VDI Wissensforum

L.KRUMM, M.GALETZ, R. WARNECKE

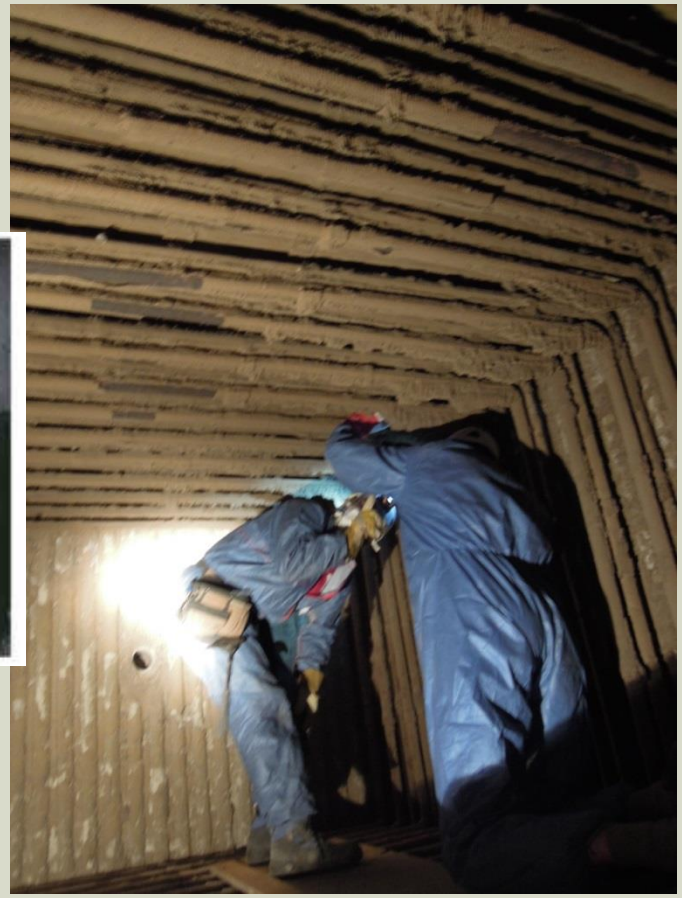
Einfluss des Sauerstoffs und der Oberflächenbelegung auf den Korrosionsschichtaufbau des unlegierten Stahls 16Mo3 in chlor- und schwefelhaltigen Atmosphären

Im Rahmen des BMBF – MatRessource - Projekts: VOKos

Bundesministerium für Bildung und Forschung

VDI Wissensforum

ÜBERHITZERROHRE NACH EINSATZ IN EINER MÜLLVERBRENNUNGSANLAGE

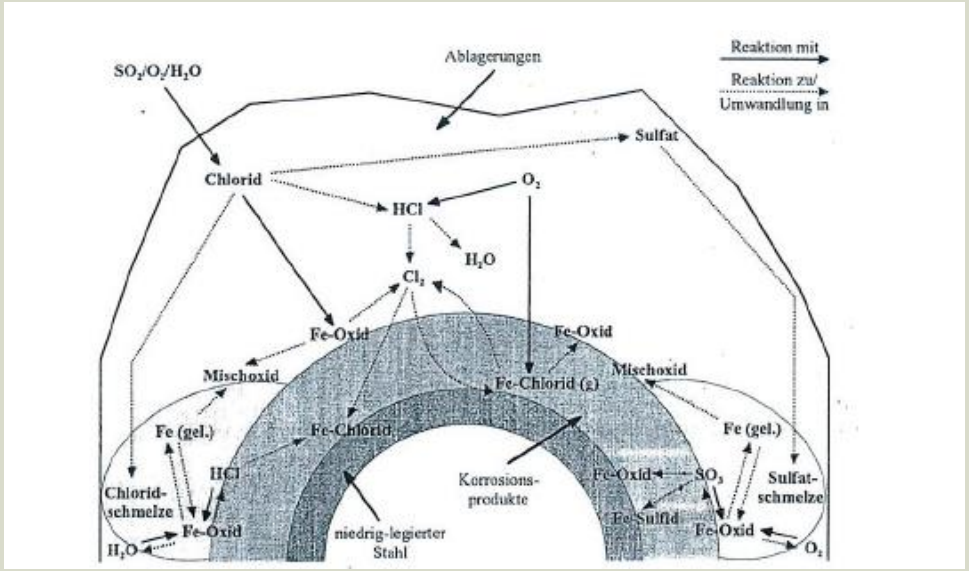


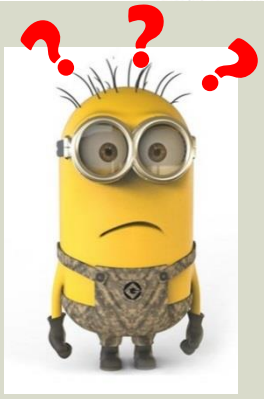
Quelle: GK Schweinfurt

RÜCKLÄUFERROHR

L13, P6, SCHEIBE 13, 4. ZUG ; AUSGEBAUT FEB. 2015

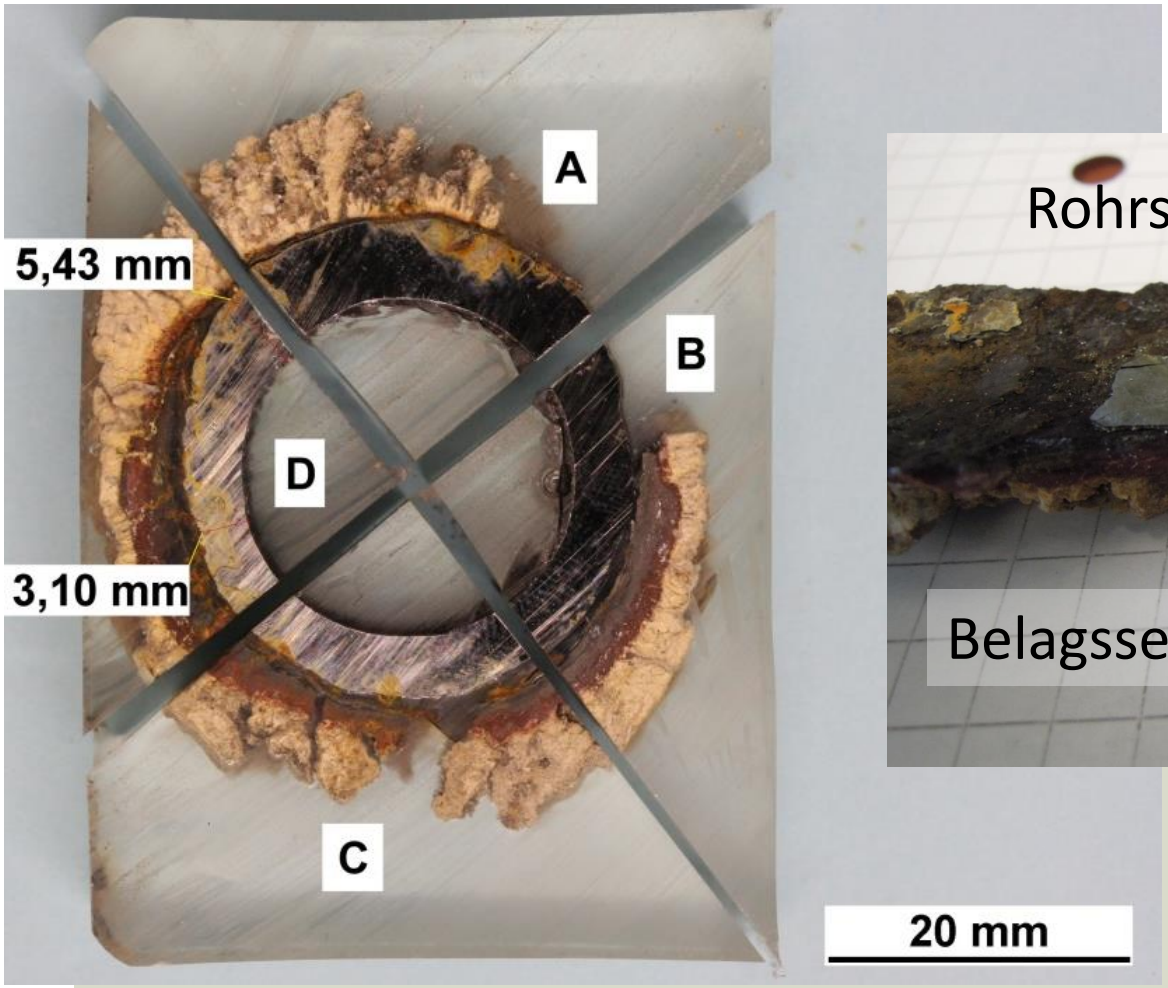
Gasflussrichtung

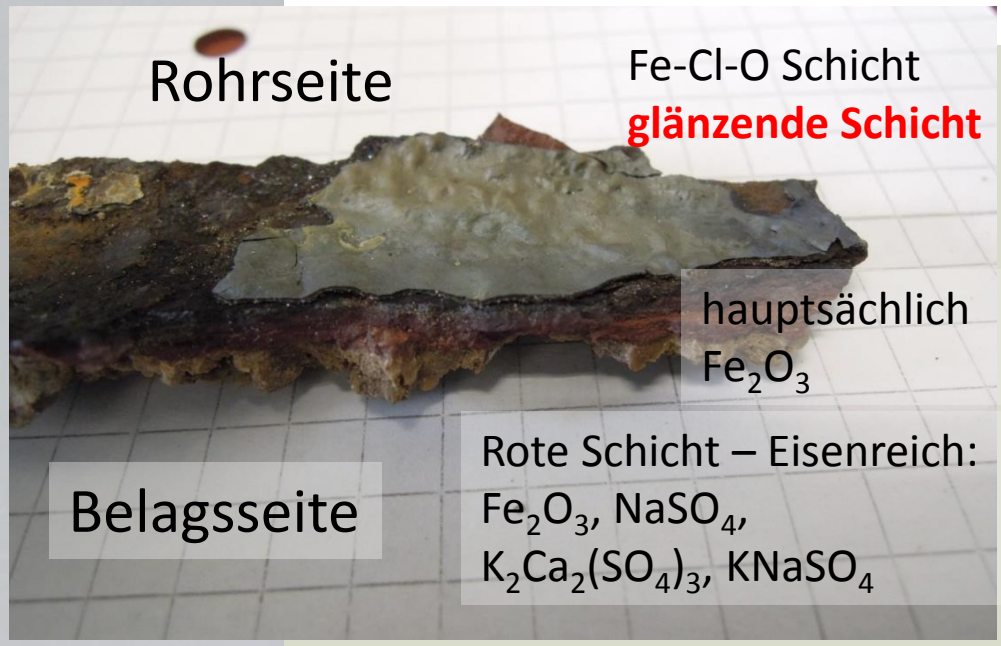




[Schroer et al., 2002]

KORROSIONSANGRIFF

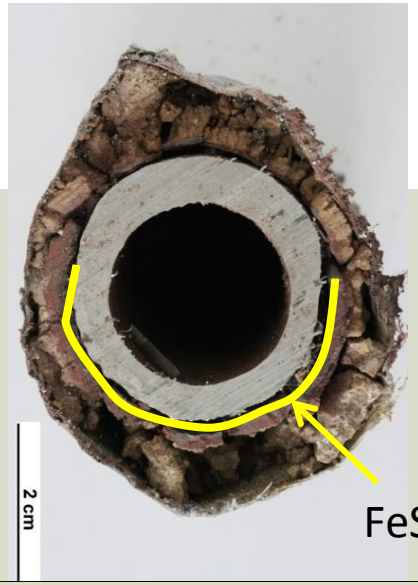


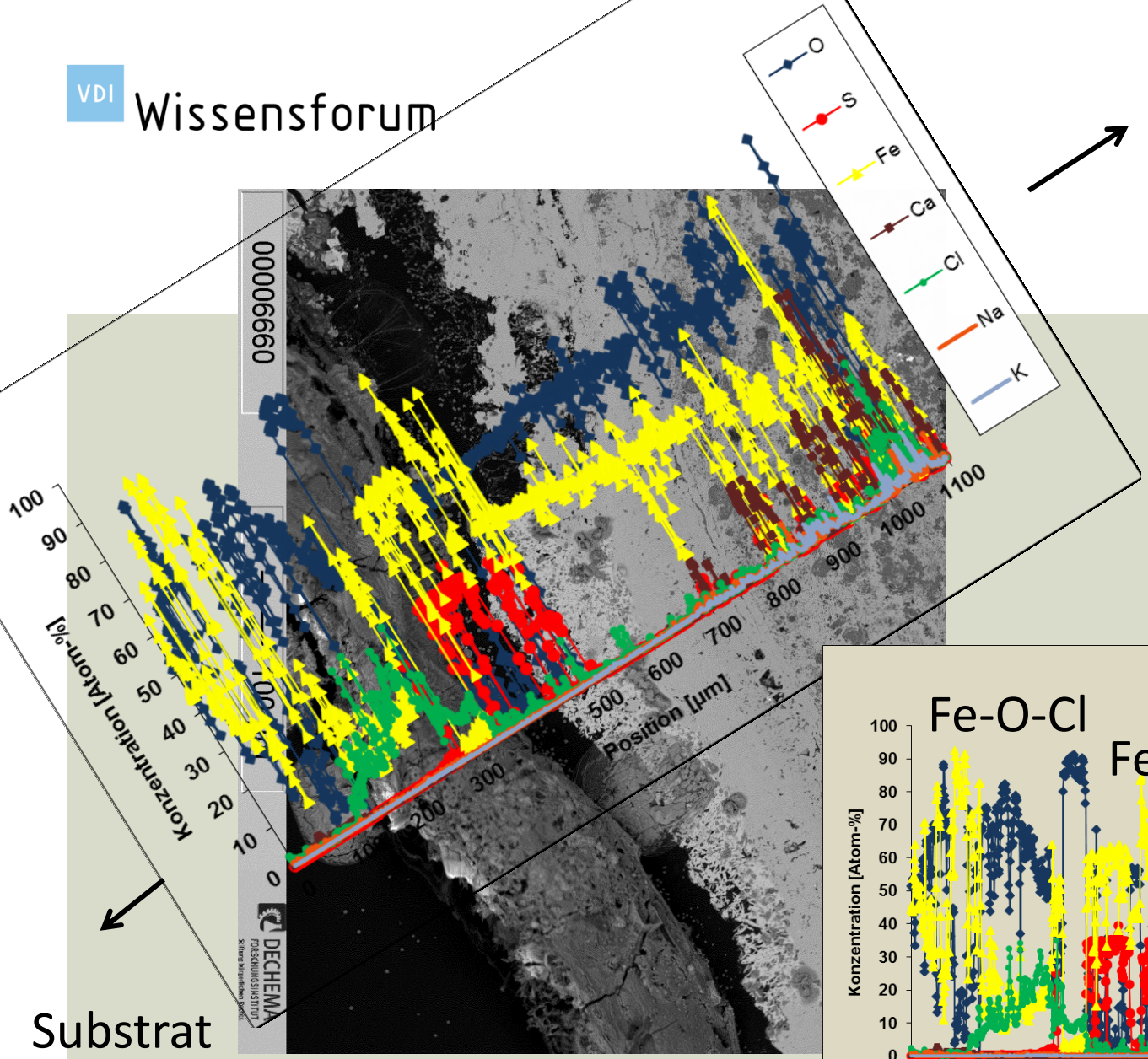


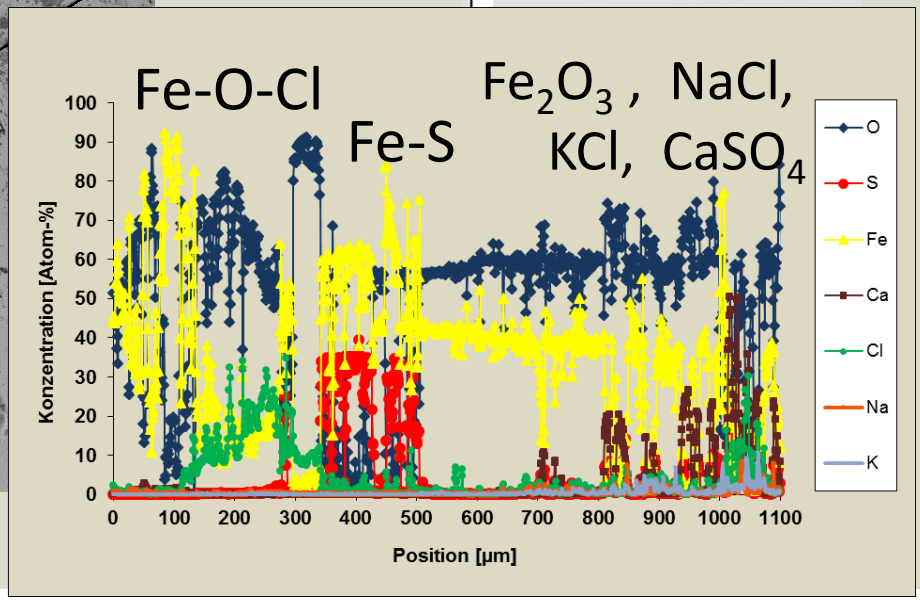
Helle äußere Schicht:
$CaSO_4$, $K_2Ca_2(SO_4)_3$,

Maximaler Materialabtrag zwischen d_{max1}= -1.4 mm/Jahr und d_{max2} = -0.26 mm/Jahr

Belag


2 cm
FeS


O
S
Fe
Ca
Cl
Na
K
Konzentration [Atom-%]
Position [µm]
Substrat


Fe-O-Cl
Fe-S
Fe_2O_3 , NaCl,
KCl, $CaSO_4$
Konzentration [Atom-%]
Position [µm]
O
S
Fe
Ca
Cl
Na
K

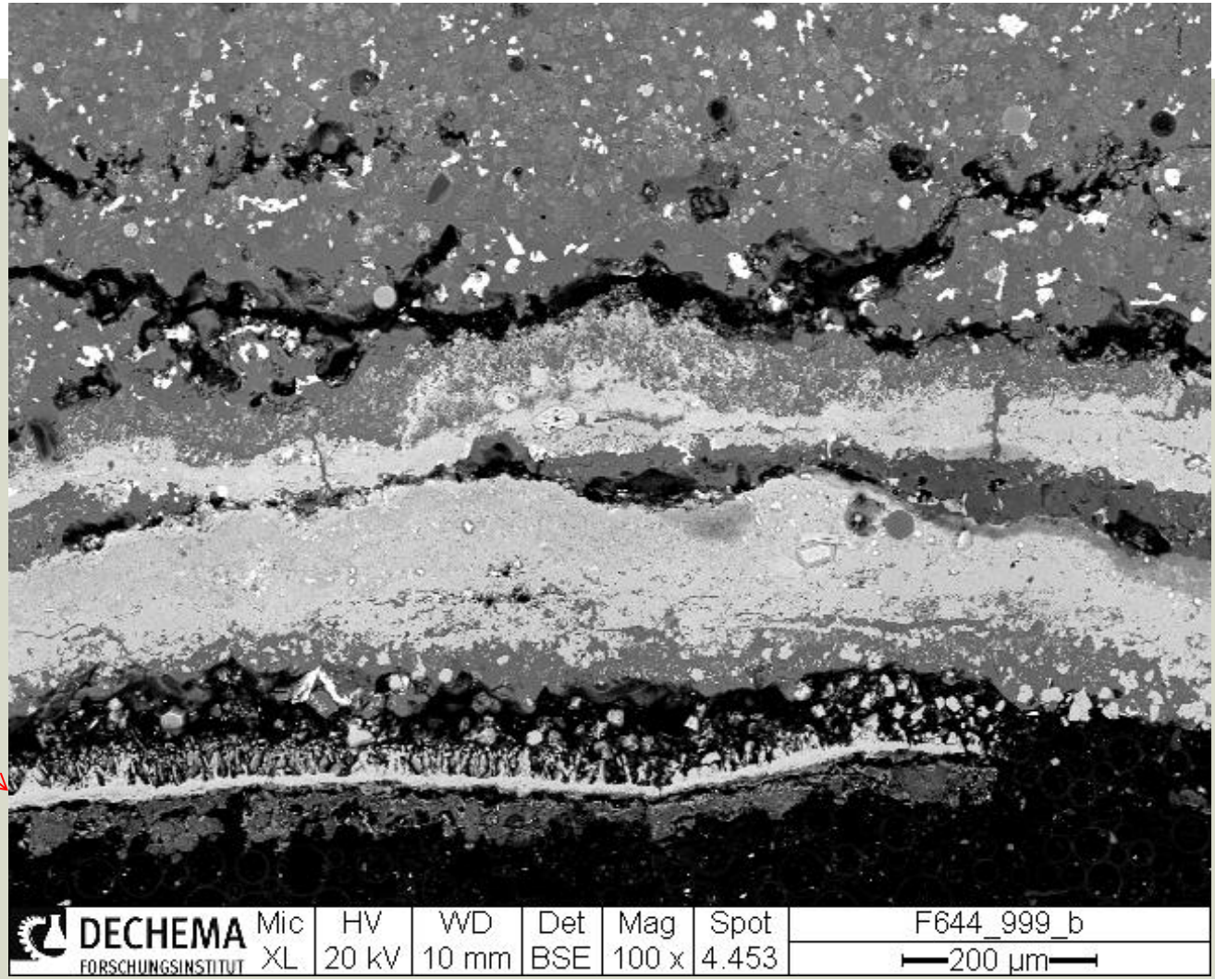
NAHAUFNAHME DER KORROSIONSSCHICHT EINES RÜCHLÄUFERROHRES

Belag
($CaSO_4$, Na_2SO_4, KCl, etc.)

Fe_2O_3

(Fe-S)

Fe-O-Cl



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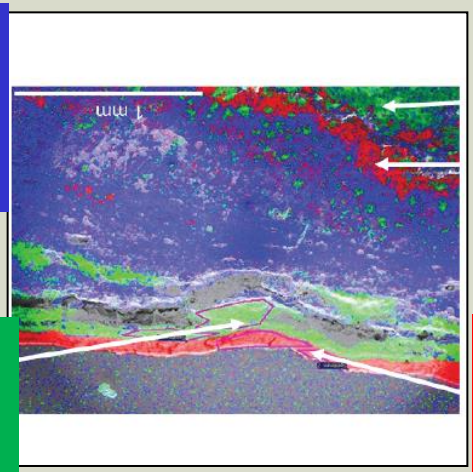
VERGLEICH DER KORROSIONSSCHICHT MIT ERGEBNISSE AUS DER LITERATUR

Hauptsächlich
Fe_2O_3
~800-1200 µm

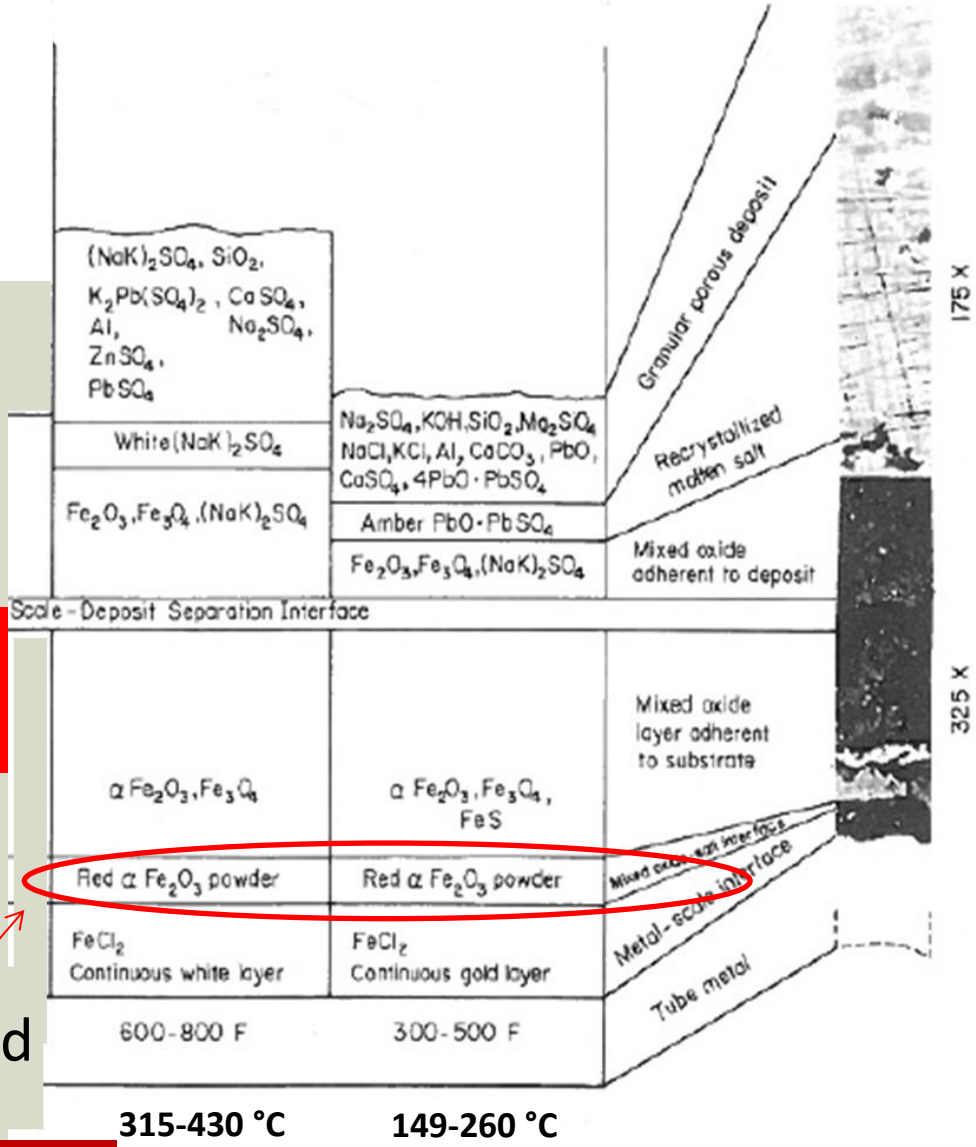


Belag

Hauptsächlich
Fe S
~100-200 µm

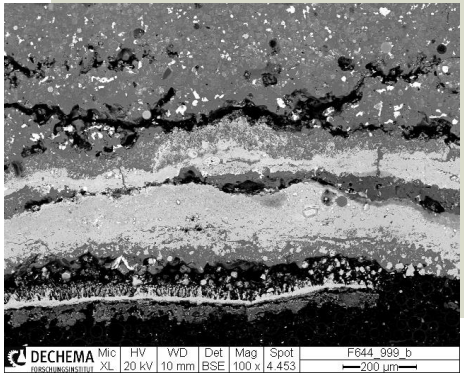
Hauptsächlich
$FeCl_2$
~100-250 µm

[B. Waldmann, Diss. 2007]



315-430 °C **149-260 °C**

und

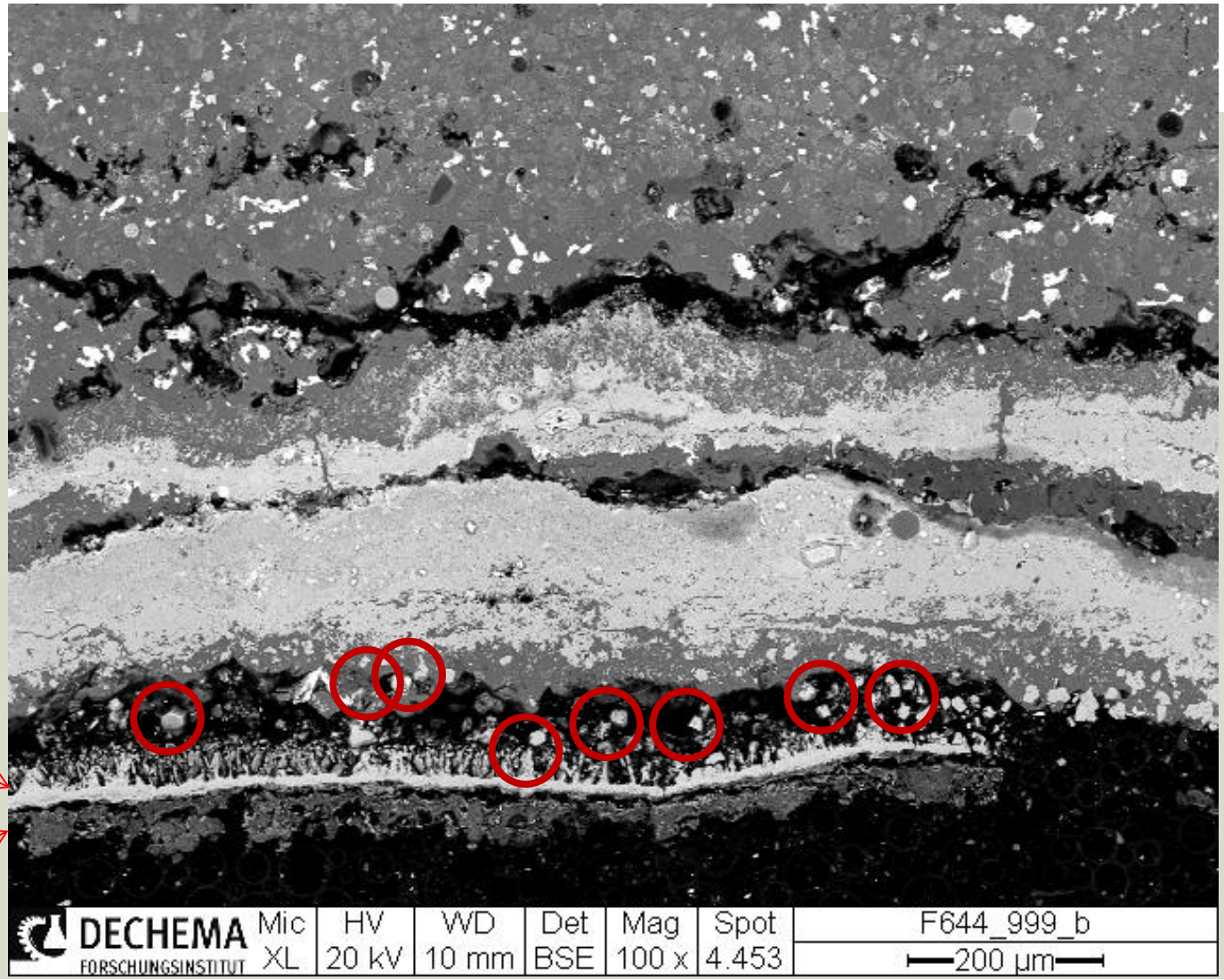


Abweichung: FeOCl

[P.D. Miller, H.H. Krause, Corrosion Vol. 28, (1972)]

NAHAUFNAHME DER KORROSIONSSCHICHT EINES RÜCKLÄUFERROHRES

Belag ($CaSO_4$, Na_2SO_4 etc.)



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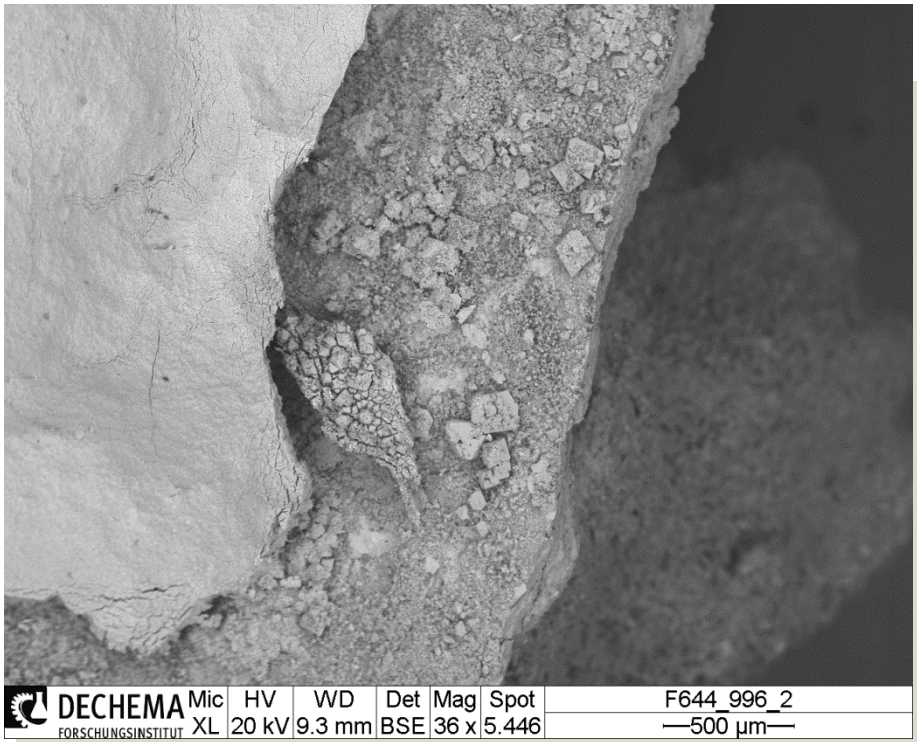
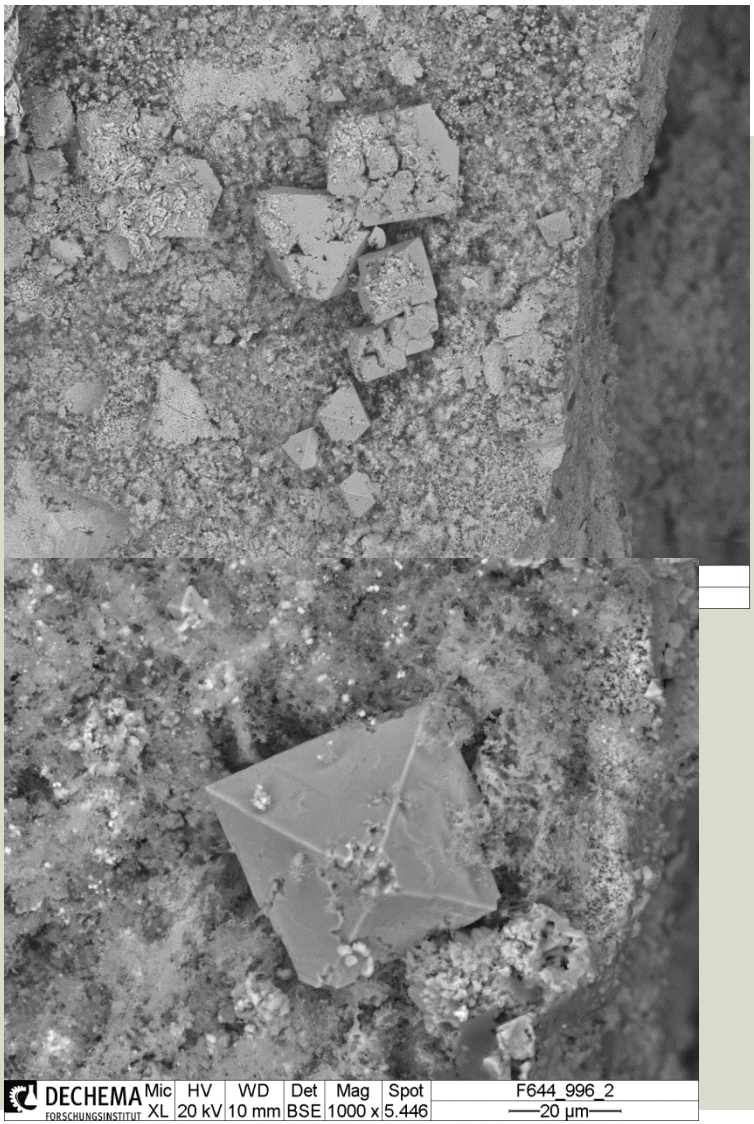
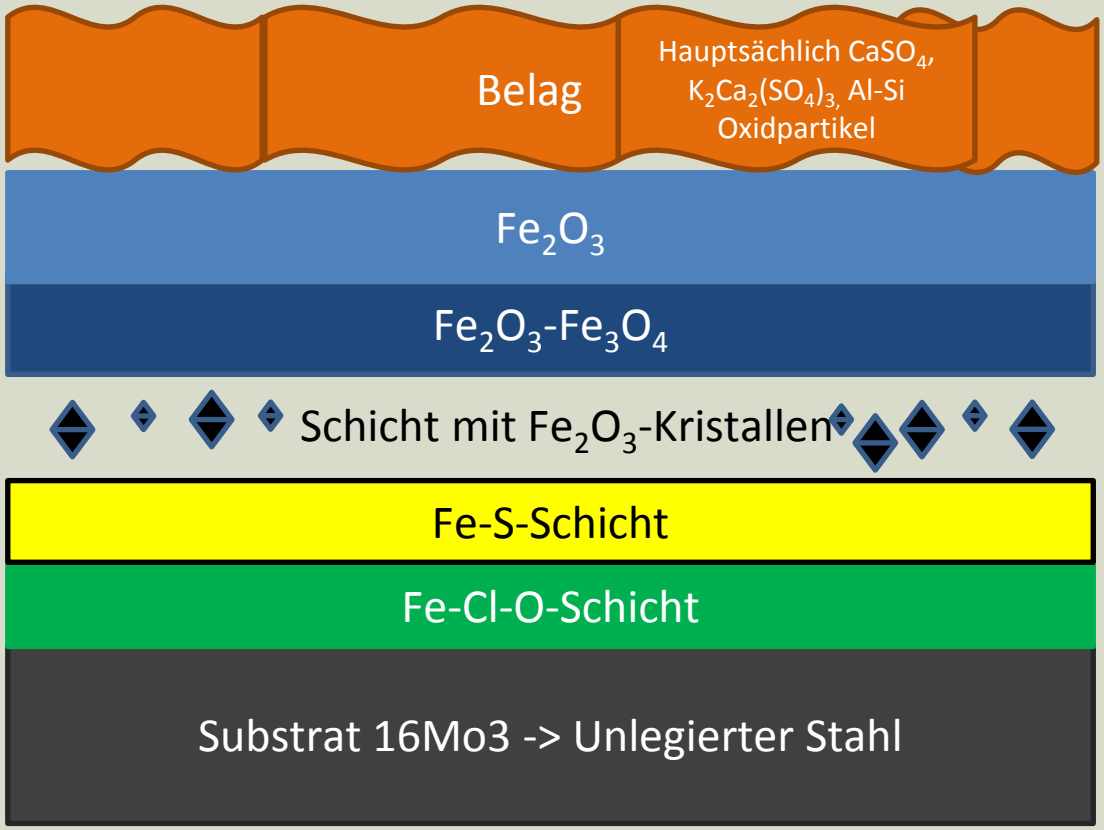
LOKALE ANREICHERUNG DER EISENOXIDKRISTALLE NAHE DER SUBSTRATOBERFLÄCHE





SCHEMATISCHER AUFBAU DER KORROSIONSSCHICHT

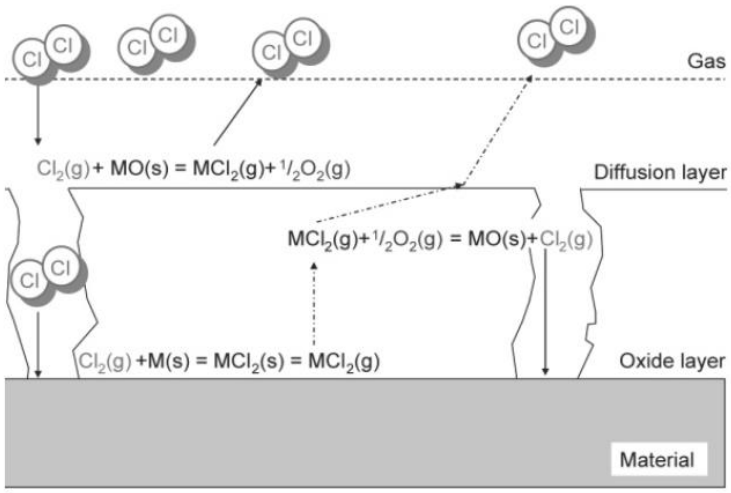


Welche Atmosphären sind unterhalb des Belags notwendig, die zu dem erhaltenen Korrosions-schichtaufbau führen?

MECHANISMEN IN DER LITERATUR DER HOCHTEMPERATUR CHLORKORROSION

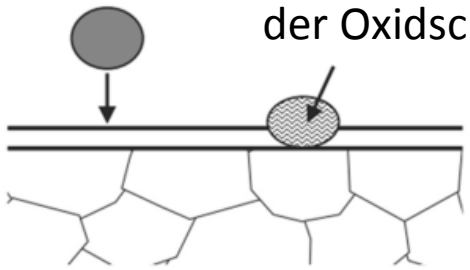
Korrosionsuntersuchungen mit Belag: zwei Hauptmechanismen werden diskutiert

Aktive Oxidation



[nach H.J. Grabke et al., 1992,
R. Bender et al. 2003, Mat. Corr.]

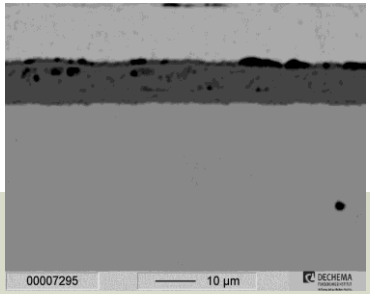
Salzschmelze



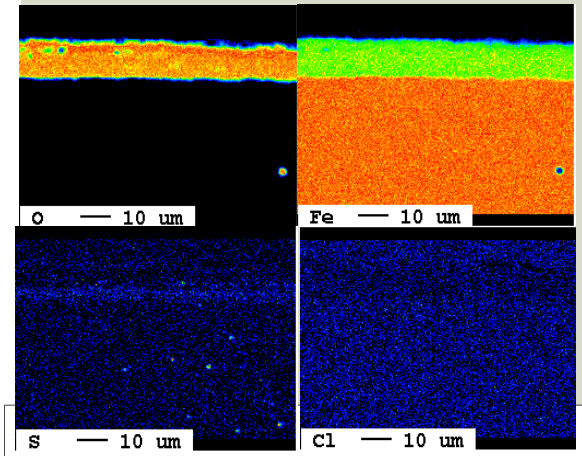
[z.B. T. Jonsson et al., Les Embiez, 2016,
M. Halverson, Gordon Conf. 2015]

Tests ohne Belag! In: N_2 - 8% O_2 – 17% H_2O-10%CO_2 -0.1HCl- 0.01 SO_2

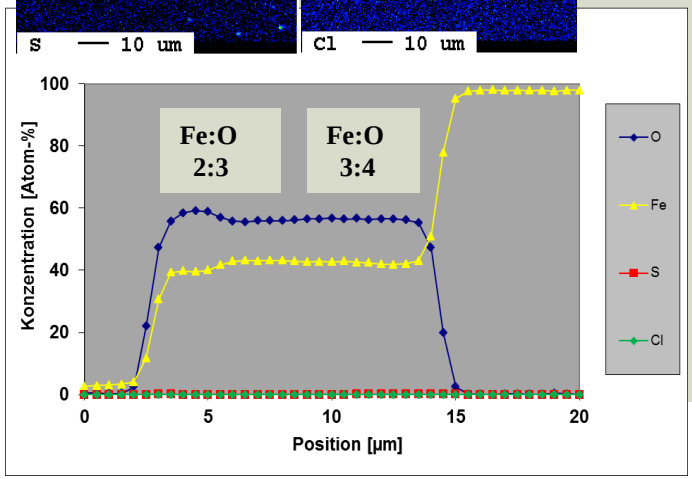
N_2 - 8% O_2 – 17% H_2O-10%CO_2 -0.1HCL- 0.01 SO_2 (MVA ATMOSPHÄRE)



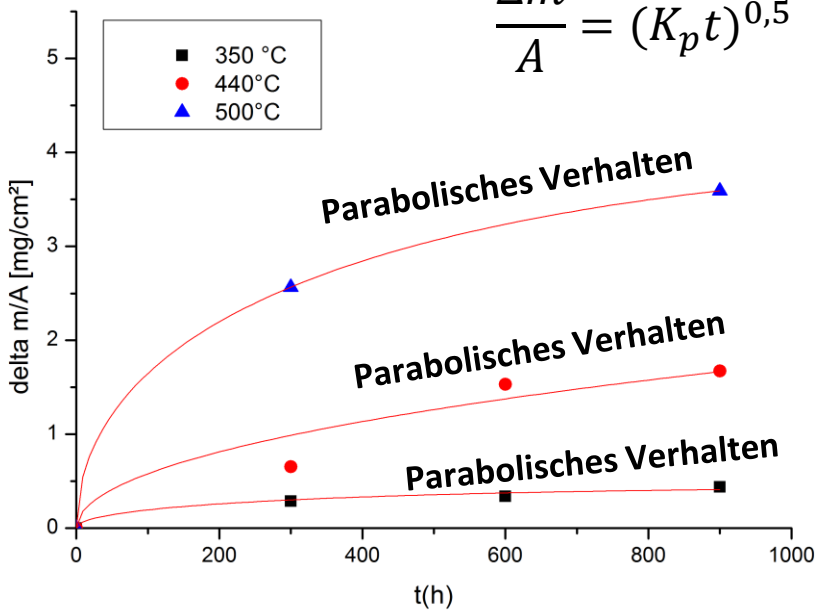
440°C 900h



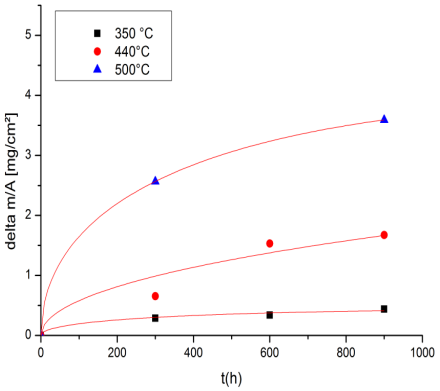
Kein
Cl oder S



$$\frac{\Delta m}{A} = (K_p t)^{0,5}$$

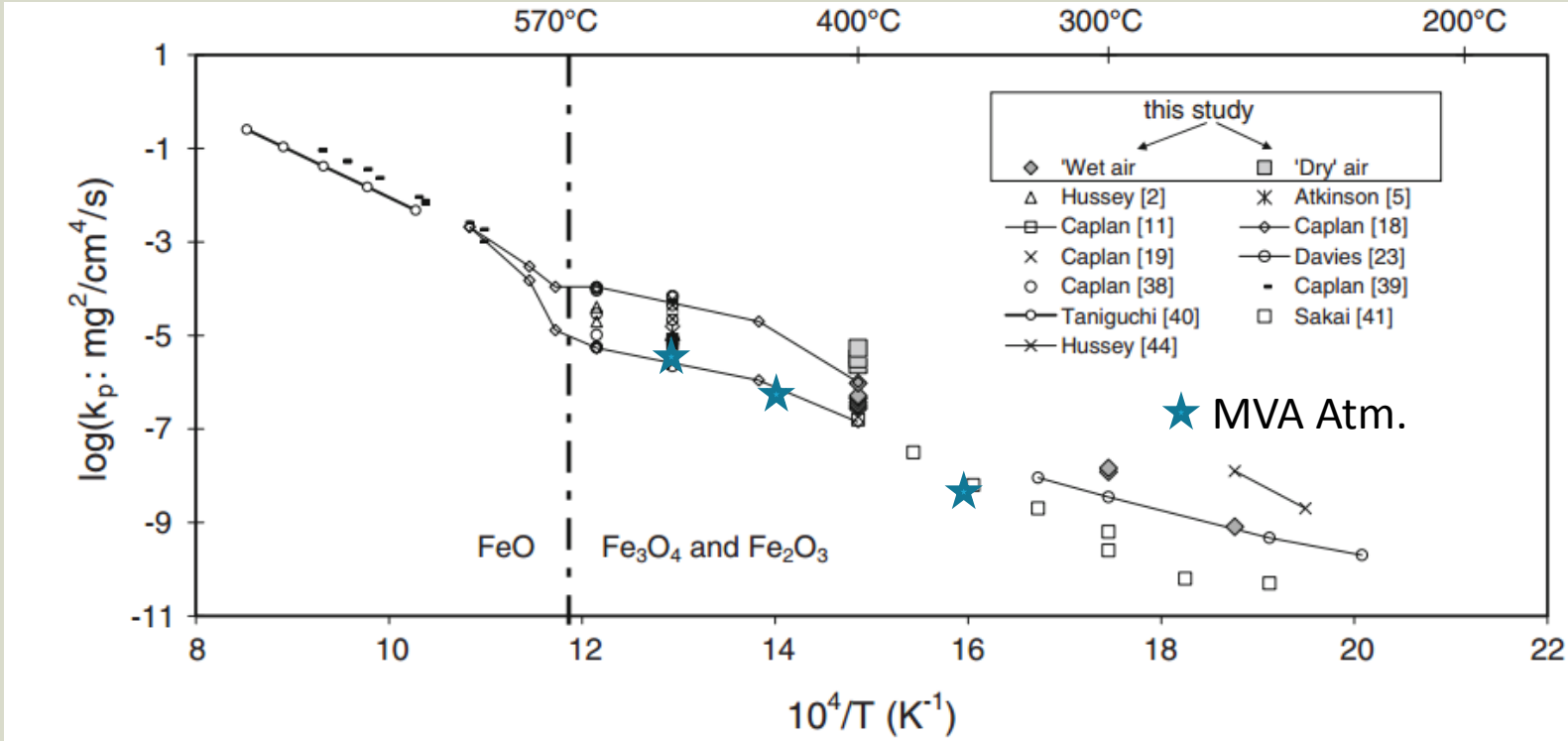


VERGLEICH DER K_P-WERTE AUS EIGENEN UNTERSUCHUNGEN MIT DEN LITERATURDATEN



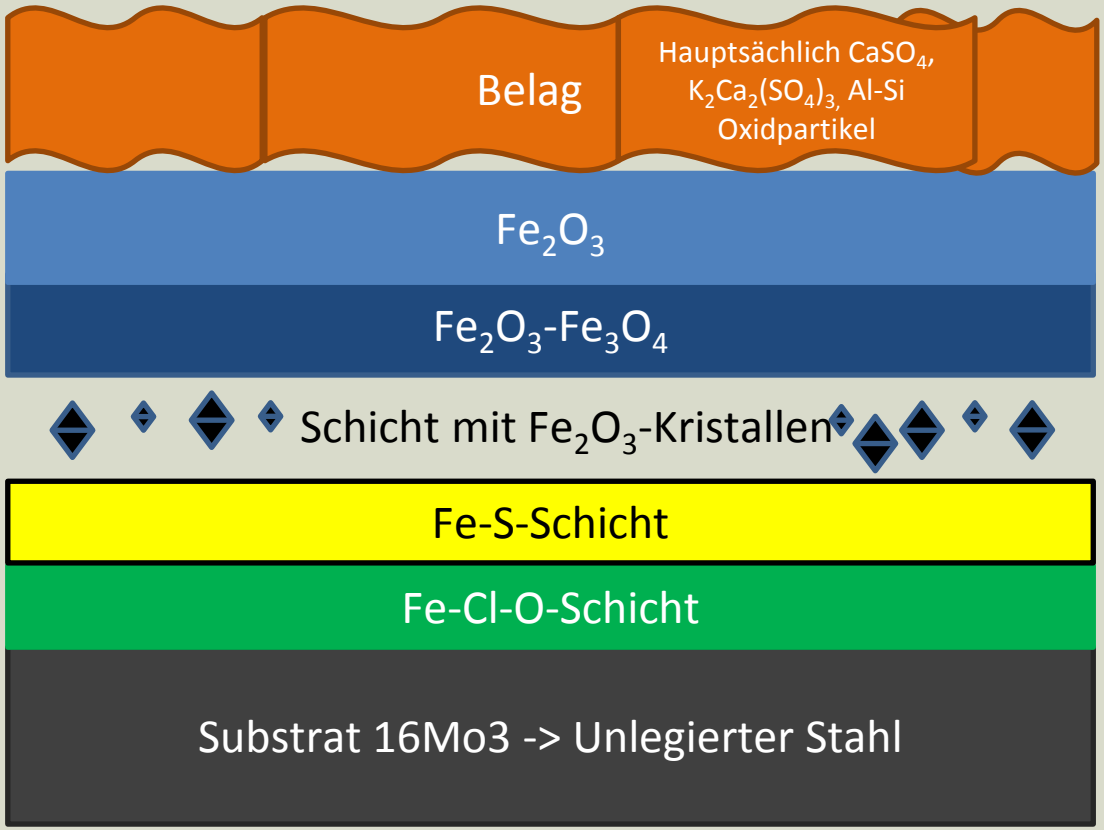
$$\frac{\Delta m}{A} = (K_p t)^{0,5}$$

T [°C]	k_p [mg²/cm⁴ s]
350	5.5 *10-8
440	8.3* 10-7
500	9,7*10-6



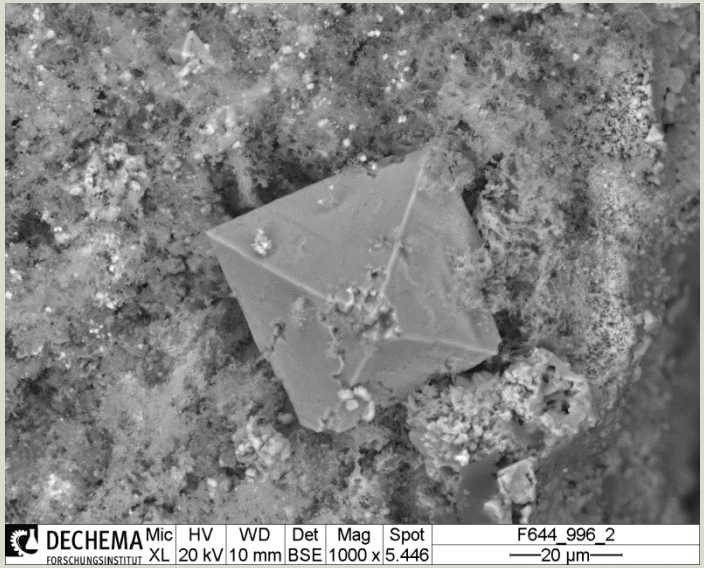
Iron Oxidation at low temperature (260–500° C) in air and the effect of water vapor
N. Bertrand, C. Desgranges, D. Poquillon, M.C. Lafont, D. Monceau, Ox. Met. 73 (2009), 139-162

SCHEMATISCHER AUFBAU DER KORROSIONSSCHICHT



N_2- 8% O_2 – 17% H_2O- 10%CO_2 -0,1HCl- 0,01 SO_2

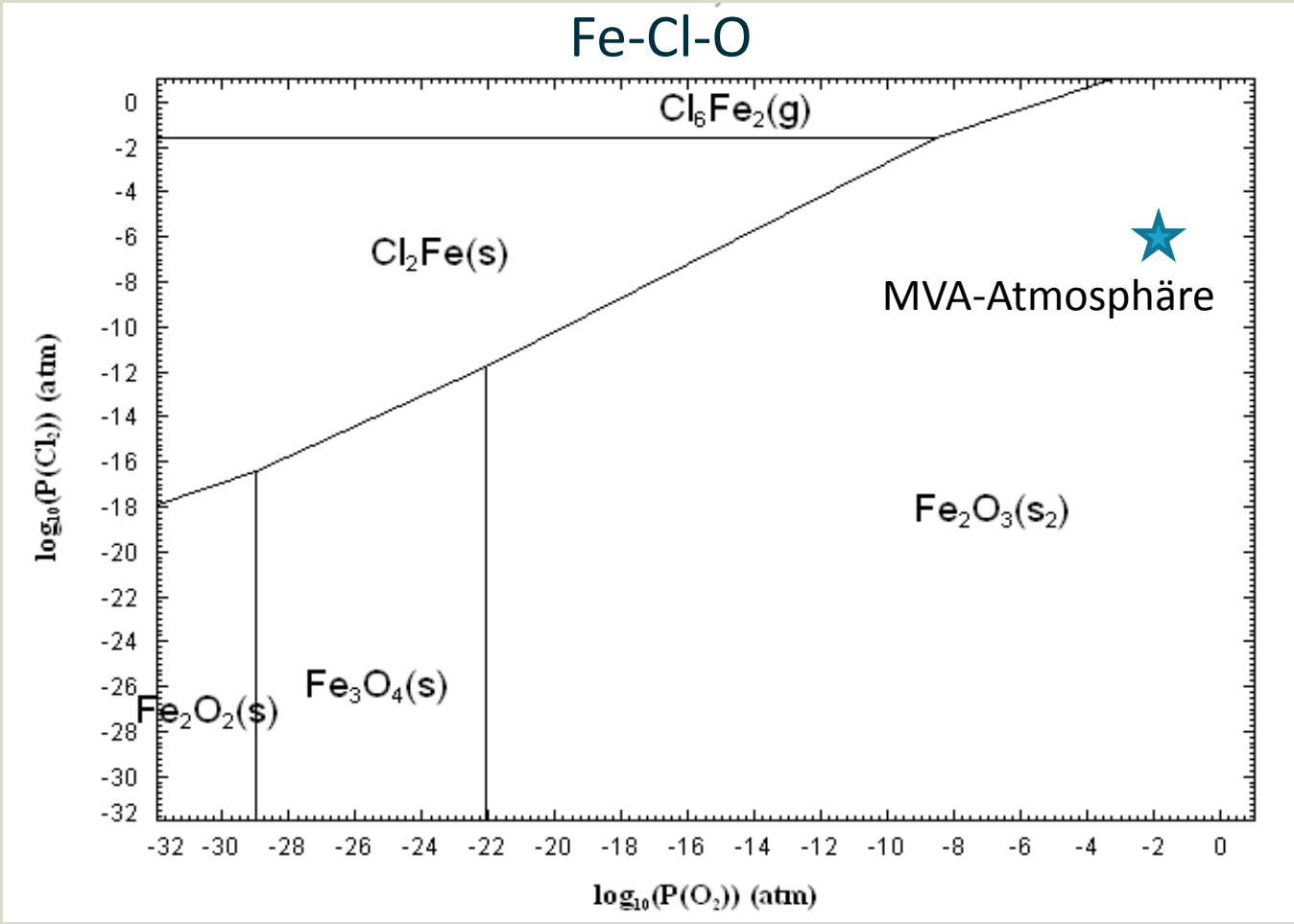
SIMULATION DER KORROSIONSSCHICHT IM LABOR

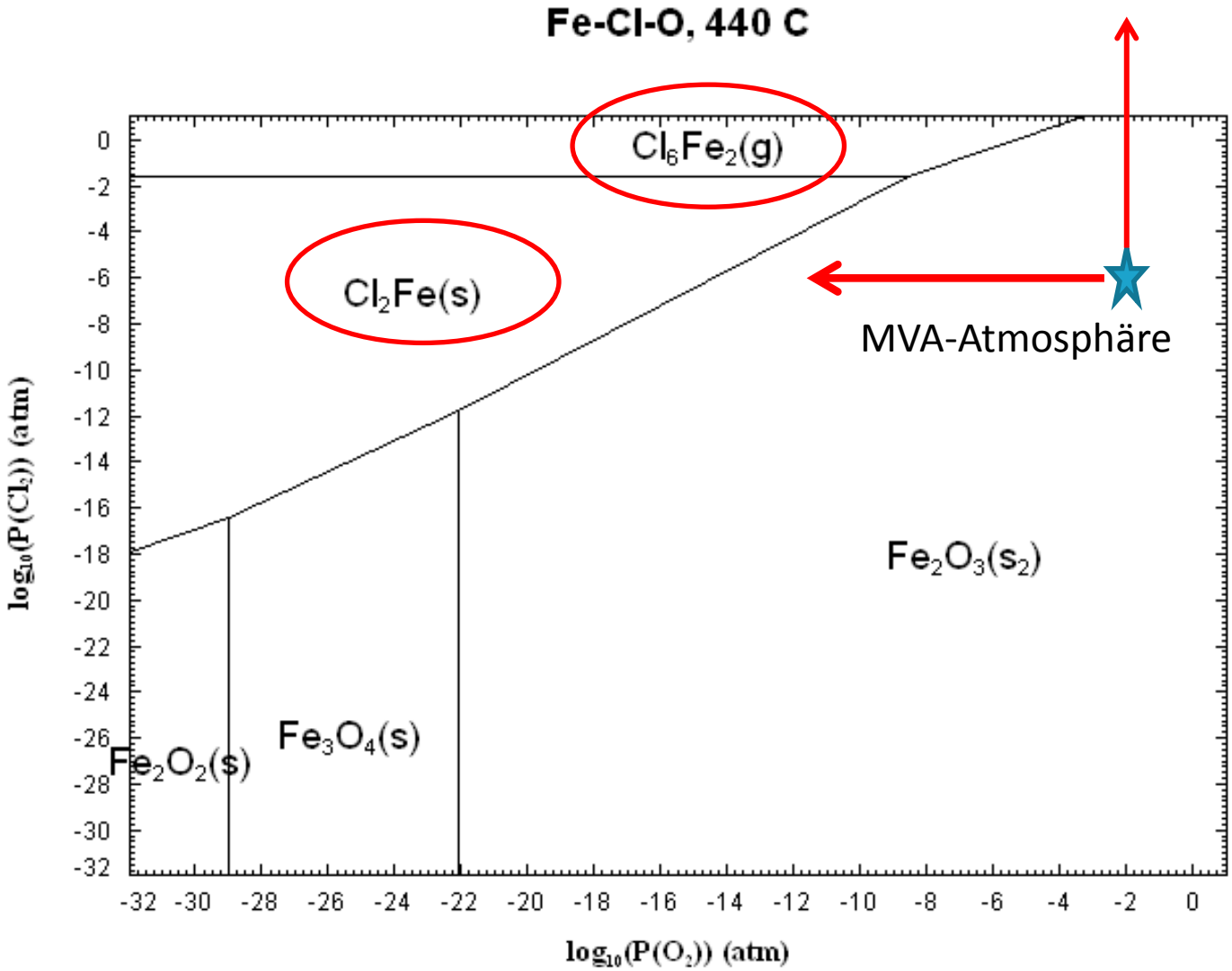


Fe_2O_3-Kristalle – Entstehung?

Welche Atmosphäre führt zur entsprechenden Kristallbildung?

PHASENSTABILITÄTSDIAGRAMM BEI 440° C (FACTSAGE)



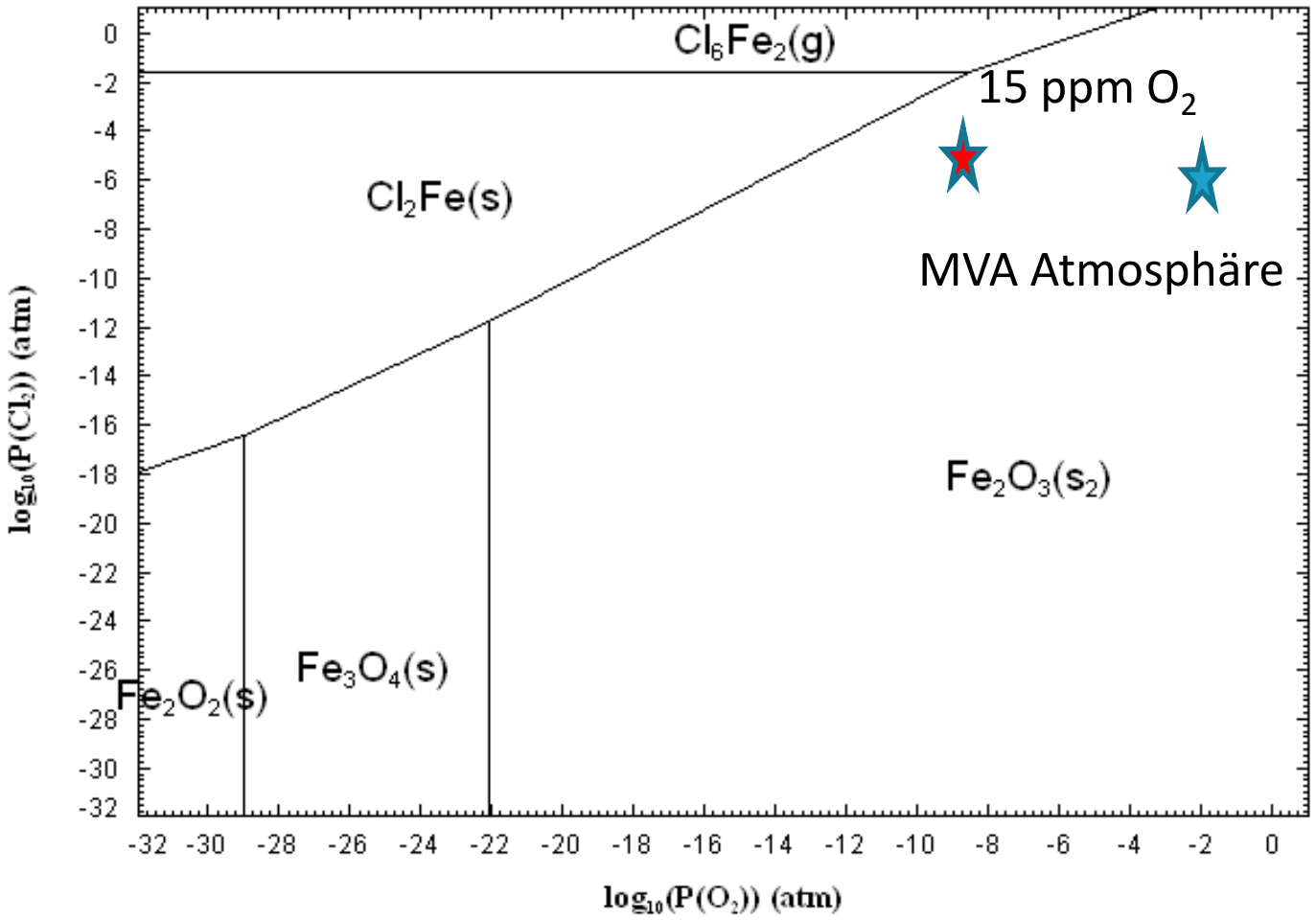

Fe-Cl-O, 440 C
Cl6Fe2(g)
Cl2Fe(s)
MVA-Atmosphäre
Fe2O3(s2)
Fe3O4(s)
Fe2O2(s)
log10(P(Cl2)) (atm)
log10(P(O2)) (atm)
0
-2
-4
-6
-8
-10
-12
-14
-16
-18
-20
-22
-24
-26
-28
-30
-32
-32 -30 -28 -26 -24 -22 -20 -18 -16 -14 -12 -10 -8 -6 -4 -2 0

ÜBERBLICK DER LABORUNTERSUCHUNGEN

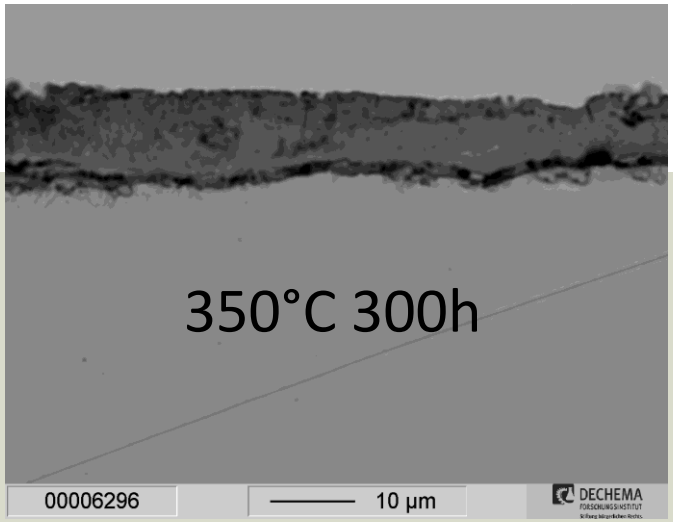
Temperatur [°C]	Zeit [h]	Gaszusammensetzung [%]
350, 380, 410, 440, 470, 500	300, 600, 900	**P(O_2) - reich:** **1)** Sythetische Luft– max. Auslagerungszeit 300h **2)** N_2 – 0,1HCl + 0,01SO_2 +8O_2 + 10CO_2 + 17H_2O + ***(Simulierte MVA Atmosphere)*** **P(O_2) - arm** **3)** N_2 – 0,1HCl - 15ppm O_2 **4)** N_2 – 0,1HCl + 15ppm O_2 + 0,01 SO_2 + N_2Rest **5)** N_2 – 0,1HCl + 450ppm O_2 + N_2Rest

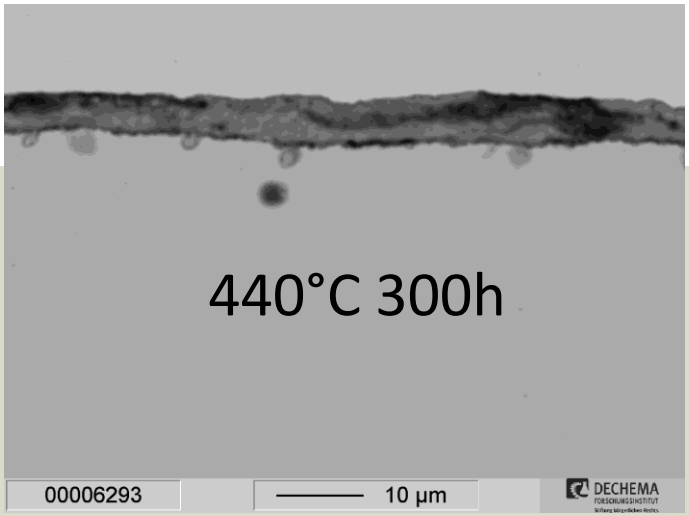
N_2 - 0,1%HCl +15ppm O_2

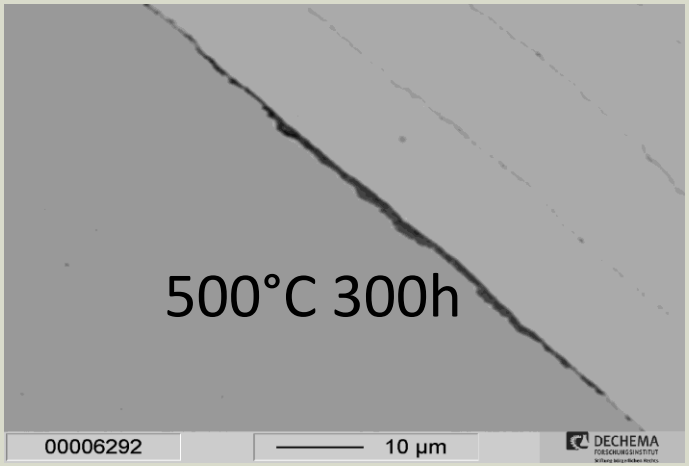
Fe-Cl-O, 440° C

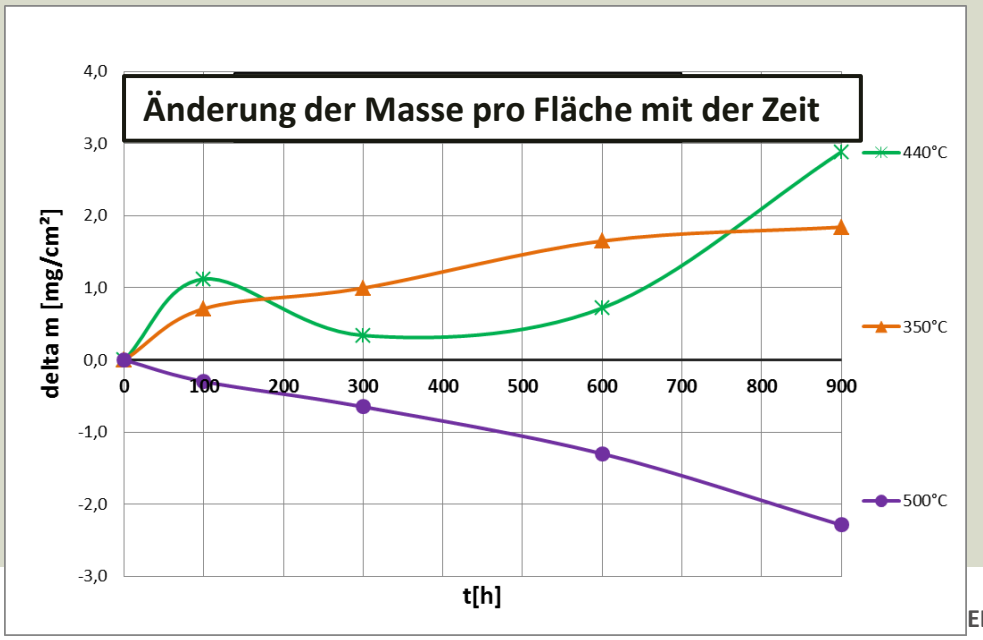


N_2 - 0,1%HCl +15ppm O_2



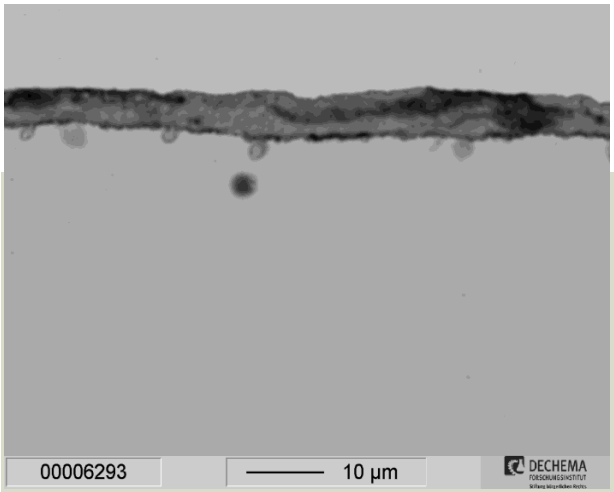


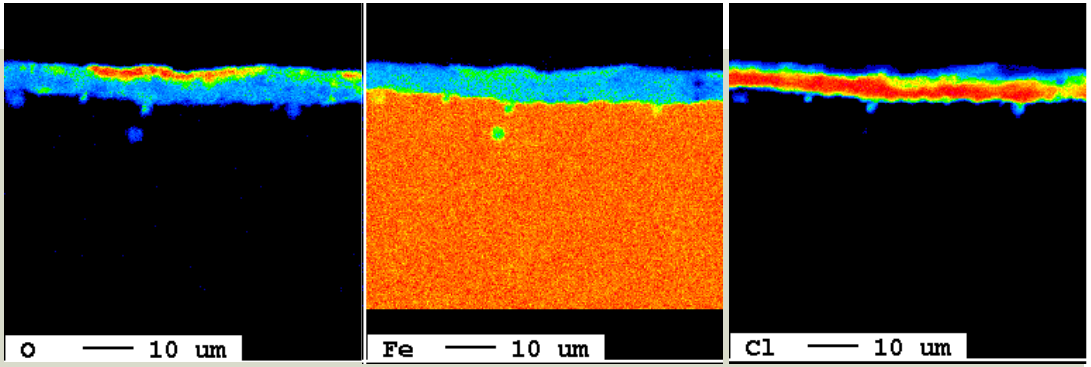


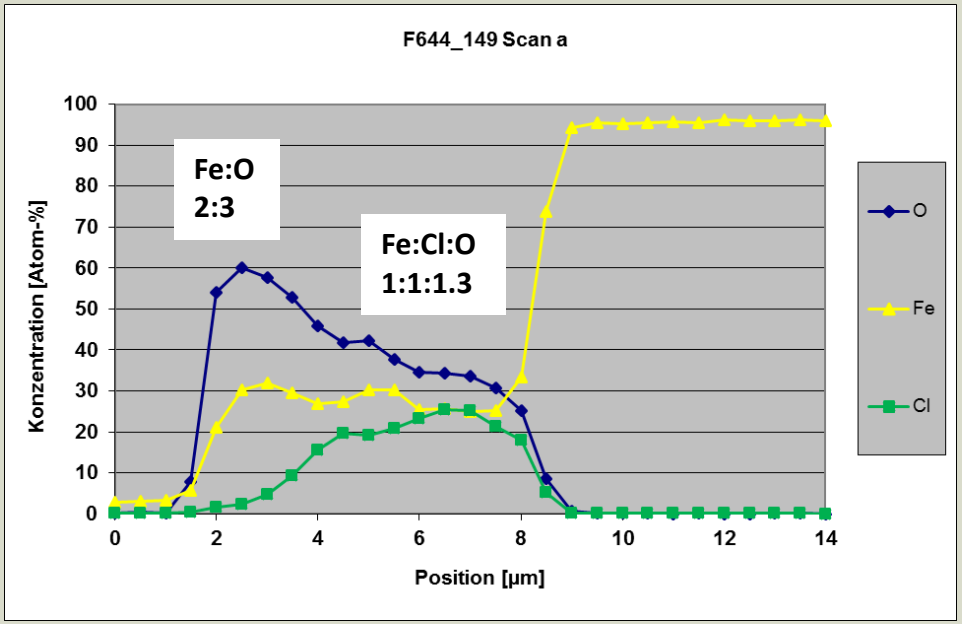


Je höher die Temperatur, desto höher der Massenverlust bedingt durch Verdampfung.

N_2 - 0,1%HCl +15ppm O_2 -300h bei 440° C







Fe_2O_3

+

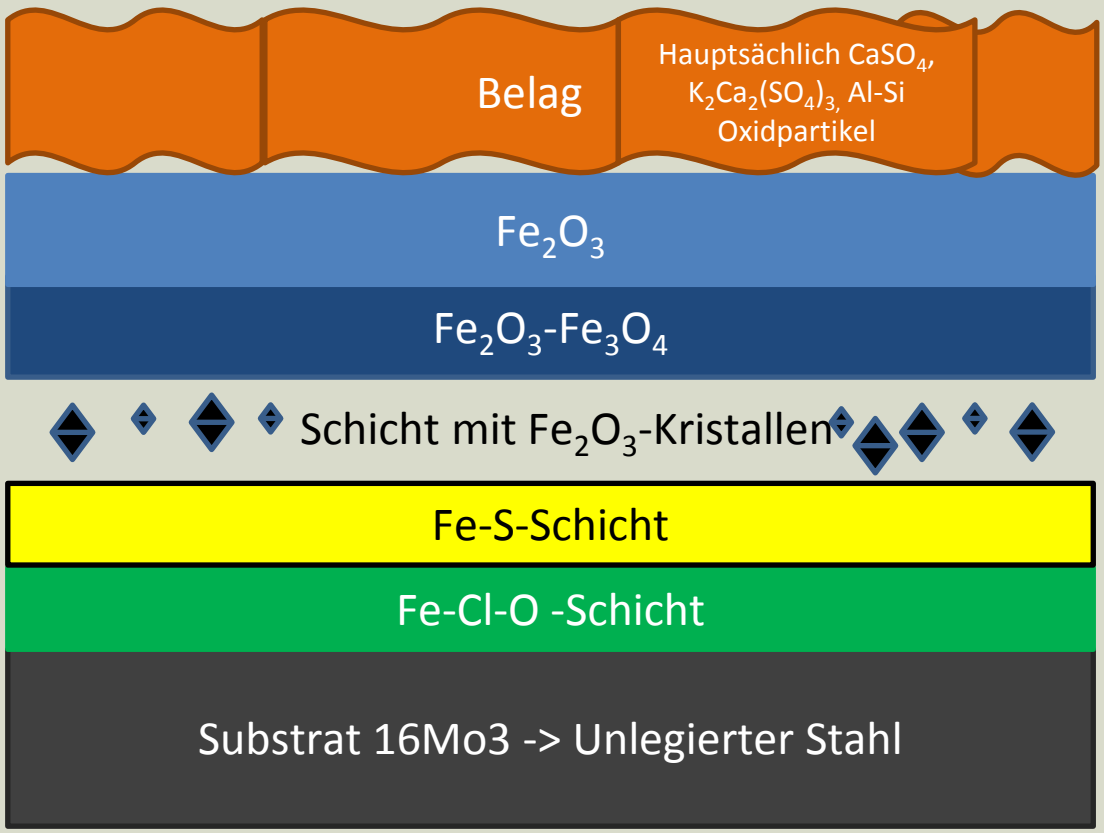
FeOCl

?

viel

wenig

SCHEMATISCHER AUFBAU DER KORROSIONSSCHICHT

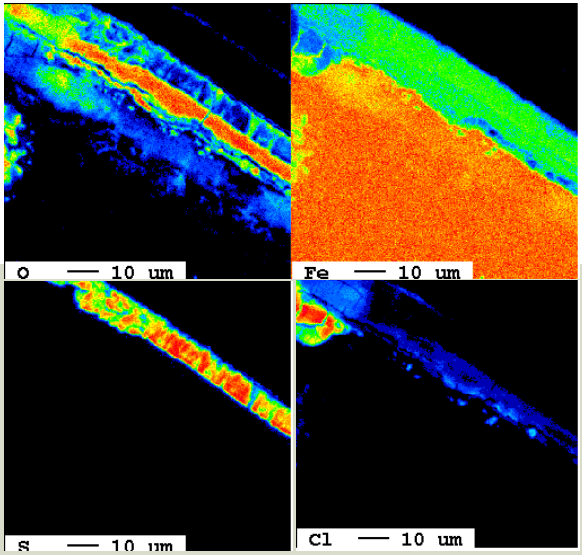


N_2 – 0,1% HCl - 15ppm O_2

ÜBERBLICK DER LABORUNTERSUCHUNGEN

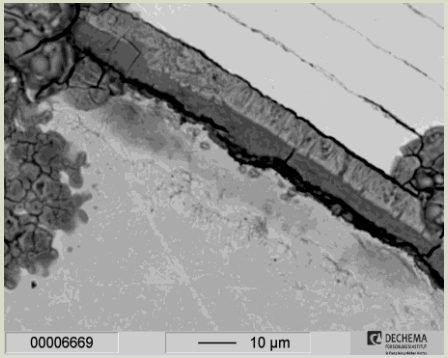
Temperatur [°C]	Zeit [h]	Gaszusammensetzung [%]
350, 380, 410, 440, 470, 500	300, 600, 900	**P(O_2) - reich:** **1)** Sythetische Luft– max. Auslagerungszeit 300h **2)** N_2 – 0,1HCl + 0,01SO_2 +8O_2 + 10CO_2 + 17H_2O + ***(Simulierte MVA-Atmosphere)*** **P(O_2) - arm** **4)** N_2 – 0,1HCl - 15ppm O_2 **5)** N_2 – 0,1HCl + 15ppm O_2 + 0,01 SO_2 + N_2Rest **6)** N_2 – 0,1HCl + 450ppm O_2 + N_2Rest

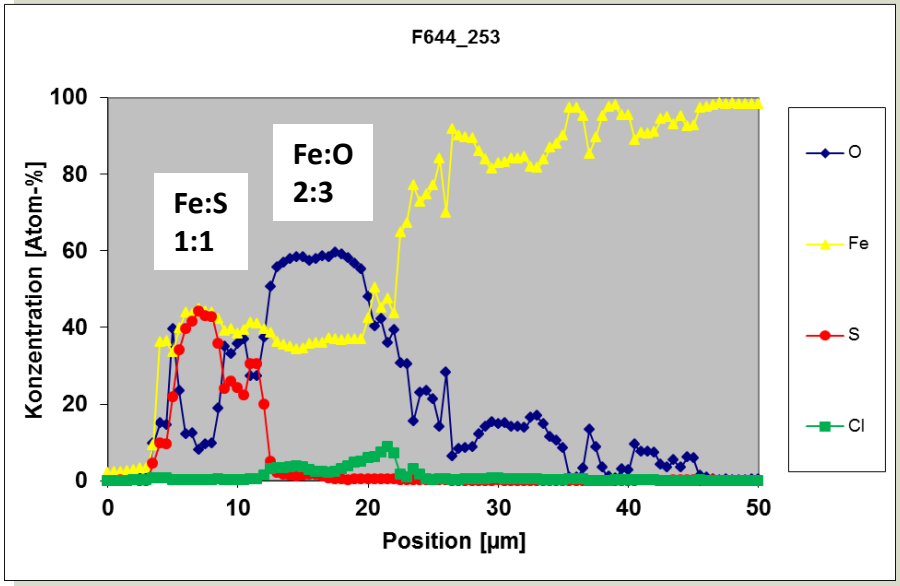
N_2 – 0,1%HCl – 0,01%SO_2 - 15ppm O_2
300h bei 440°C

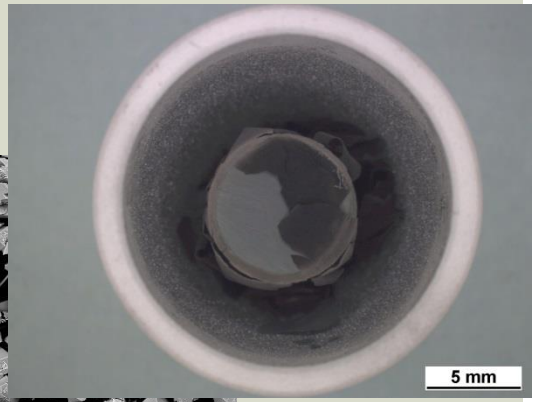


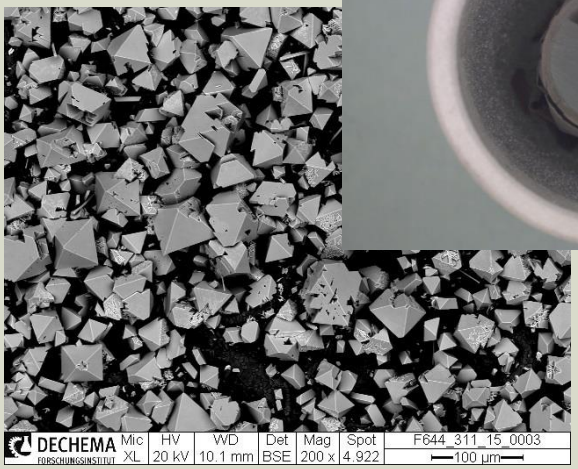
viel

wenig





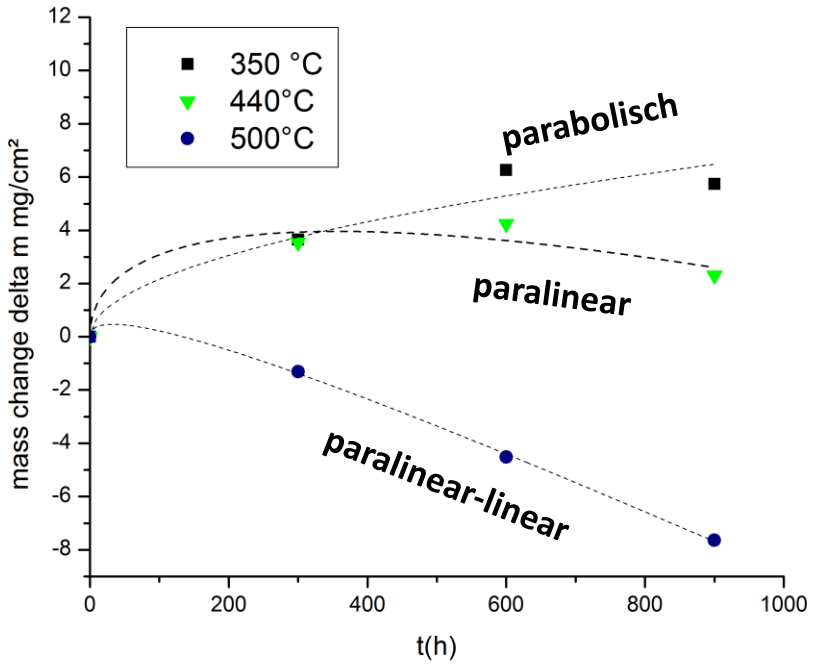




T > 410°C

T < 500°C

N_2 – 0,1%HCl – 0,01%SO_2 - 15ppm O_2



Fit:

Parabolisch: $\frac{\Delta m}{A} = (K_p t)^{0,5}$

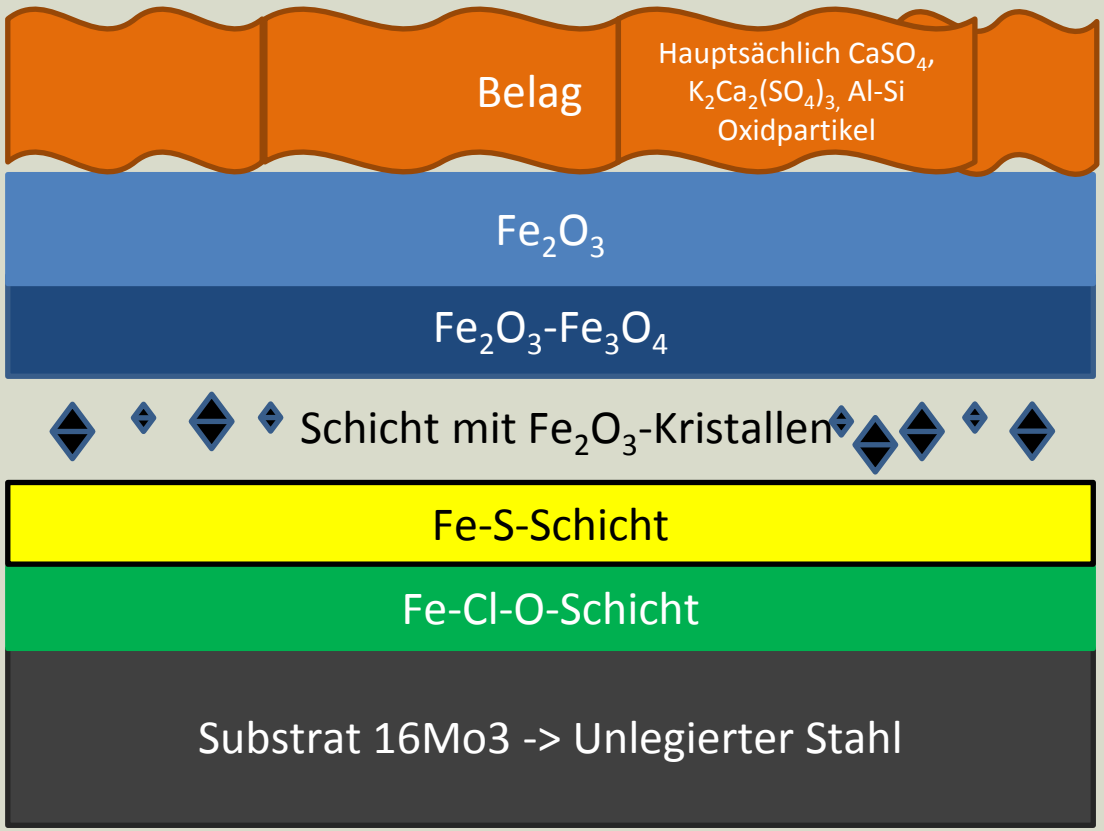
Paralinear*: $\frac{\Delta m}{A} = (K_p t)^{0,5} - K_v * t$

Δm: *Massenänderung*
A: *Fläche*
t: *Zeit*
K_p: *parabolische Ratenkonstante*
K_v: *lineare Verdampfungsrate*

T [°C]	k_p [mg²/cm⁴ s]	k_v [mg/cm² s]
350	**2,3*10-5**	0
440	**4,9*10-5**	**3,0*10-6**
500	**8,3*10-6**	**3,9*10-6**

* Hagel, Trans. Am. Soc. Met., 56, 1963, 583-599

SCHEMATISCHER AUFBAU DER KORROSIONSSCHICHT



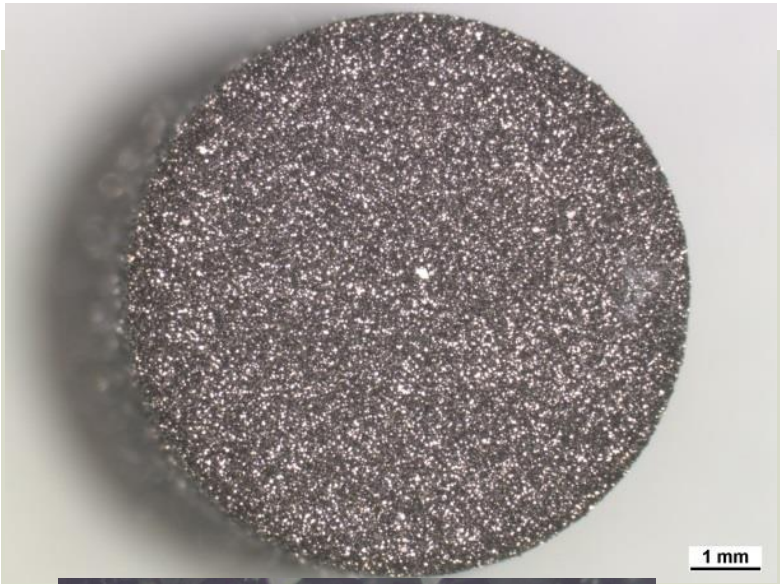
N_2 – 0,1%HCl – 0,01%SO_2 - 15ppmO_2

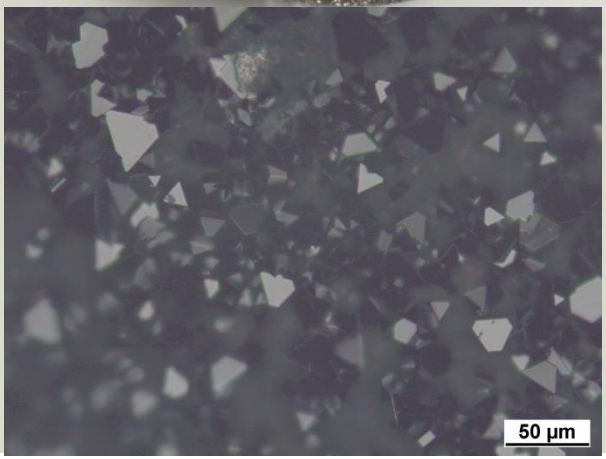
N_2 – 0,1%HCl - 15ppmO_2

ÜBERBLICK DER LABORUNTERSUCHUNGEN

Temperatur [°C]	Zeit [h]	Gaszusammensetzung [%]
350, 380, 410, 440, 470, 500	300, 600, 900	**P(O_2) - reich:** **1)** Sythetische Luft– max. Auslagerungszeit 300h **2)** 0,1HCl + 0,01SO_2 +8O_2 + 10CO_2 + 17H_2O + N_2Rest ***(Simulierte MVA-Atmosphere)*** **P(O_2) - arm** **4)** N_2 – 0,1HCl - 15ppm O_2 **5)** N_2 – 0,1HCl + 15ppm O_2 + 0,01 SO_2 + N_2Rest **6)** N_2 – 0,1HCl + 450ppm O_2 + N_2Rest

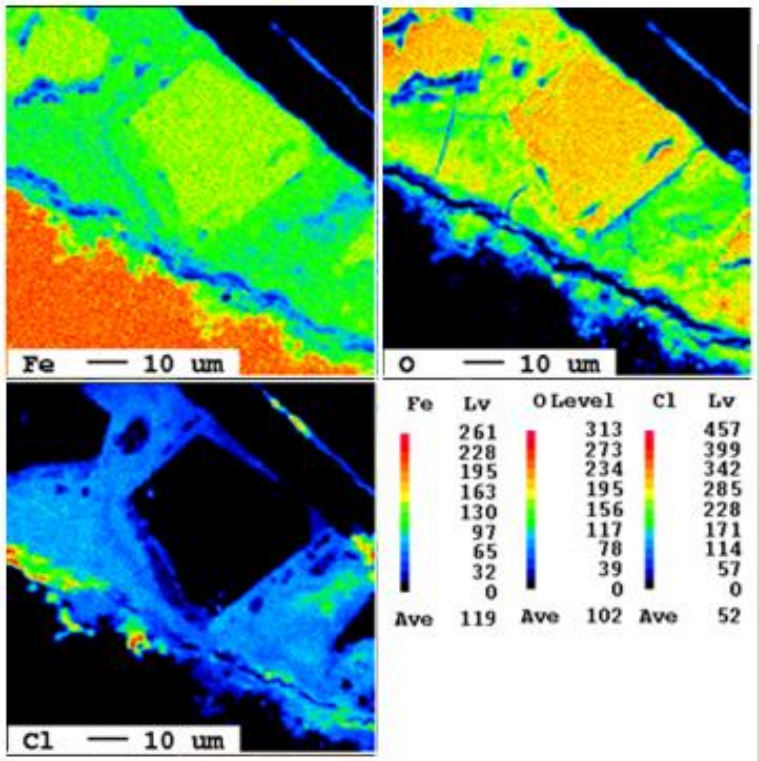
N_2 – 0,1%HCl - 15ppmO_2 – 300h bei 440°C

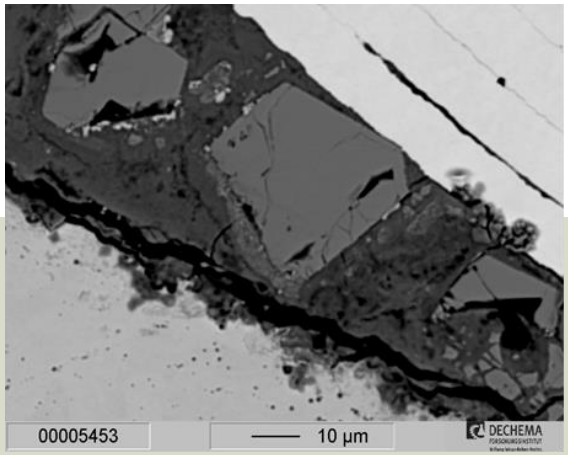


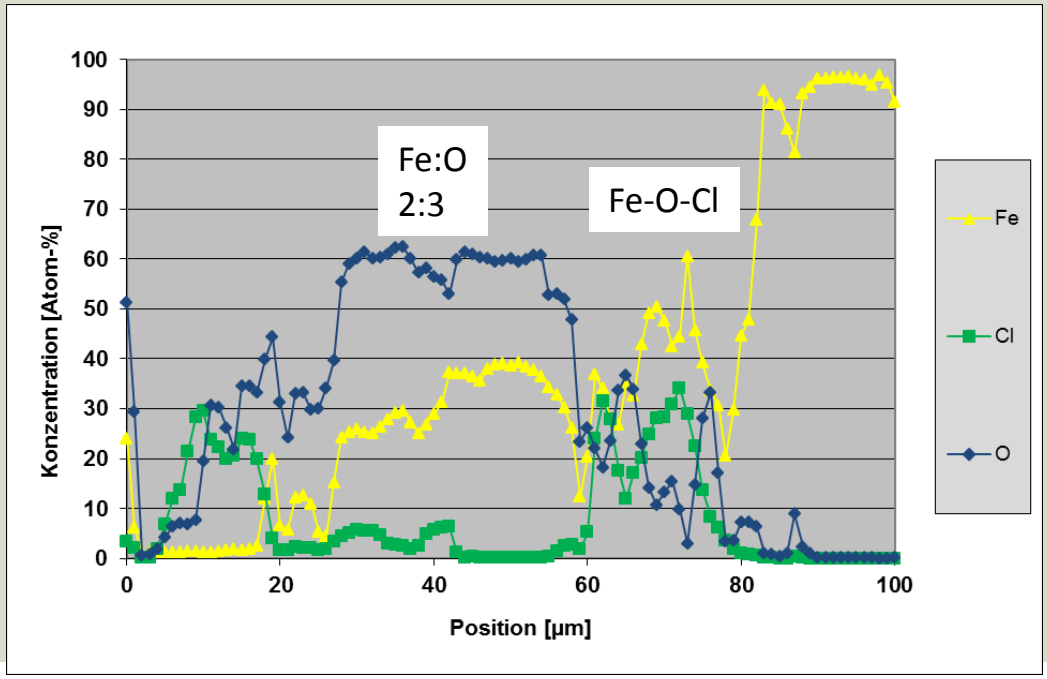


Kristallbildung erfolgt direkt an der Substratoberfläche!

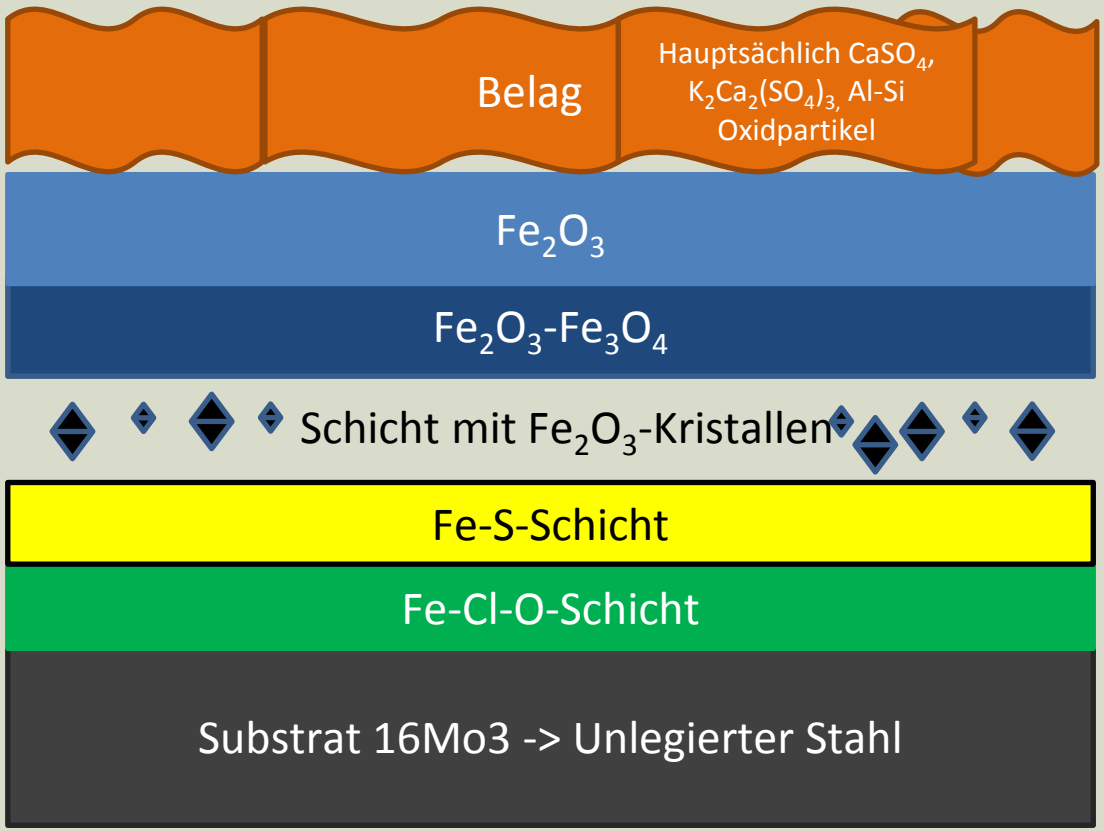
N_2 – 0,1%HCl – 450ppm O_2
300h bei 440°C







SCHEMATISCHER AUFBAU DER KORROSIONSSCHICHT

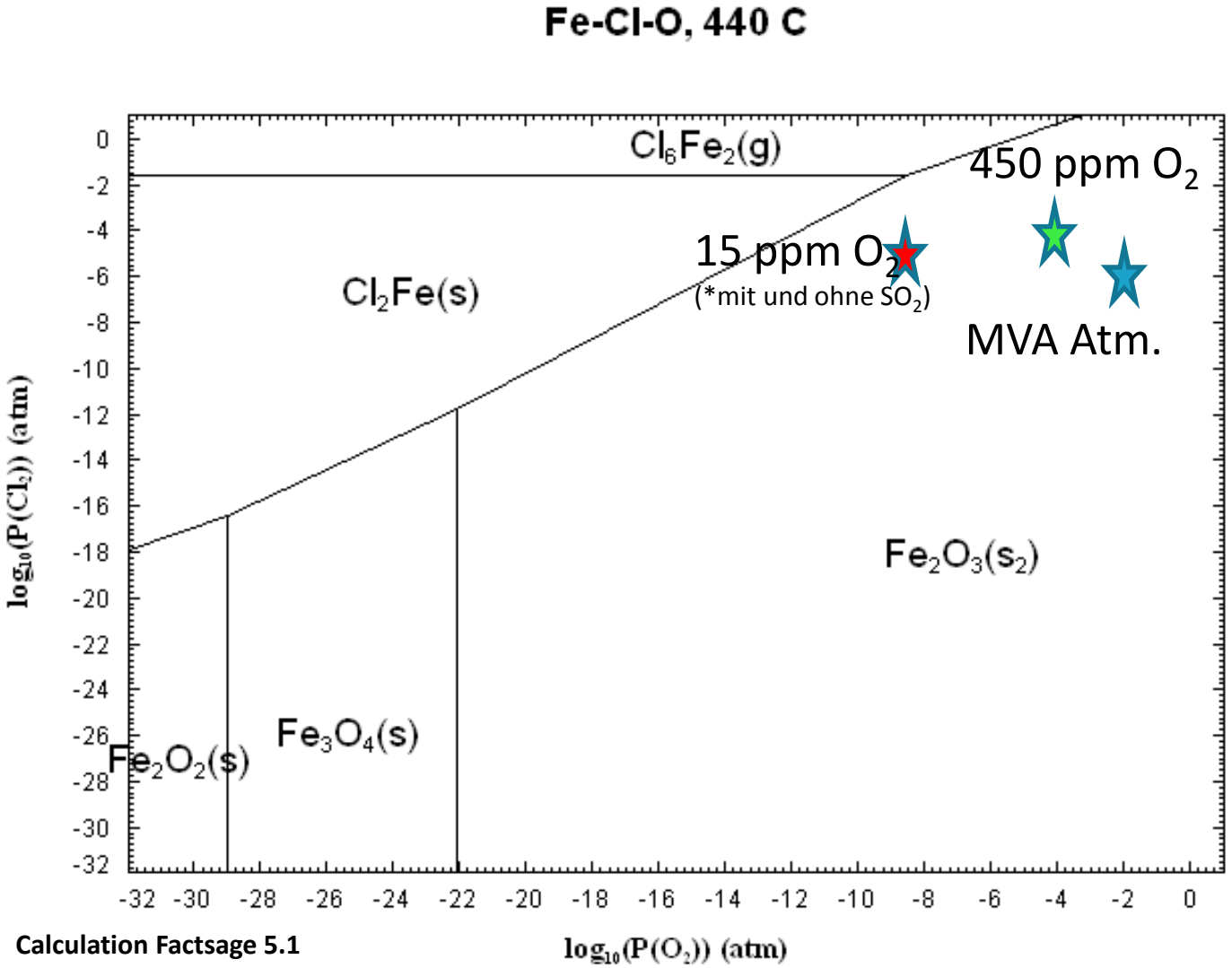


N_2 – 0,1%HCl – 450ppm O_2

N_2 – 0,1%HCl – 0,01%SO_2 - 15ppm O_2

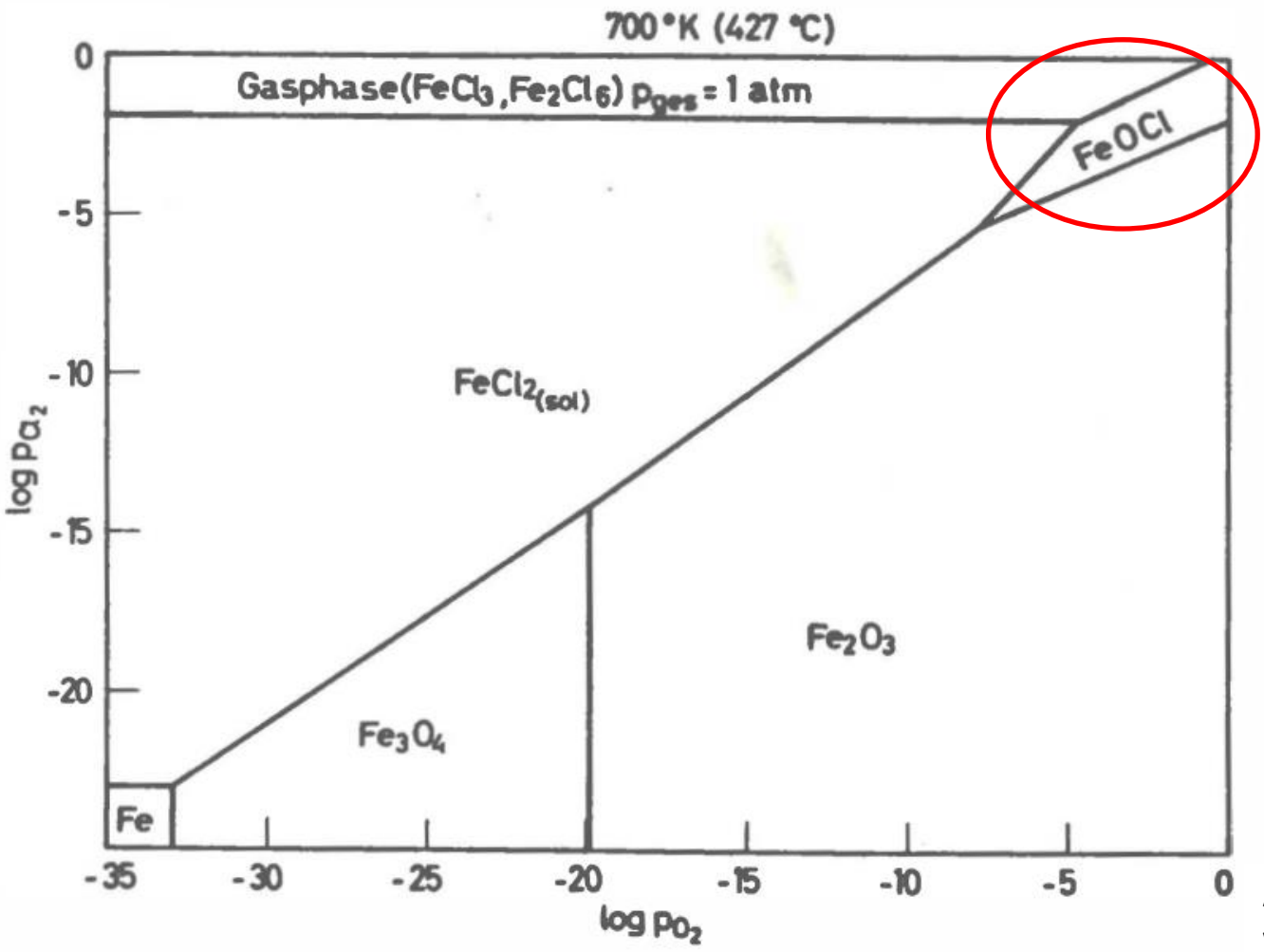
N_2 – 0,1%HCl - 15ppm O_2

ÜBERBLICK DER VERWENDETEN ATMOSPHÄREN



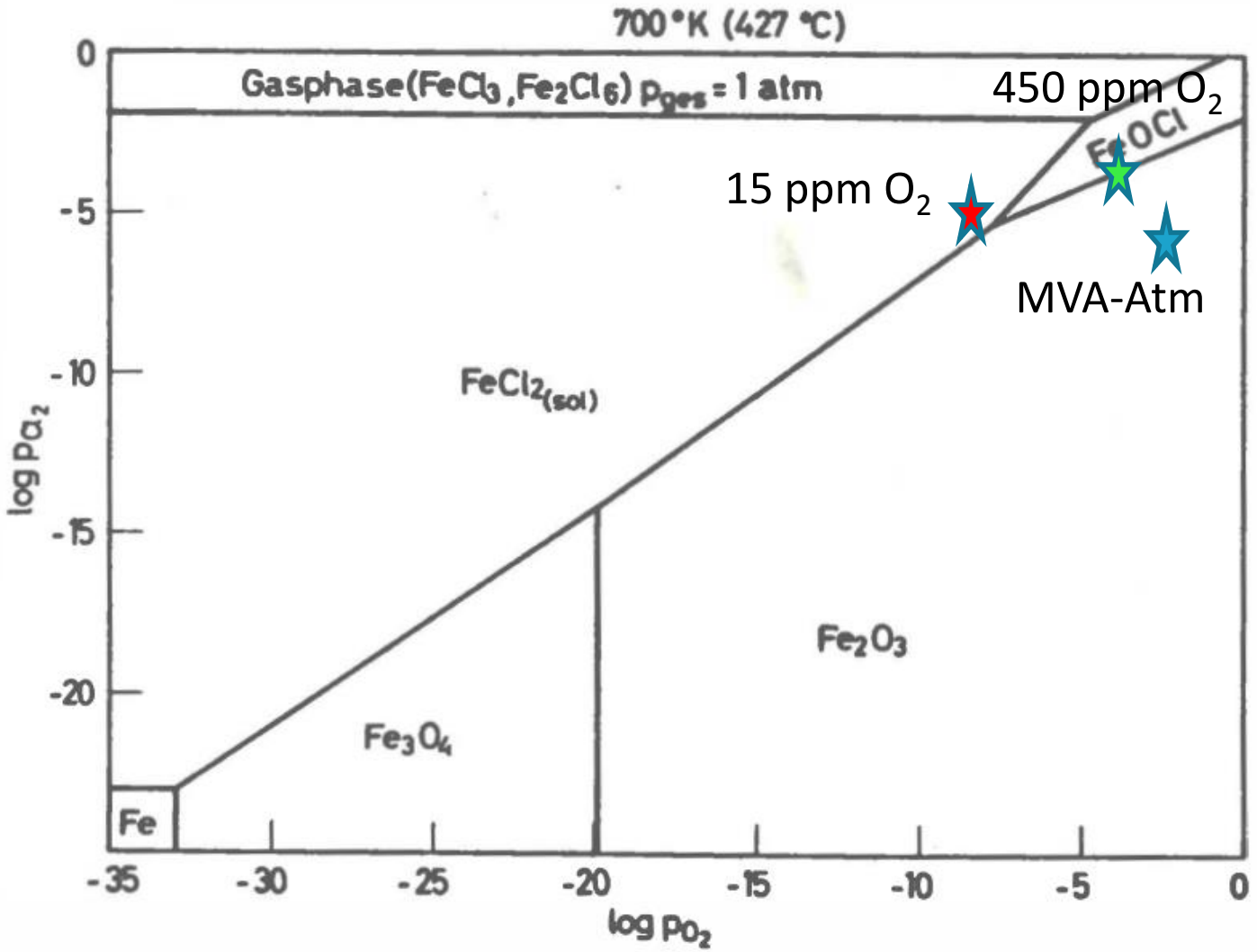
Calculation Factsage 5.1

Phasenstabilitätsdiagramm aus Literatur für Fe-Cl-O bei 427°C

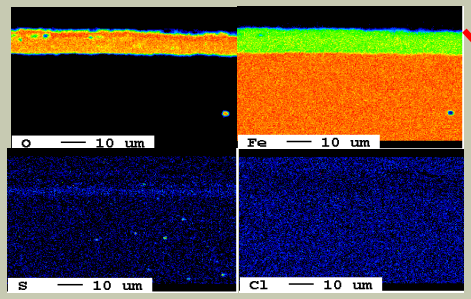
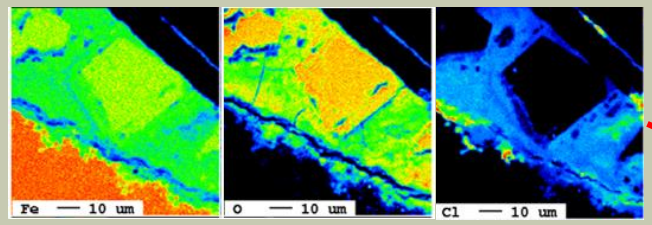
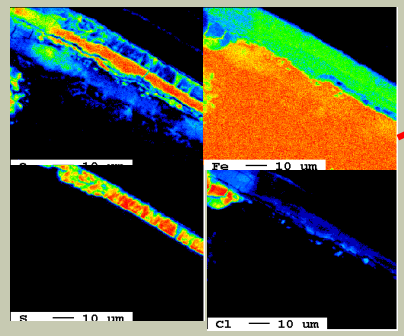
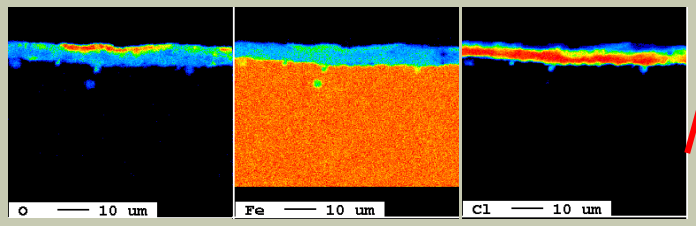


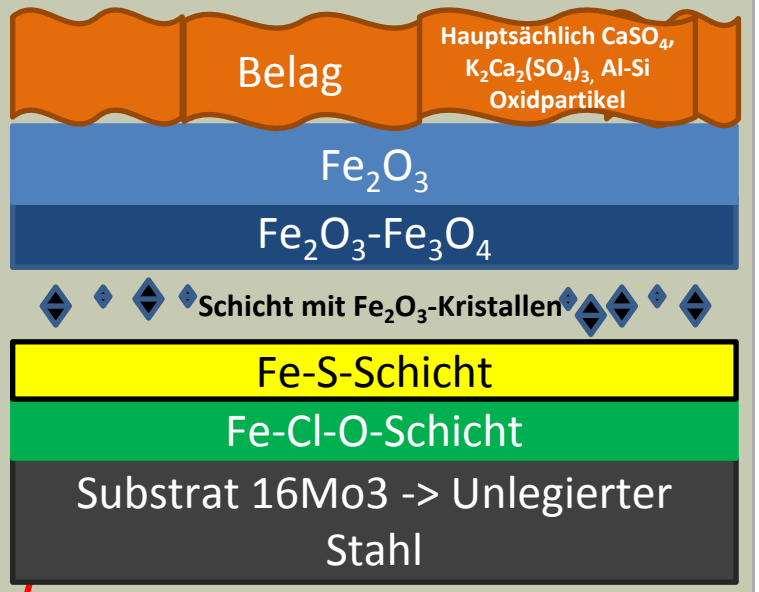
Aus Dissertation von E. Mann, 1972

ÜBERBLICK DER VERWENDETEN ATMOSPHÄREN



Aus Dissertation von E. Mann, 1972

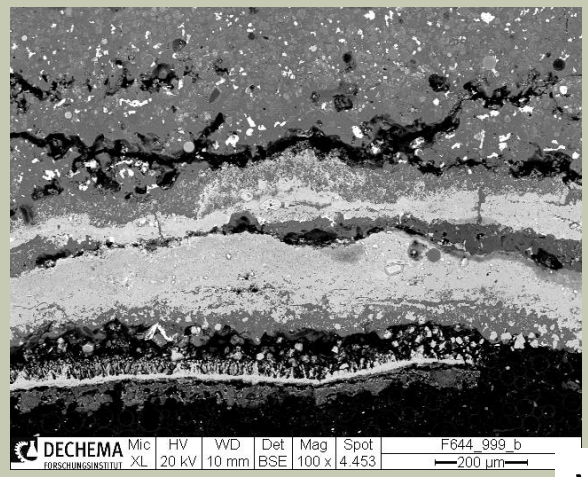
Atmosphäre	Korrosionsschicht nach 300h bei 440° C
MVA Atmosphäre	
N_2 – 0,1%HCl - 450 ppm O_2	
N_2 – 0,1%HCl – 0,01%SO_2	
N_2 – 0,1%HCl - 15ppm O_2	

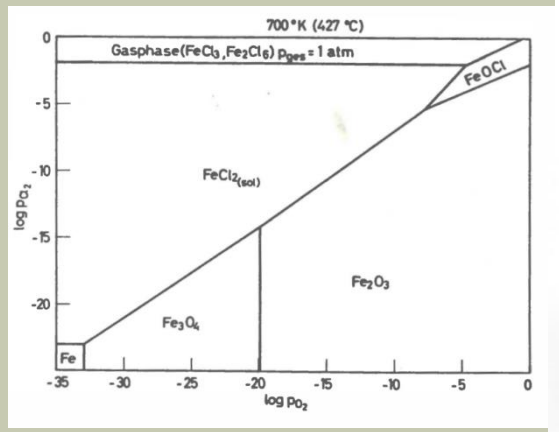


ZUSAMMENFASSUNG

Aktive Oxidation wird durch die Kristallbildung nachgewiesen.
$\underline{p(O_2) \downarrow}$ ist entscheidend für die Korrosion, nicht $\underline{p(Cl_2) \uparrow}$

Bereits unterhalb des Belags und oberhalb der äußeren Fe_2O_3-Schicht ist der Sauerstoffpartialdruck stark abgesenkt!!!





Welchen Einfluss hat FeOCl?