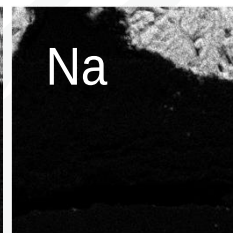
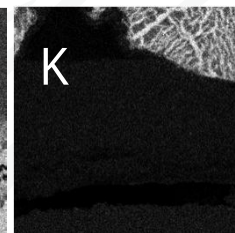
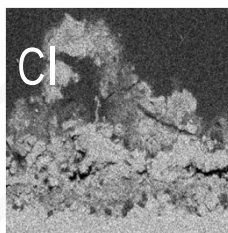
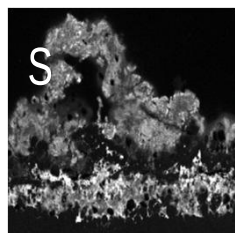
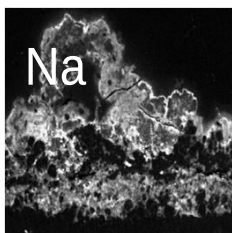
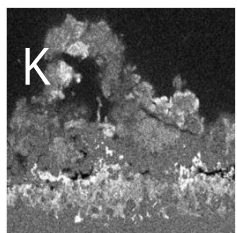
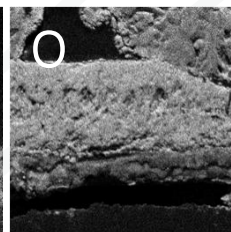
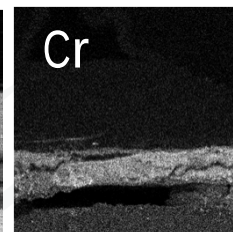
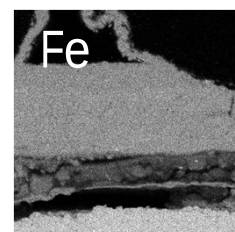
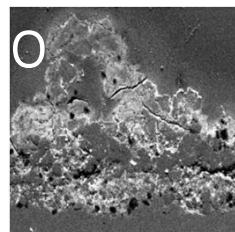
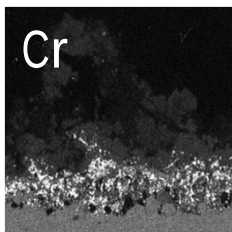
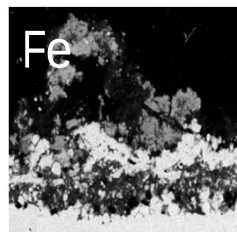
10CrMo, red
 $\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4$
+ NaCl + KCl
Salt 8

334 μm



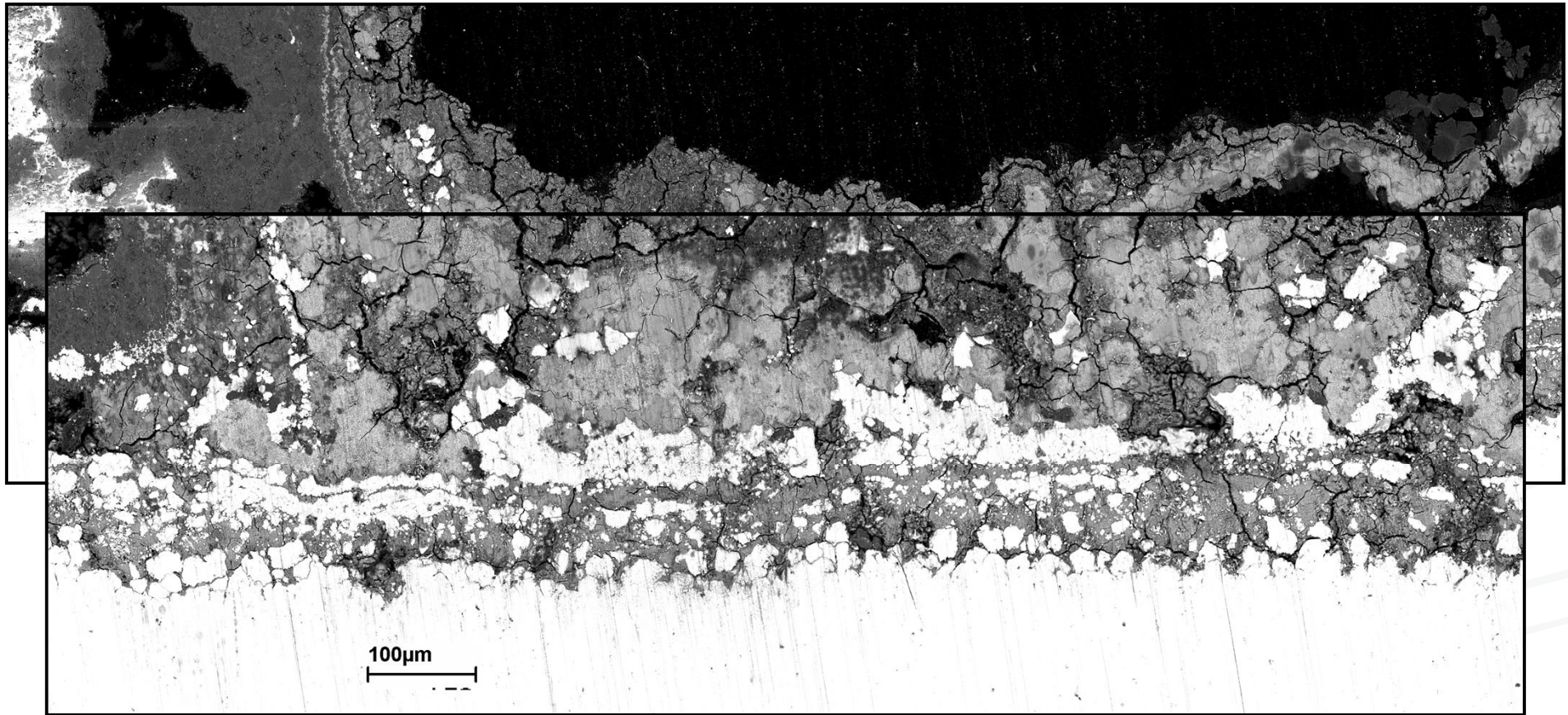
10CrMo,
ambient
 $\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4$
+ NaCl + KCl
Salt 8

52 μm



Skyrec – results

10CrMo at 600°C with salt 8 attacked by the grain boundary corrosion



Skyrec – preliminary conclusions

- Ambient atmosphere seems to be more harmful than reducing under tested temperature and salts
- K containing salts show more detrimental effect
 - especially $\geq 500^{\circ}\text{C}$ for low grade steels, $\geq 550^{\circ}\text{C}$ for all steels - at ambient conditions
 - $\geq 550^{\circ}\text{C}$ for all steels - at reducing conditions(T_0 of the K containing salts slightly above 500°C)
- In reducing conditions and high temperature:
 - Low grade steels are destroyed mainly by grain boundary corrosion
 - Austenitic steels undergo heavy Cr leaching
- *Sulfur* often found on the corrosion front, deep in the pores
- Reducing conditions induce mainly internal attack of the steel*
- In ambient conditions growth of the oxide layer is promoted*

* Under tested temperatures and salts

Skyrec – To be done

- Final reporting (date to be decided)
- Corroded samples will be reported in a printed version of the report
- All the results (SEM/EDX) will be delivered on the CD