



Ein Unternehmen der Salzgitter Gruppe

Corrosion of heat exchanger materials

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Aachen, den 5.06.2008

Oxidation and Passivation

550 °C

Low alloyed
steels

2.25 Cr-1Mo
St. 35.8

$\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$

600 – 1200 °C

Ferritic, austenitic steels
Ni-based alloys, IMP

Fe-9-12%Cr, Fe-18Cr-10Ni
MCrAlY, FeAl, NiAl

Oxide layers

Spinelle

Cr_2O_3

Al_2O_3

> 1200 °C

Ceramics

MoSi_2 , SiC ,
 Si_3N_4

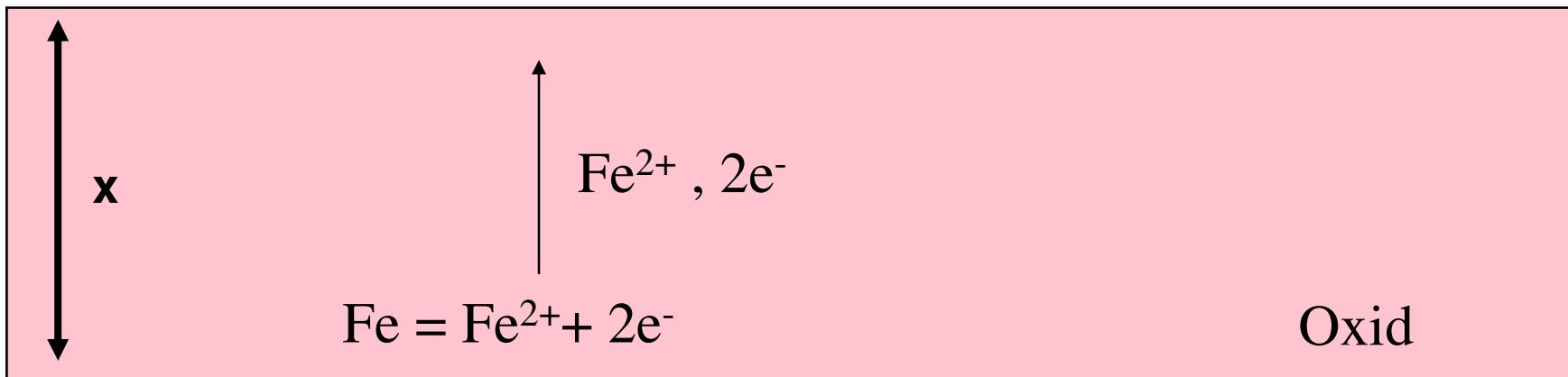
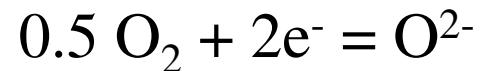
SiO_2

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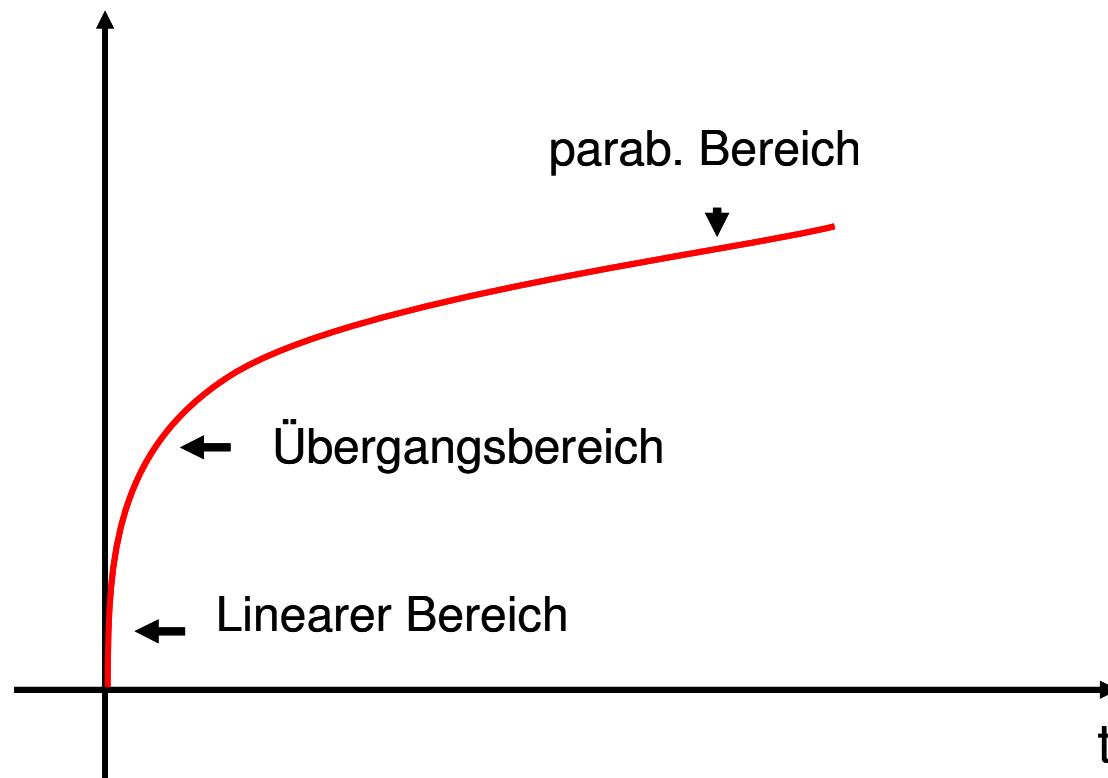
24/06/08

EDWW

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X or Δm



$$\frac{dx}{dt} = \frac{k' p}{x}$$

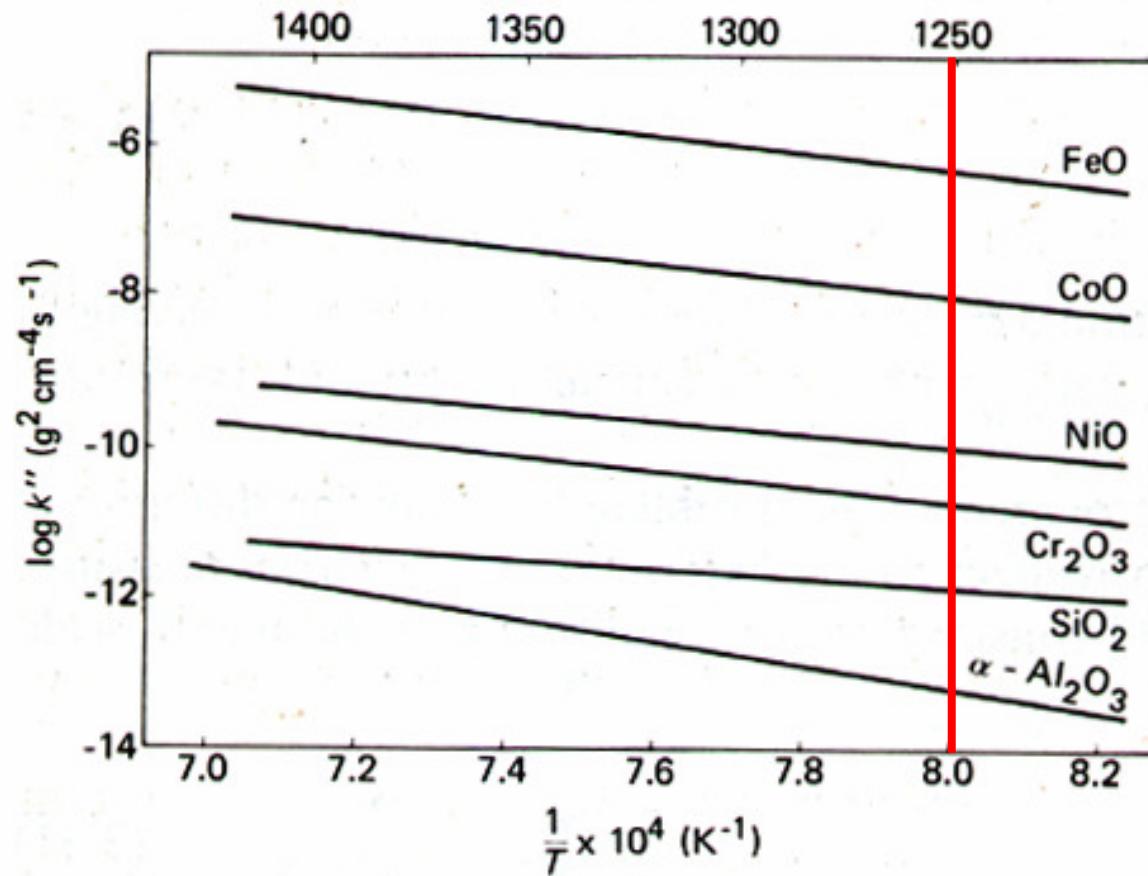
$$x^2 = 2k' p t$$

$$[k' p] = \text{cm}^2/\text{s}$$

$$[k'' p] = \text{g}^2 / \text{cm}^4 \text{ s}$$

Parabolic growth: Diffusion control

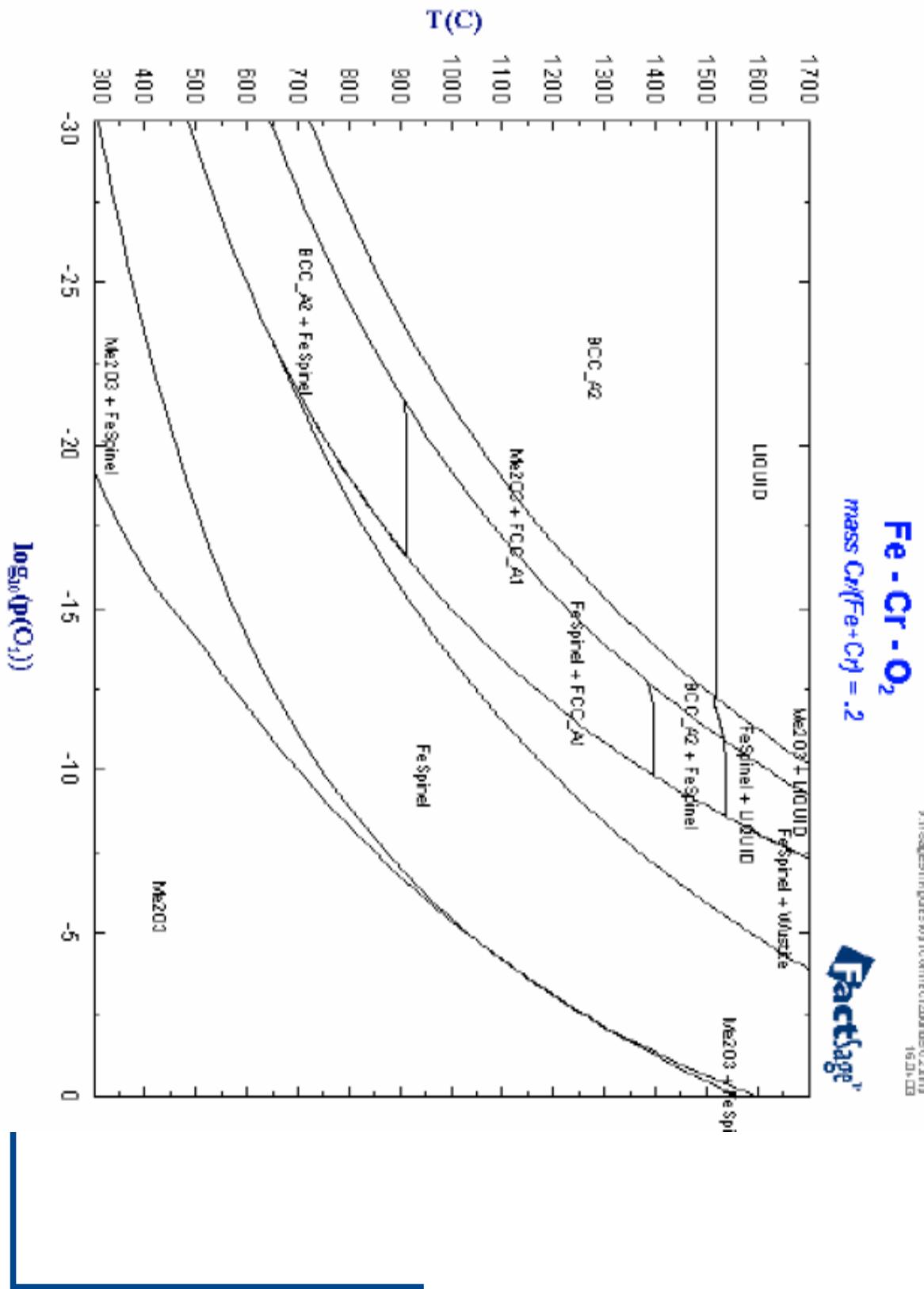
Parabolic constants of oxides



Oxidation and Passivation

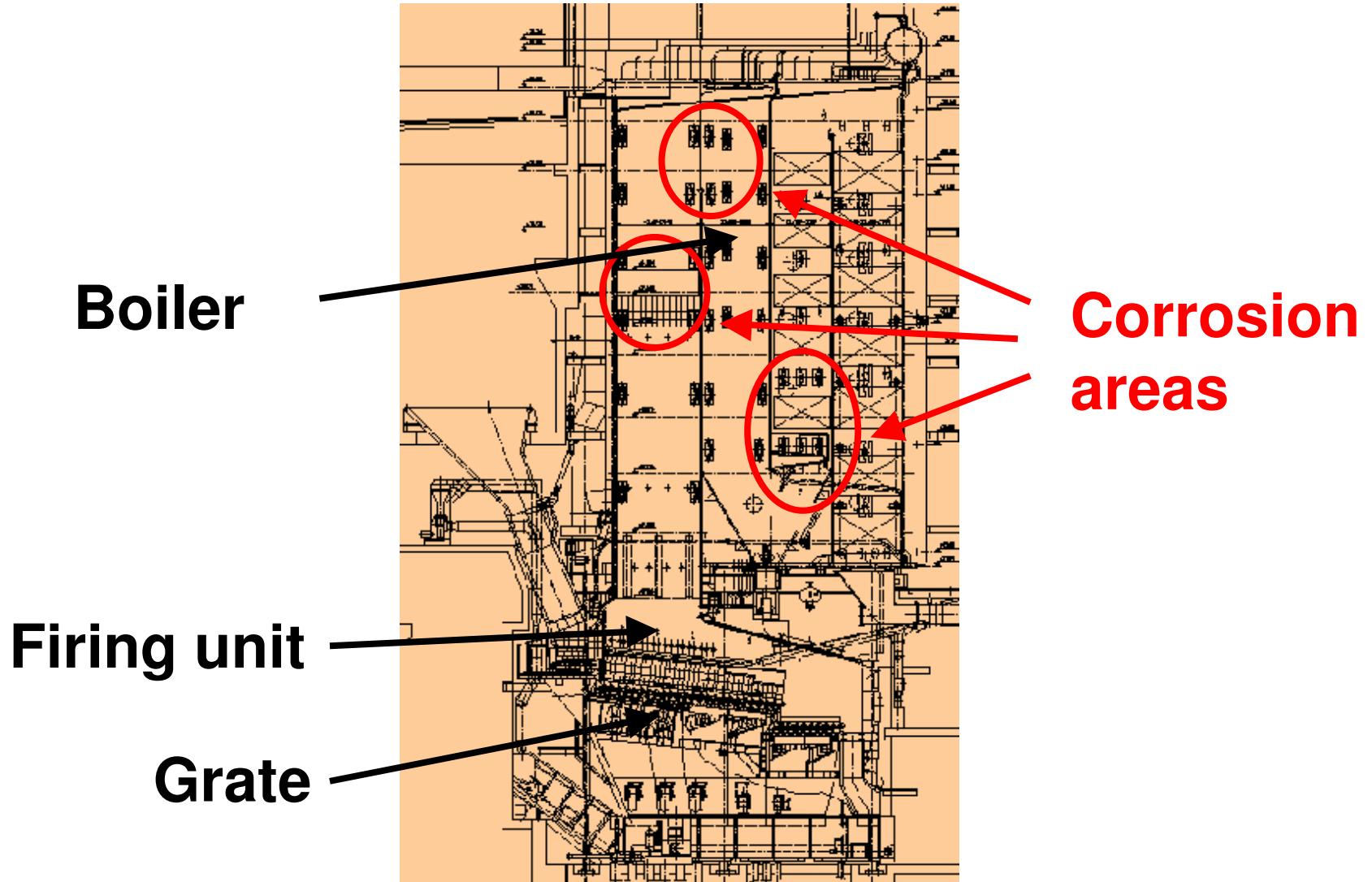
Introduction

**BALZGITTER
MANNESMANN
FORSCHUNG**
Ein Unternehmen der Salzgitter Gruppe



Corrosion in power plants

Introduction



Gaseous and solid combustion products

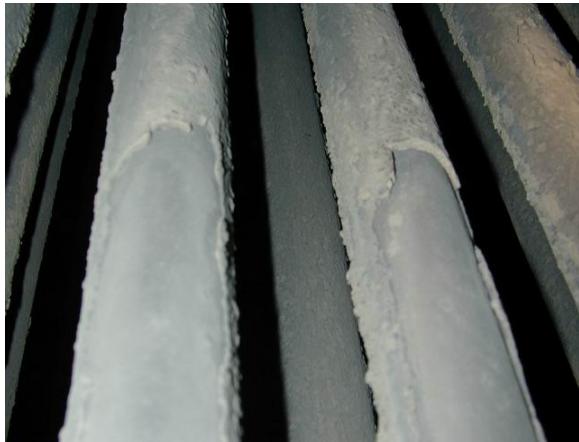
	Cl wt.%	S wt.%	Na ₂ O wt.%	K ₂ O wt.%	CaO mg/kg	Pb mg/kg	Zn mg/kg
RA	0.5	0.2	1.5	0.3	3.0	1000	1500
Altholz	0.01-0.44	0.02-0.58	0.05	0.7	4.5	40-700	170-950
Holz	0.005-0.02	0.02-0.1	0.02-0.05	0.2-0.5	0.35-1	<5	<35
Braunkohle	0.005- 0.012	0.1-2	0.01-0.3	0.002- 0.1	2-3.5	1.5-5	20-30
Steinkohle	<0.2	0.5-1.1	0.01-0.1	0.05-0.4	0.05-5.5	20-80	20-120

Chlorine > Sulfur > heavy metals > Alkali-elements

Waste > Biomass > Coal

Corrosion in power plants

Materials issues

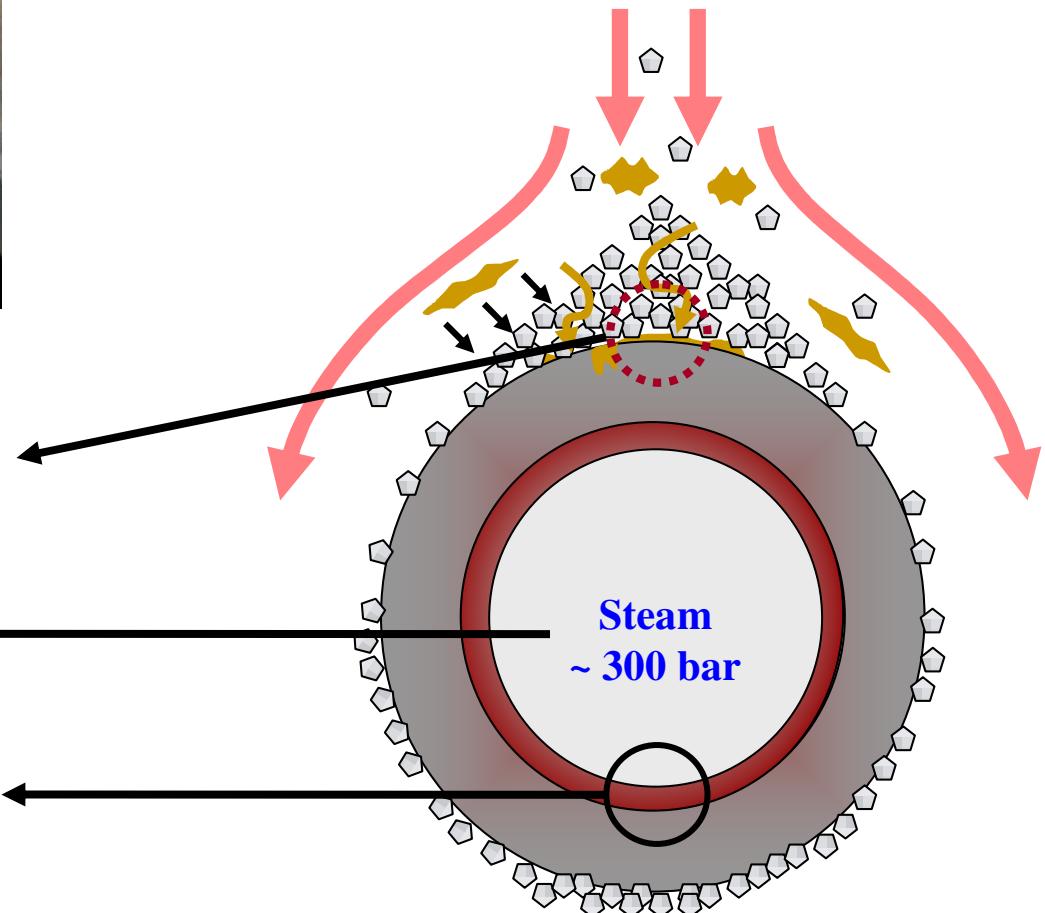


Combustion gas (CO, HCl, SO₂, ..., solids)

Fireside Corrosion
Condensate-Metal-Gas

Creep strength

Steam oxidation

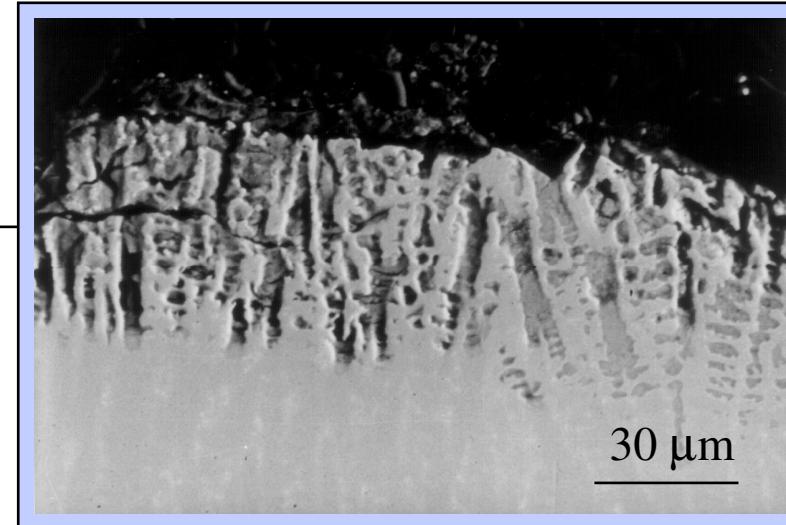
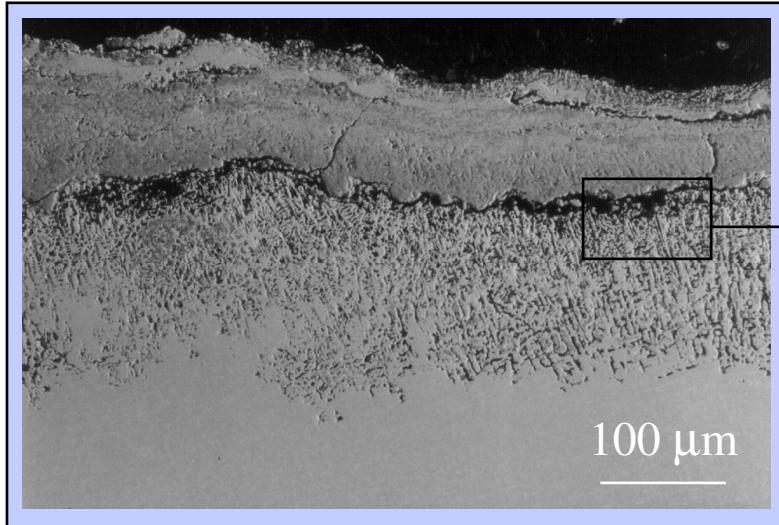


Corrosion of heat exchangers **Examples**



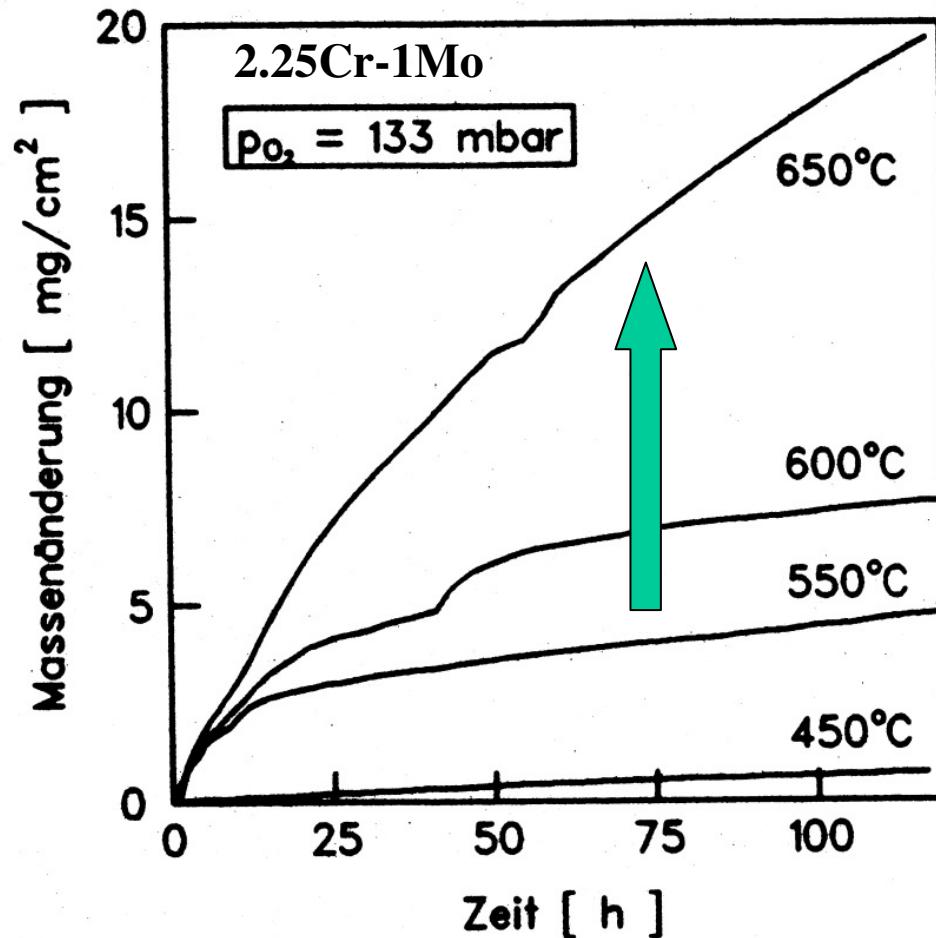
Corrosion of heat exchangers

Examples



Corrosion layer of (Fe, Cr, Ni) - oxides, Metal-chlorides (Ni, Cr, Fe)

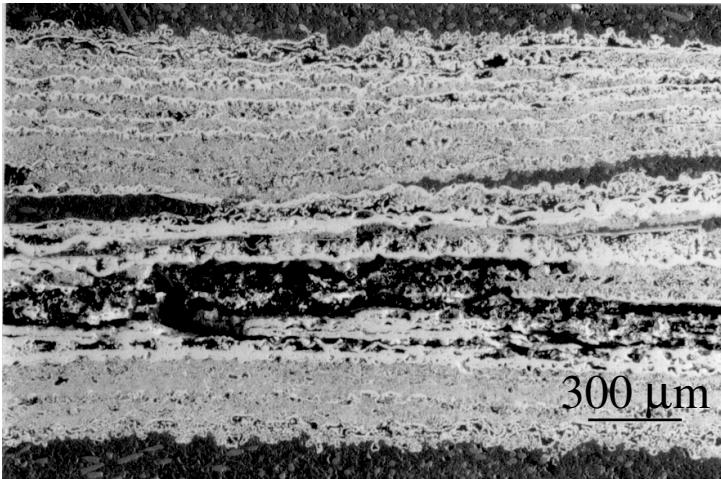
Corrosion penetrates along dendritic structures

Ar - 500 vppm HCl – O₂

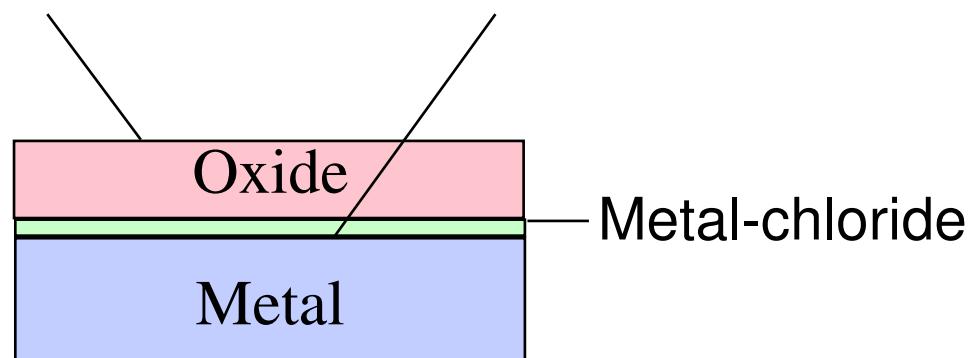
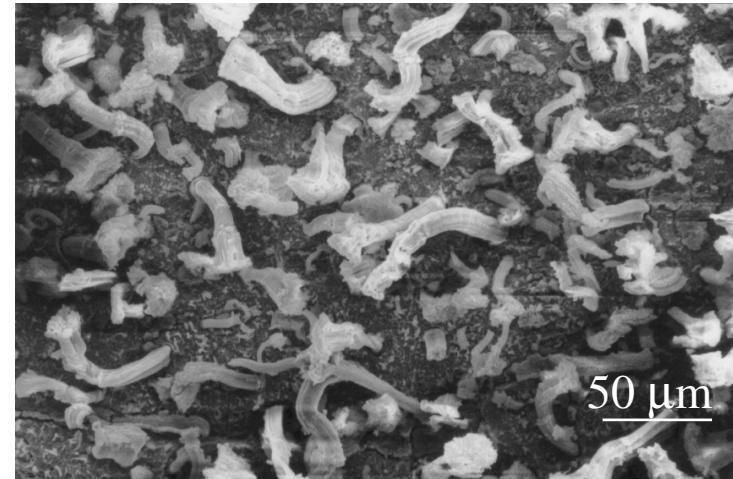
Strong accelerated oxidation

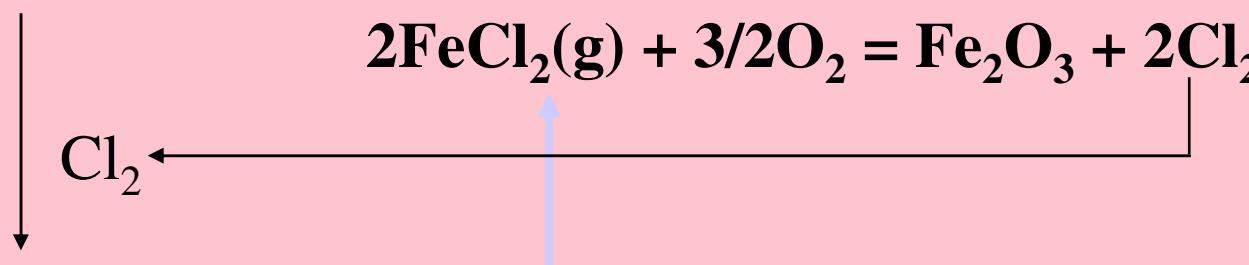
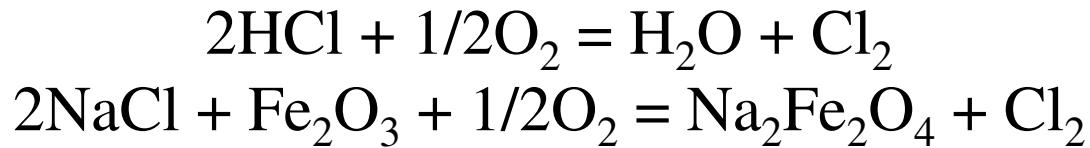
Temperature dependent

Thick and porous oxide layer



Formation of FeCl_2 at the Metal/oxide interface

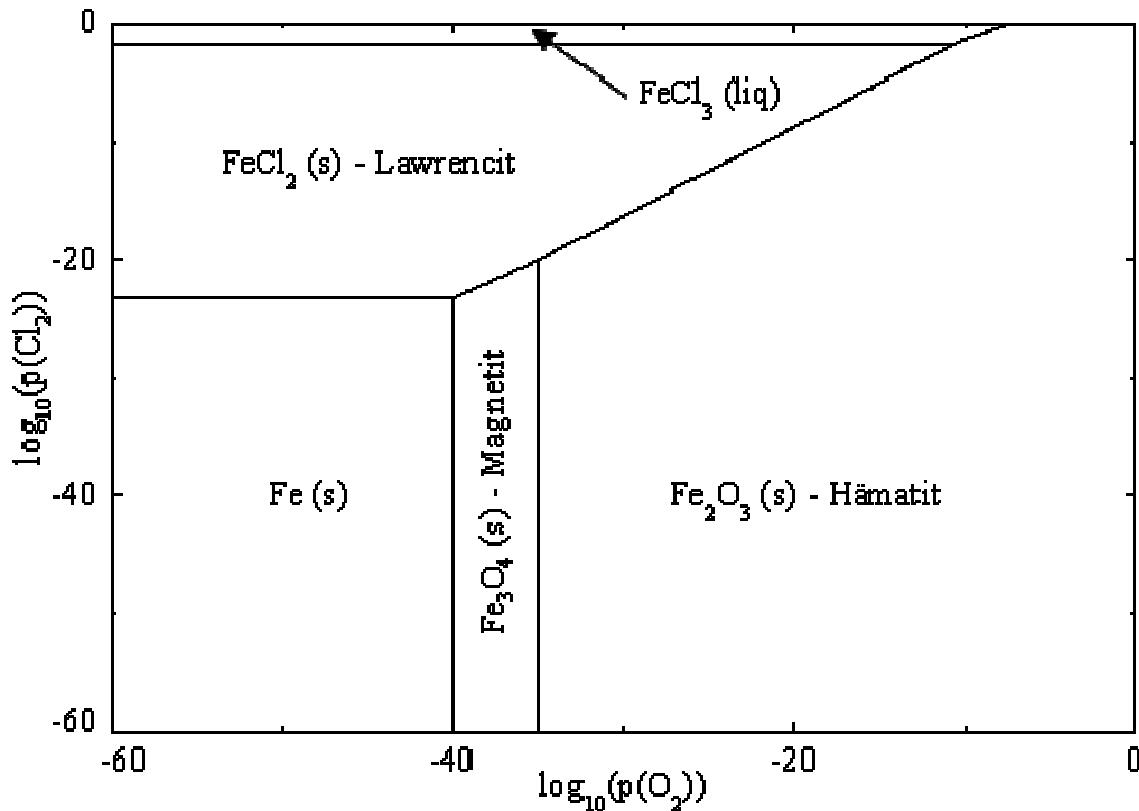




Oxide

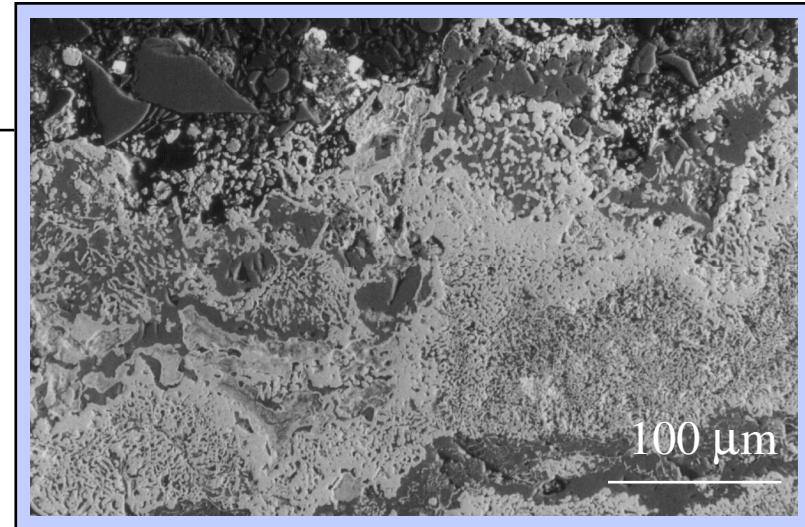
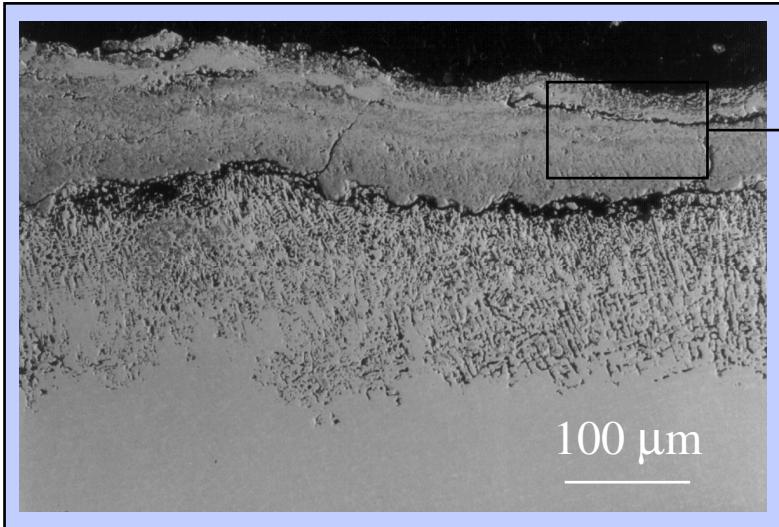
tube surface

320 °C, FactSage calculation



Corrosion of heat exchangers

Fireside Corrosion: molten salts



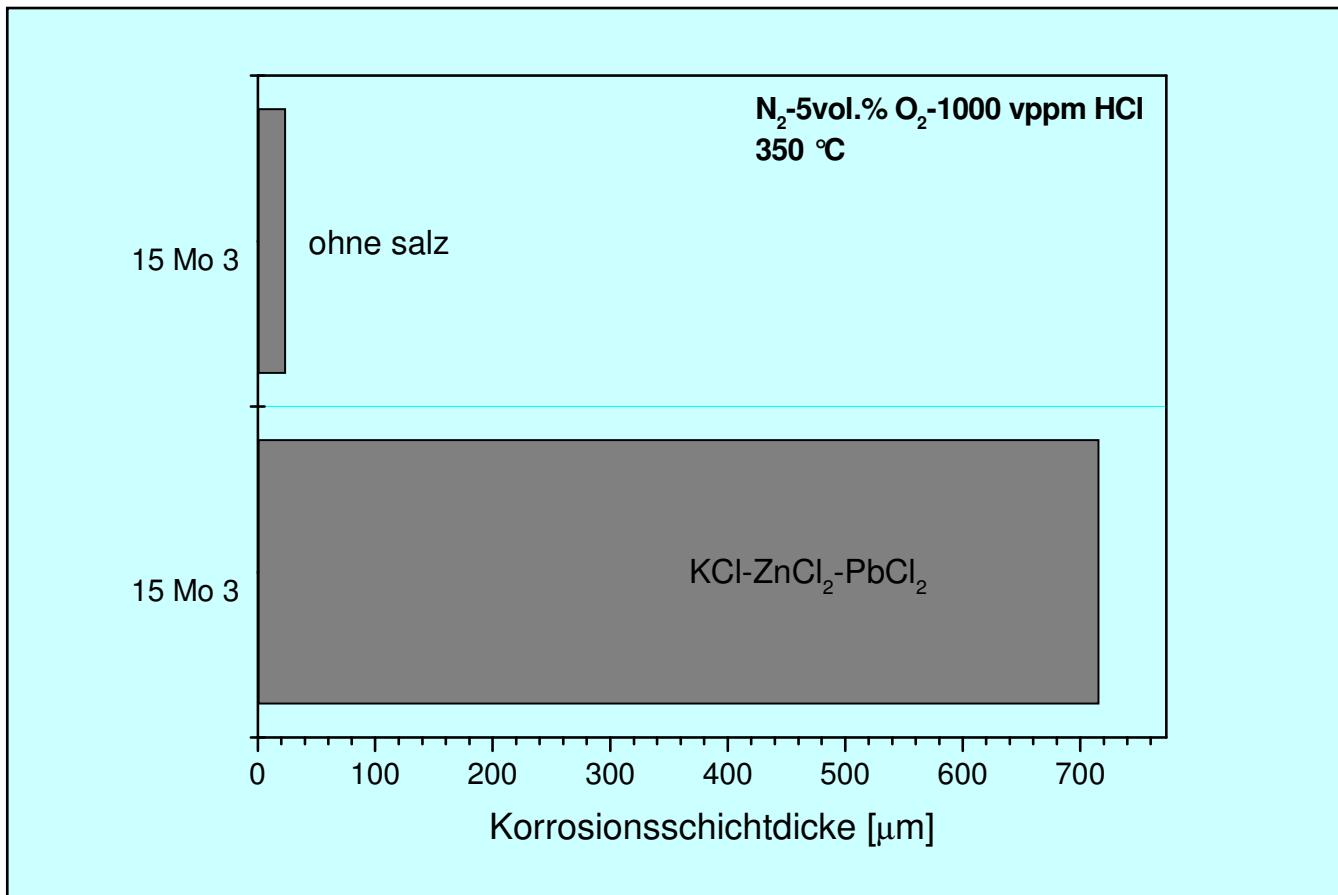
Corrosion layer of (Fe, Cr, Ni) -
oxides, Metal-chlorides (Ni, Cr,
Fe)

porous oxides in solidified
melts

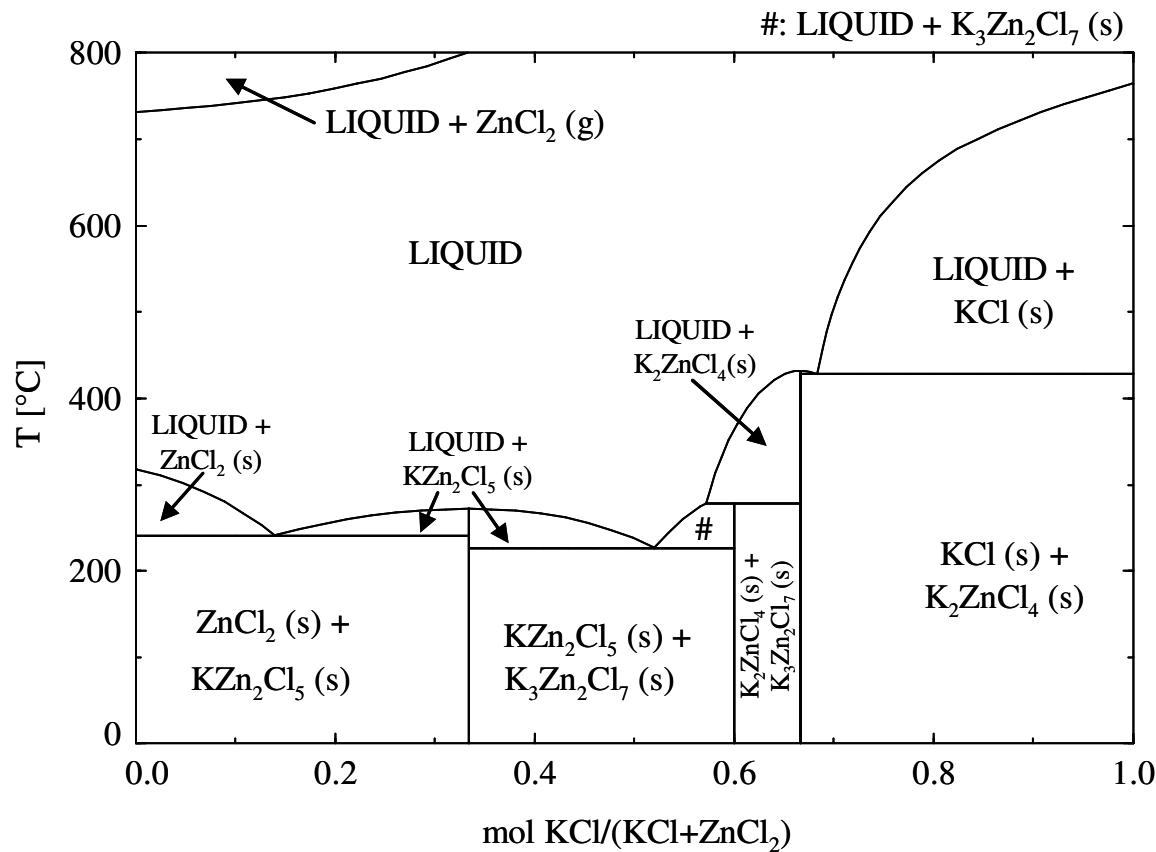
composition [wt. %]	Melting point [°C]
ZnCl ₂	318
PbCl ₂	498
48ZnCl ₂ - 52 KCl	250
82ZnCl ₂ - 18 KCl	262
84ZnCl ₂ - 16 KCl	262
73ZnCl ₂ - 27PbCl ₂	300
31NaCl - 69PbCl ₂	410
21KCl - 79PbCl ₂	411
17NaCl - 83PbCl ₂	415
39ZnCl ₂ - 50KCl - 11PbCl ₂	275
35ZnCl ₂ - 48NaCl - 17PbCl ₂	350
16NaCl - 40KCl - 44PbCl ₂	400
K ₂ SO ₄ - Na ₂ SO ₄ - ZnSO ₄	384
KCl - ZnCl ₂ - K ₂ SO ₄ - ZnSO ₄	292
K ₂ SO ₄ - Na ₂ SO ₄ - CaSO ₄	776

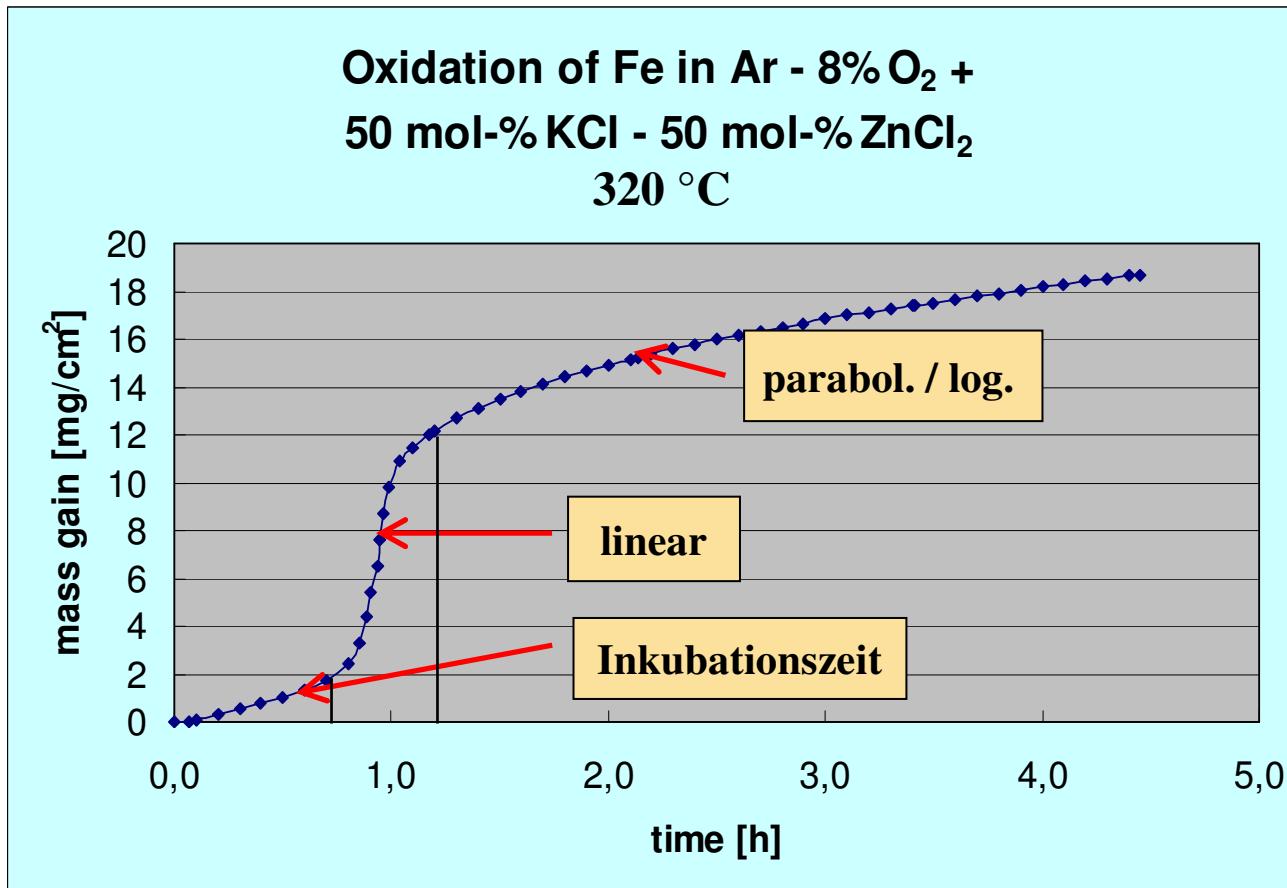
Corrosion of heat exchangers

Fireside Corrosion: molten salts



Phase diagramm: FactSage calculation

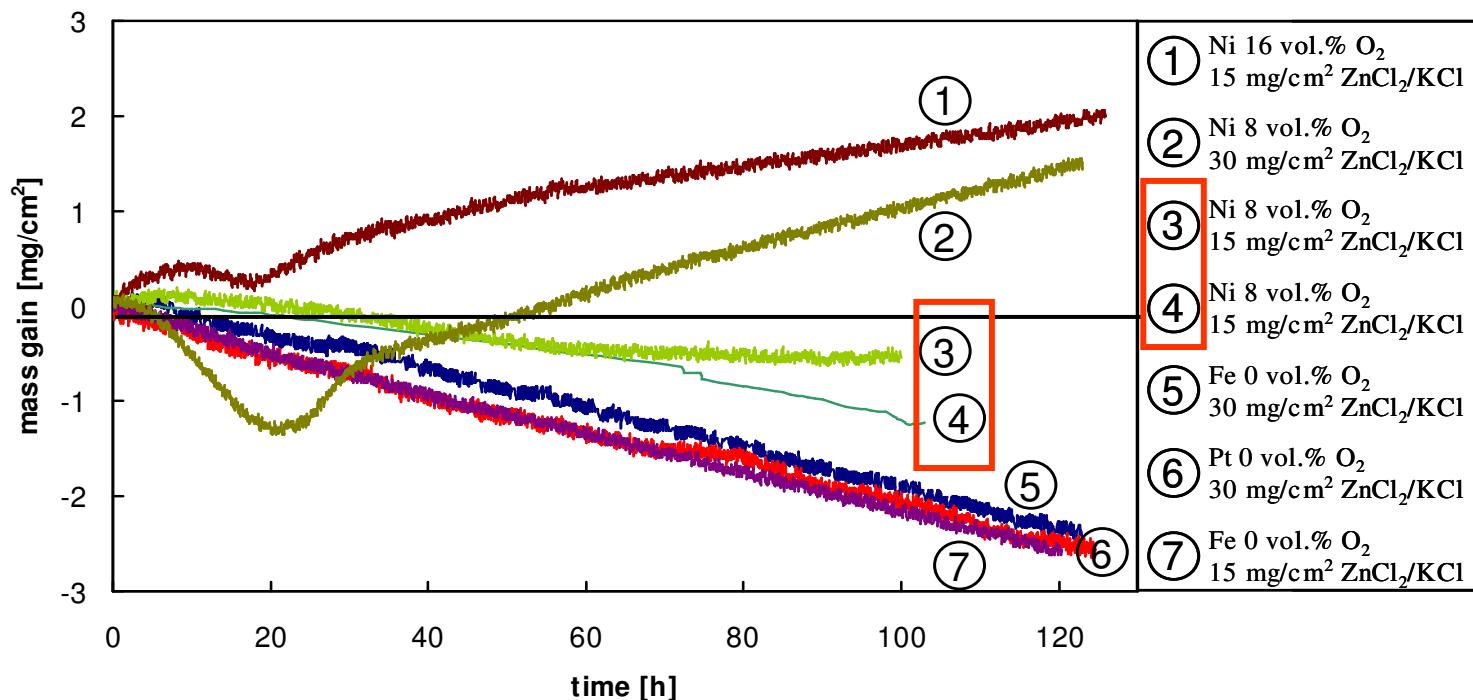


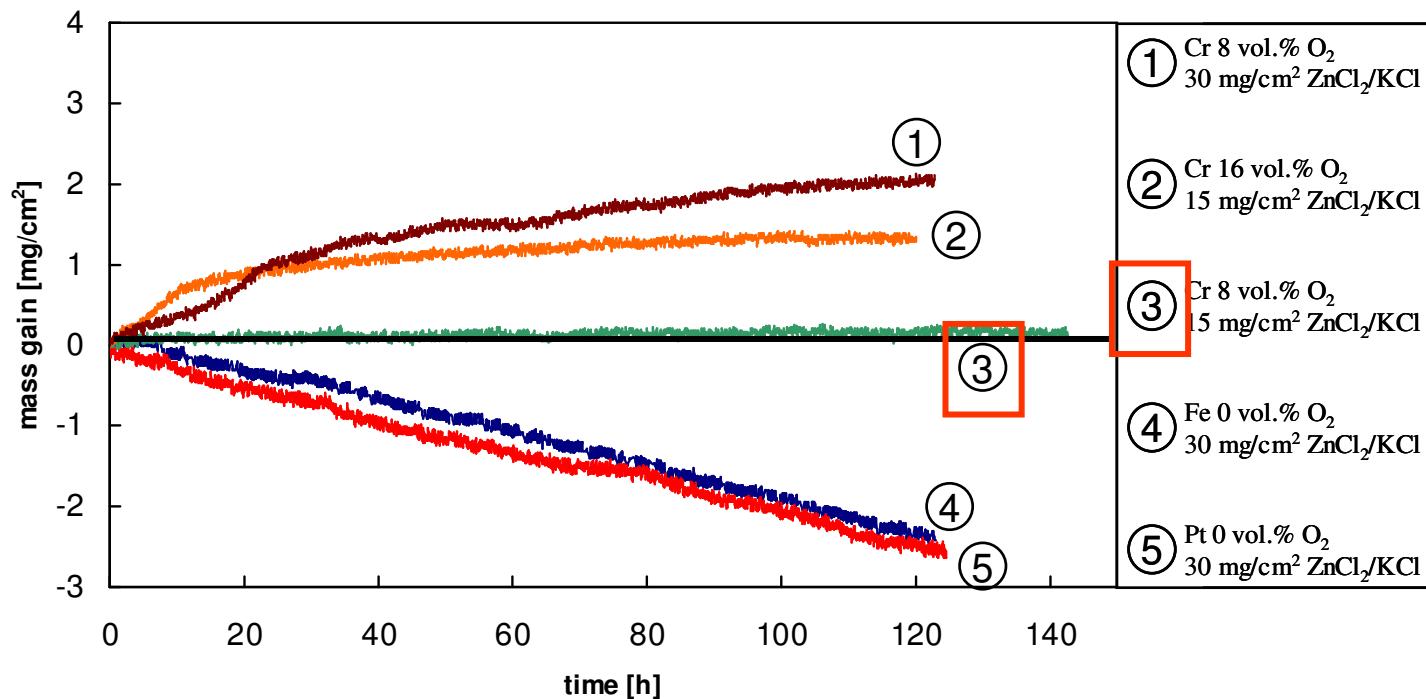


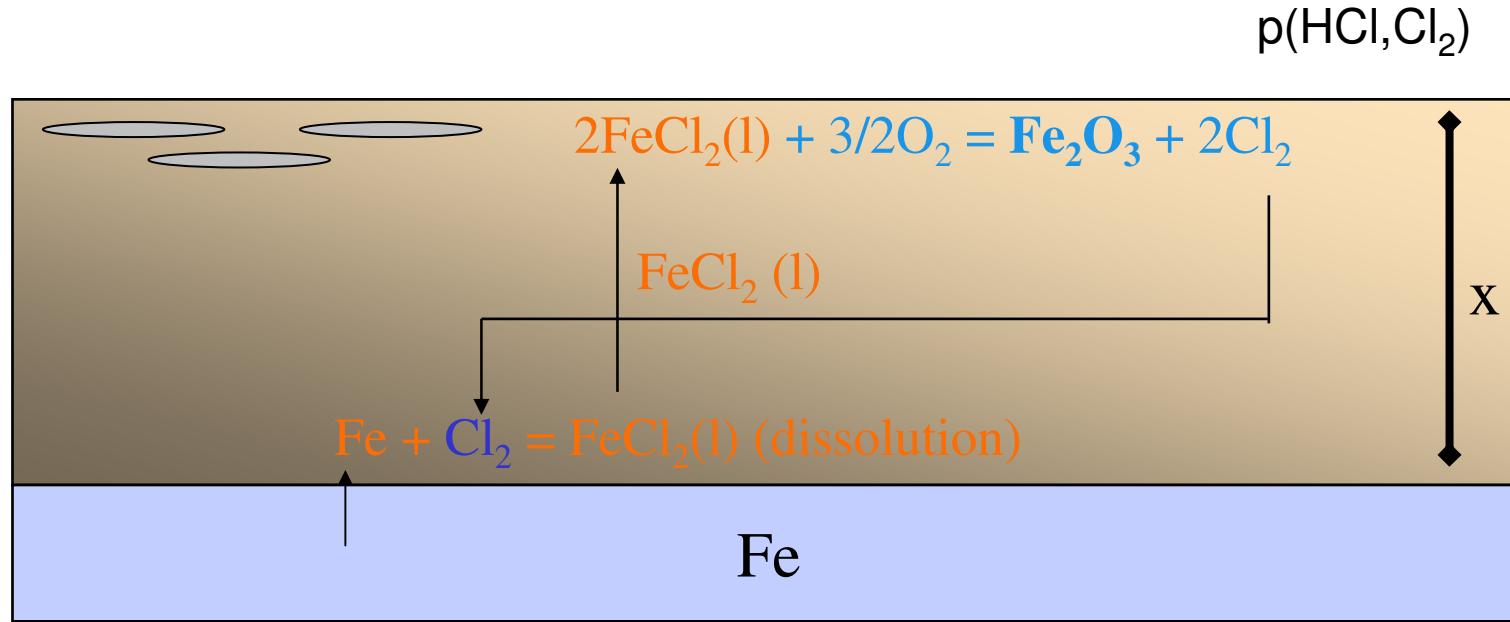
Corrosion of heat exchangers

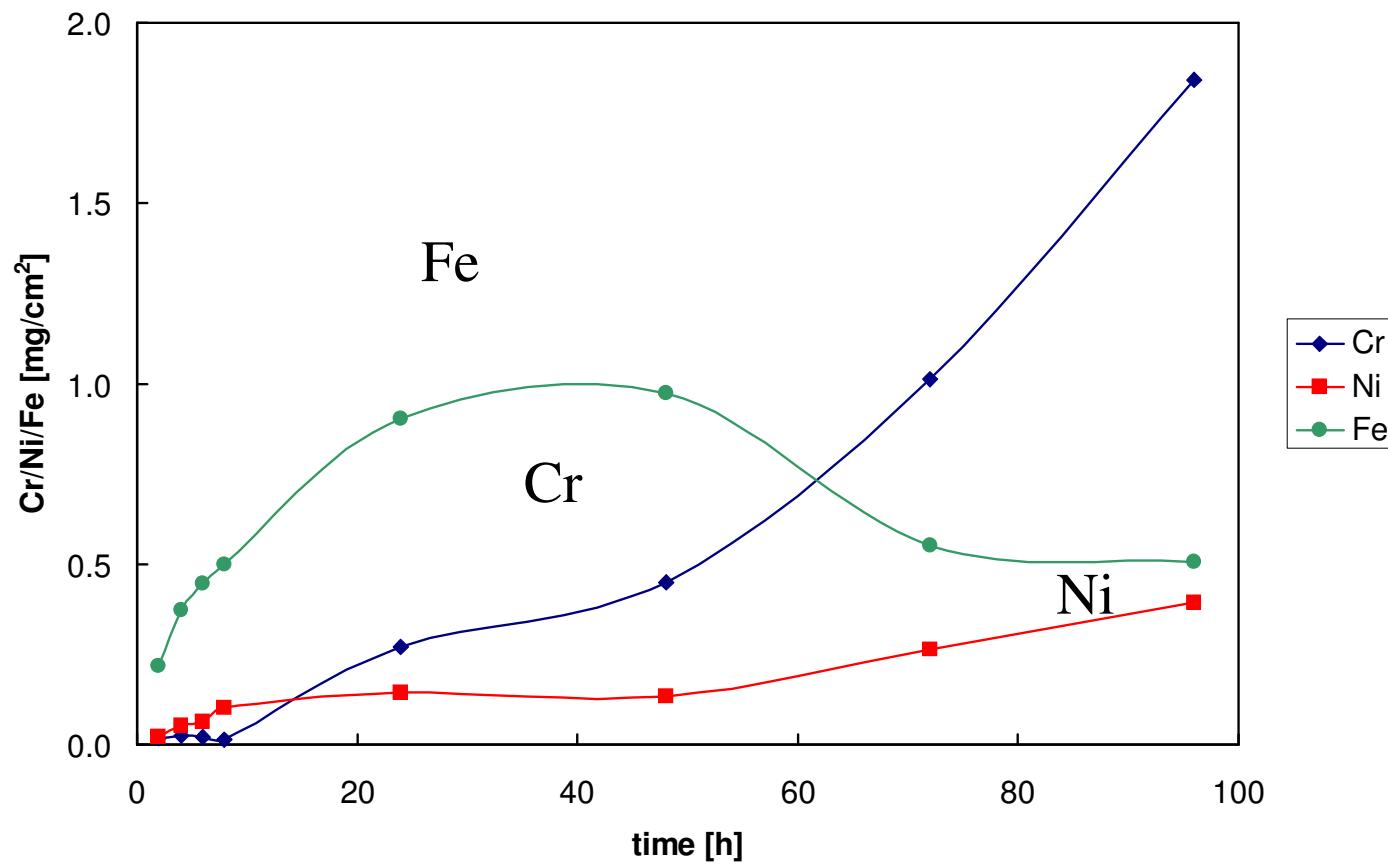
Fireside Corrosion: $\text{ZnCl}_2\text{-KCl}$ eutectic

Nickel, 320 °C, KCl-ZnCl_2



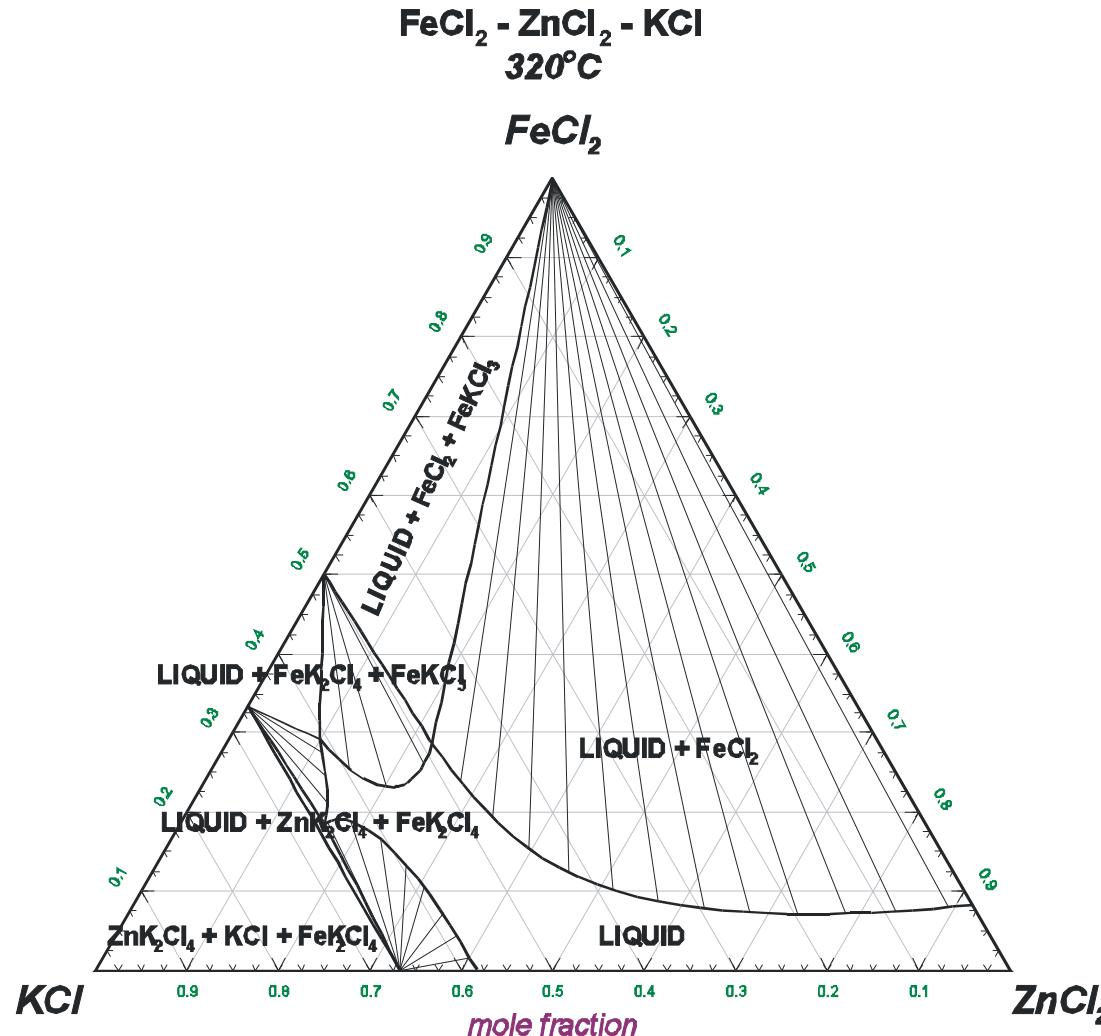
Chromium, 320 °C, KCl-ZnCl₂



Measured solubility of chloride at 320 °C and $\text{N}_2\text{-}8\% \text{O}_2$ 

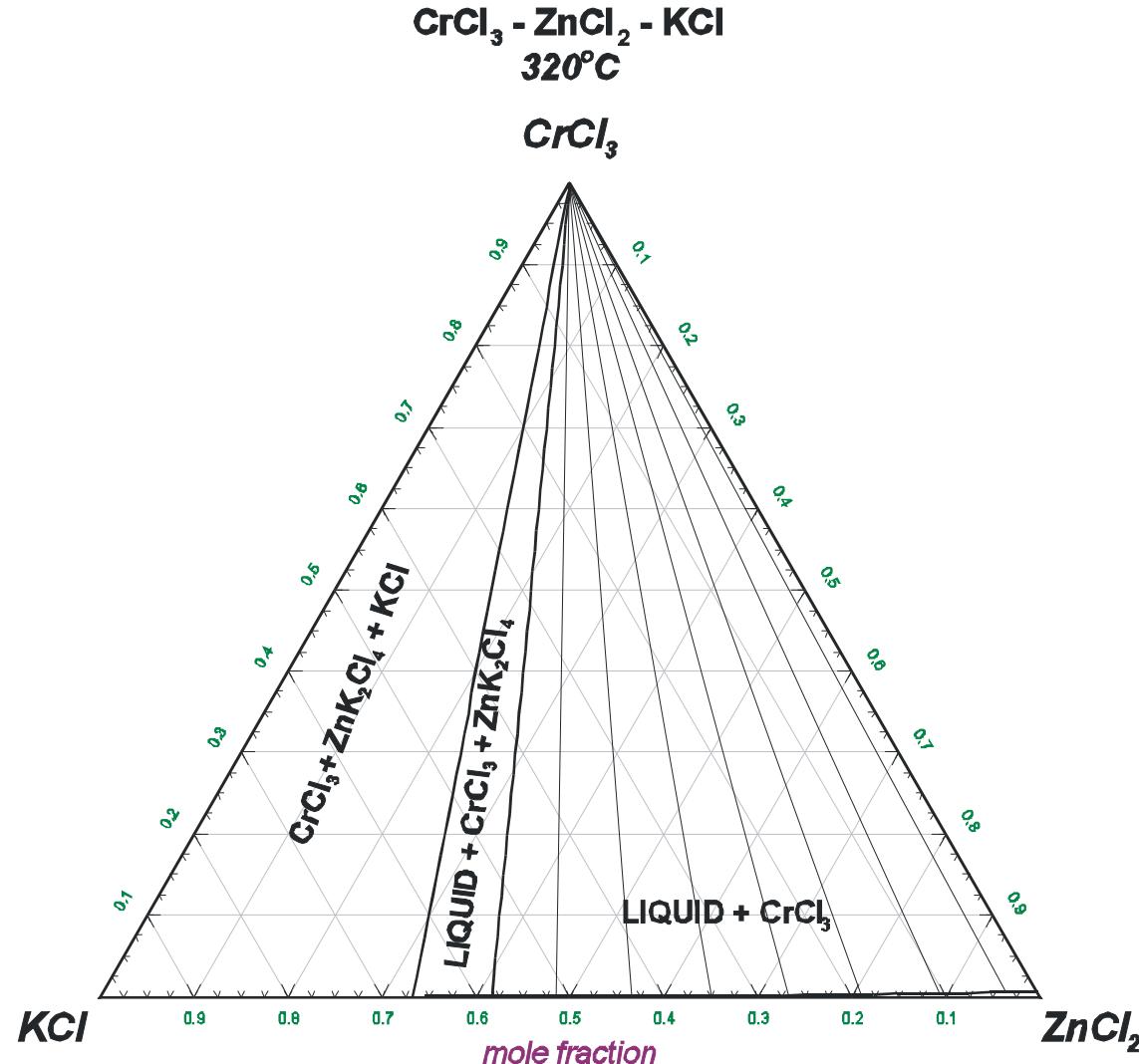
Corrosion of heat exchangers

Fireside Corrosion: $\text{ZnCl}_2\text{-KCl}$ eutectic



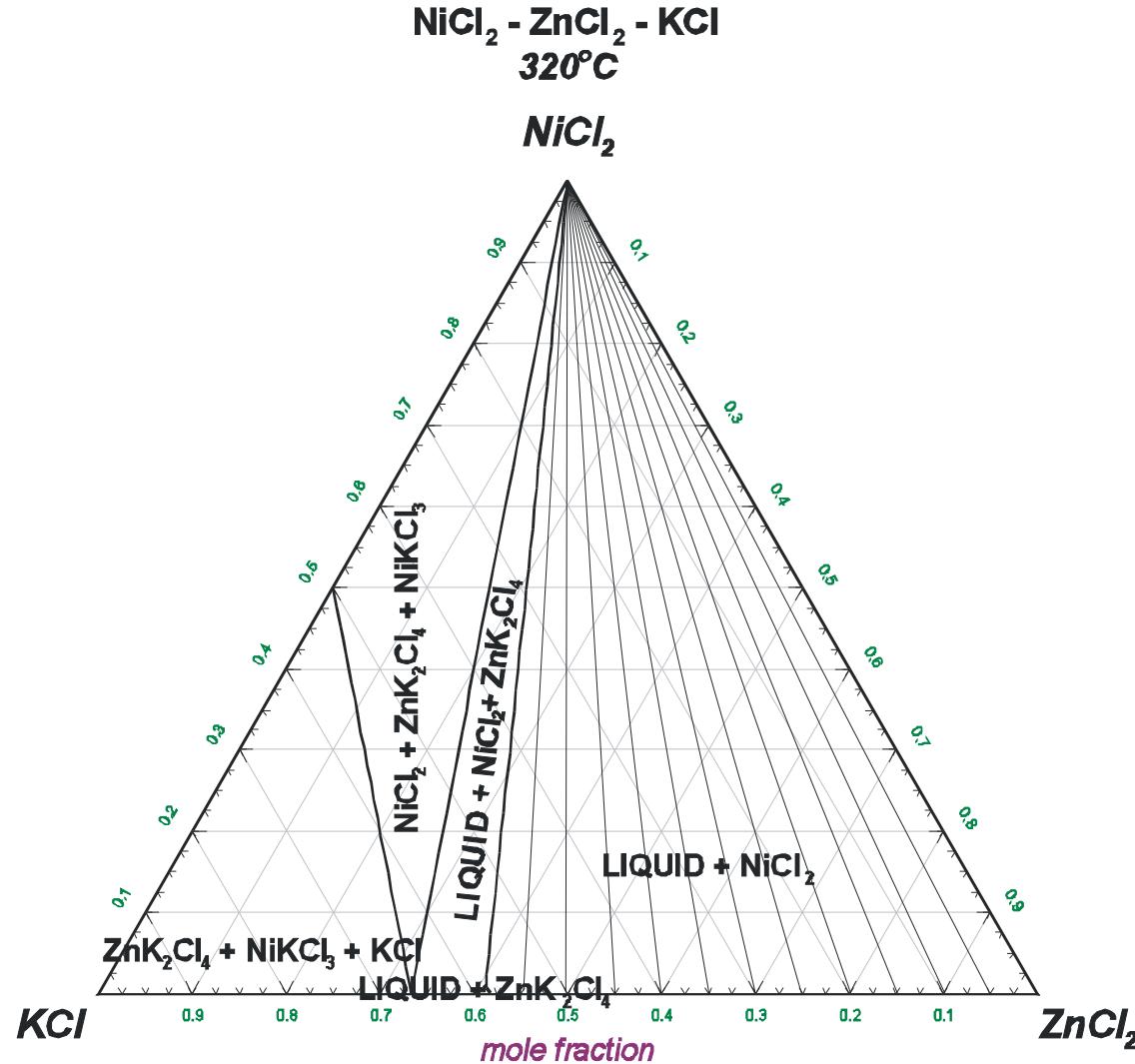
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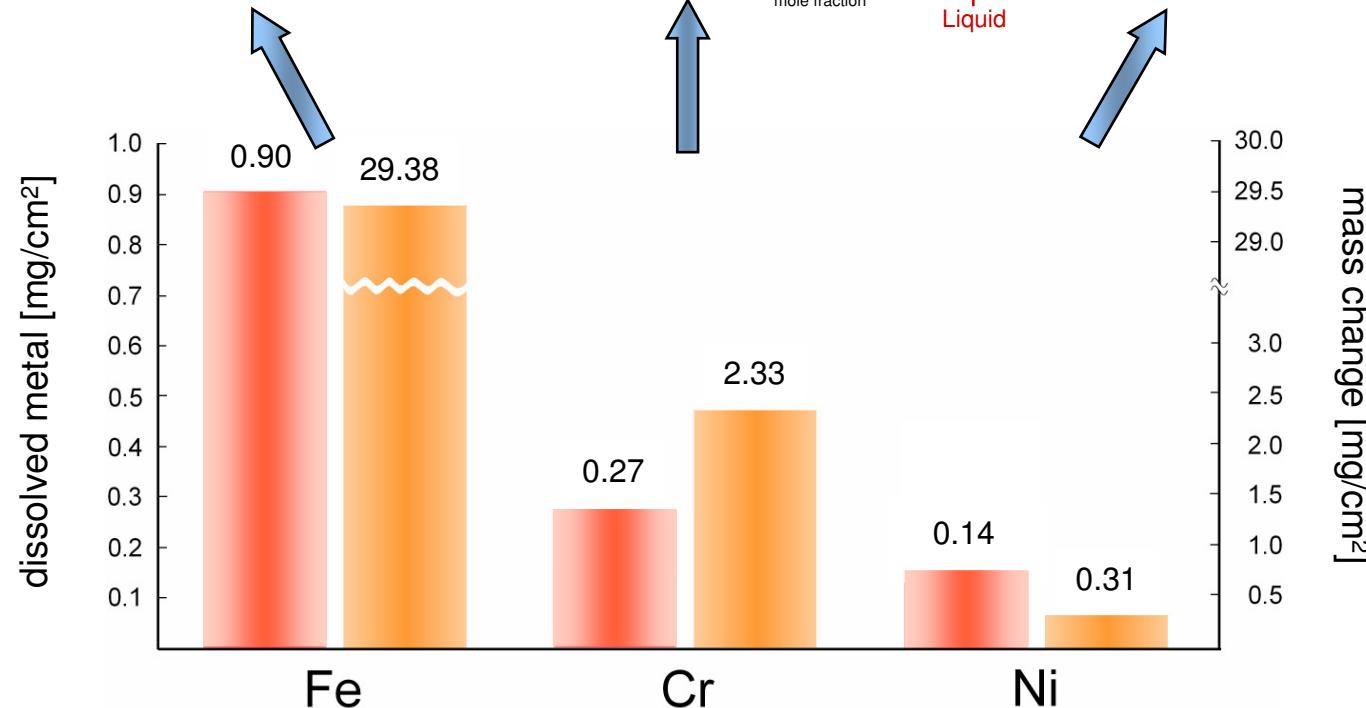
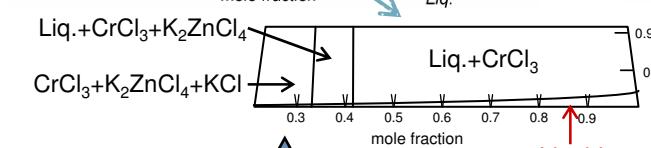
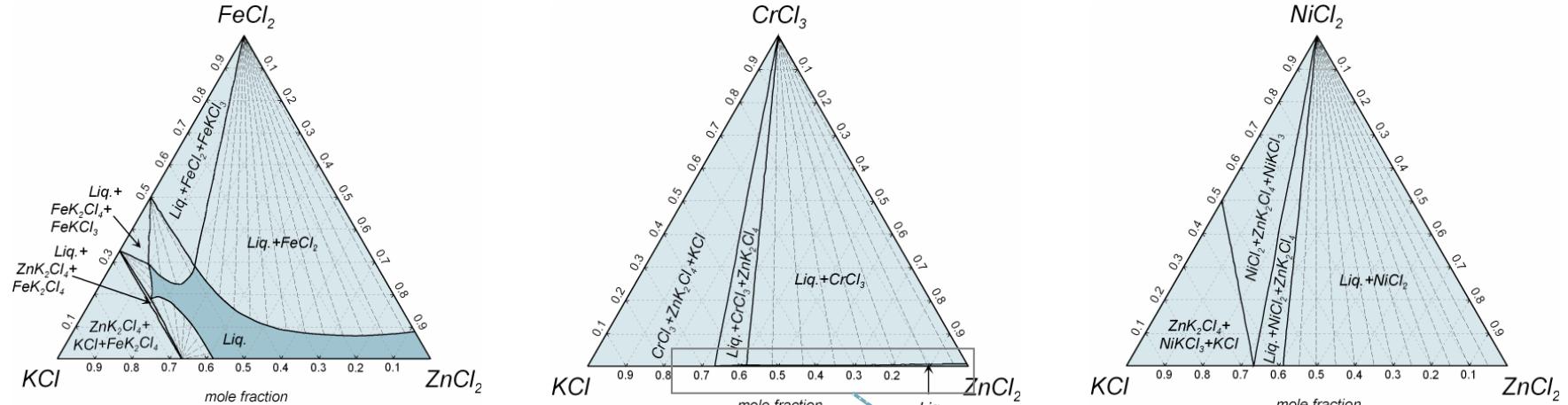
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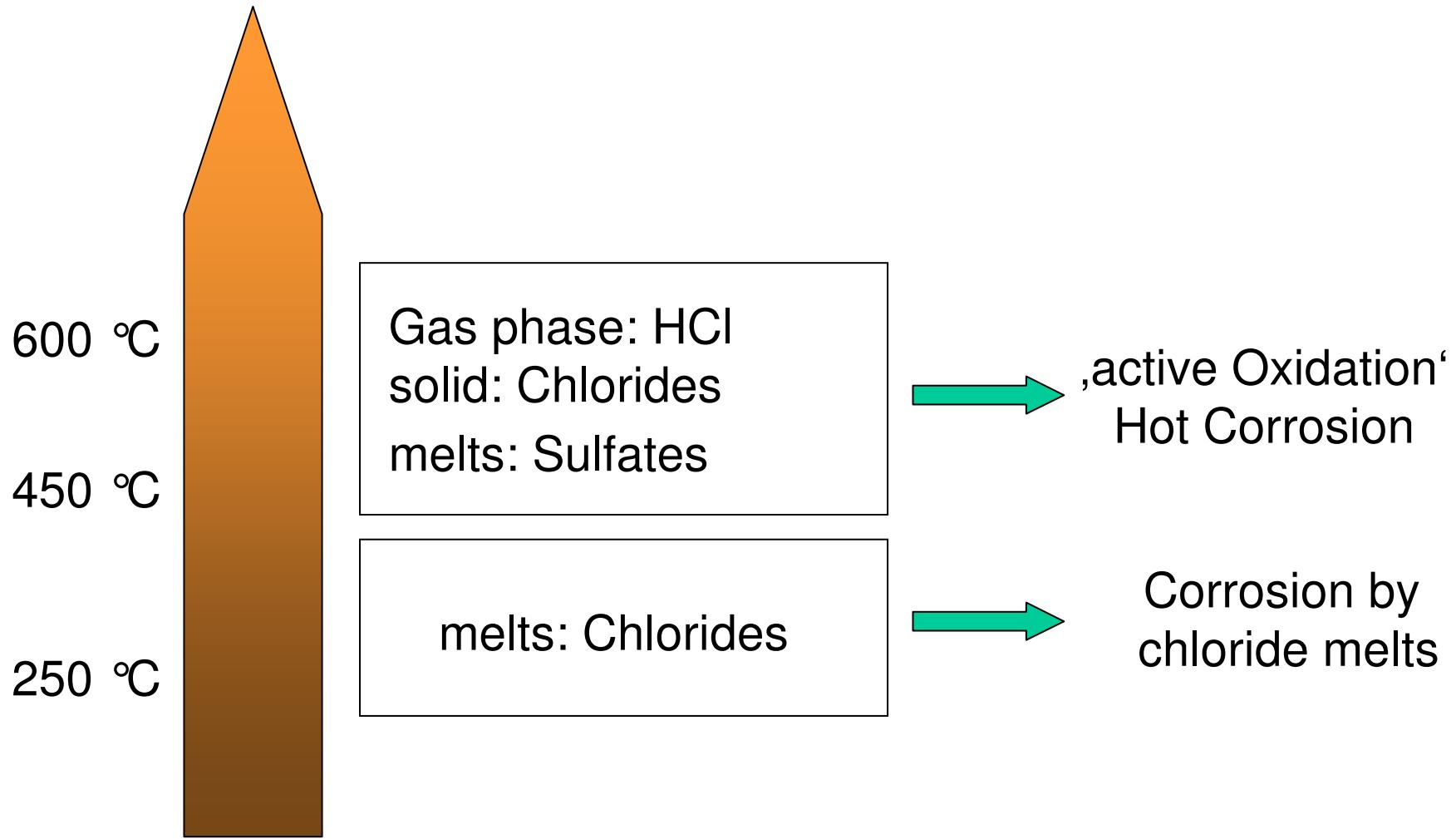
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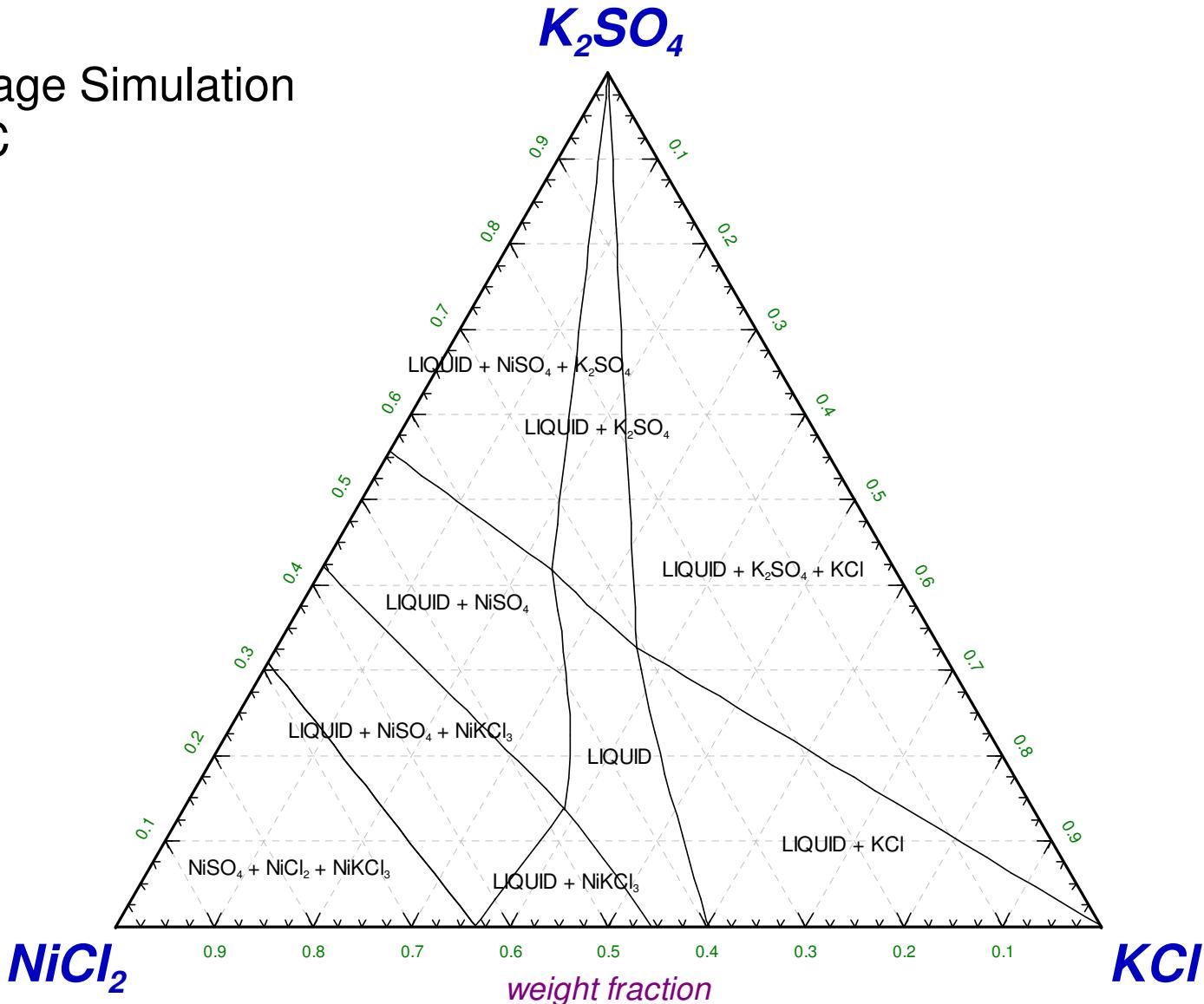




Temperature dependent corrosion mechanisms



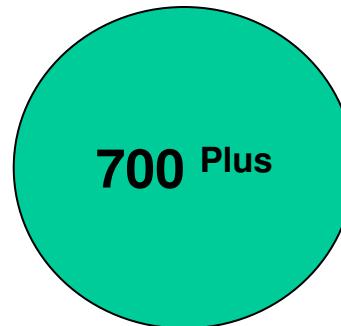
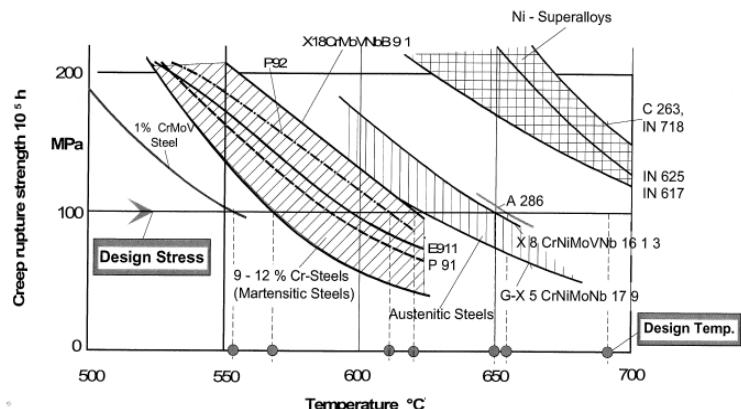
FactSage Simulation
550 °C



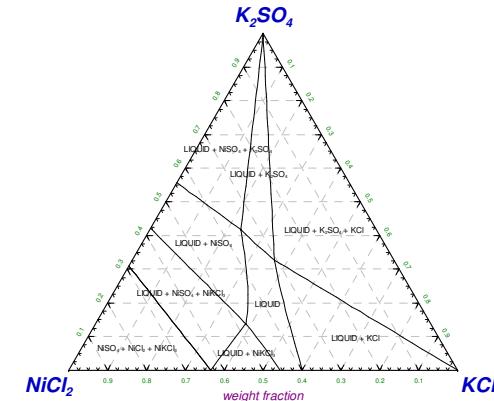
Corrosion in power plants

Outlook

creep strength



fireside corrosion



steam oxidation

