BAM

Bundesanstalt für Materialforschung und -prüfung

Sicherheit in Technik und Chemie

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CORROSIVE CO_2-STREAM COMPONENTS, CHALLENGING FOR MATERIALS TO BE USED IN CC(U)S APPLICATIONS

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THE WORLD CORROSION ORGANIZATION

EFC EUROPEAN FEDERATION OF CORROSION

Background

CO_2-Quality in CCUS Technology

corrosion

safety in transport technology

different sources = different impurities

costs

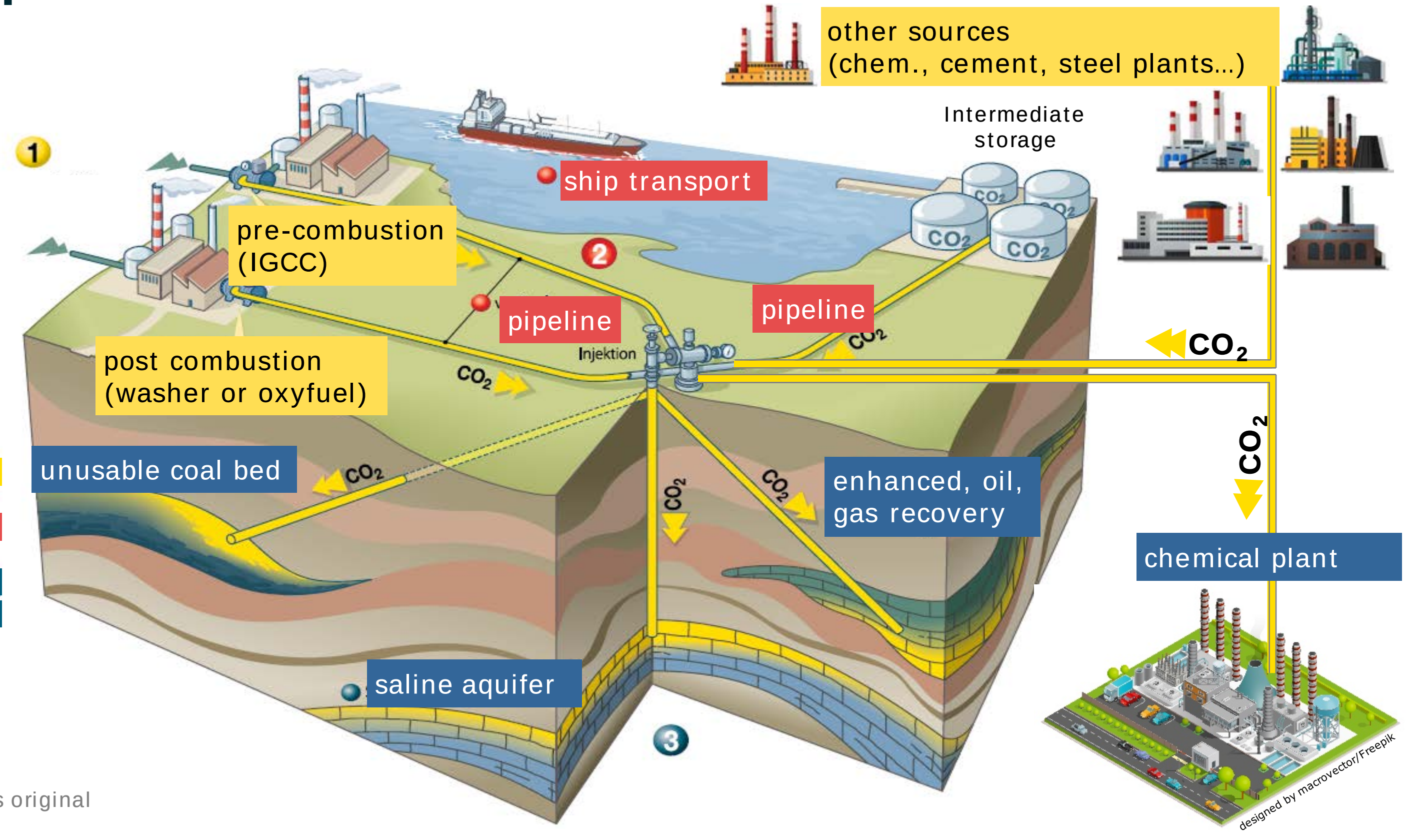
potential effect on environment

required strorage volume

Background
Process Chain

CC(U)S is a 3 step process

1 Capture
2 Transport
3 Storage
Utilization



modified from Total's original

Background

German CCS Research Programs

Directive 2009/31/EC

(38) Access to CO_2 transport networks and storage sites, irre-

- **How to define "…reasonable minimum composition thresholds…"?**
- **Which reasonable impurity levels may be viable in practical applications?**

to be met through CCS. Pipelines for CO_2 transport should, where possible, be designed so as to facilitate access of CO_2 streams meeting reasonable minimum composition thresholds. Member States should also establish dispute settlement mechanisms to enable expeditious settlement of disputes regarding access to transport networks and storage sites.

MLU

Background

Chemical Reactions within the CO_2-Stream

Equilibrium and Interactions between NO_x, SO_x, O_2:

$2\ NO + O_2 \rightarrow 2\ NO_2$
$2\ NO_2 + O_2 \rightarrow 2\ NO_3$

$NO_2 + NO \leftrightarrow N_2O_3 \rightarrow HNO_2$
$2\ NO_2 \leftrightarrow N_2O_4 \rightarrow HNO_2 + HNO_3$
$NO_2 + NO_3 \leftrightarrow N_2O_3 \rightarrow HNO_3$

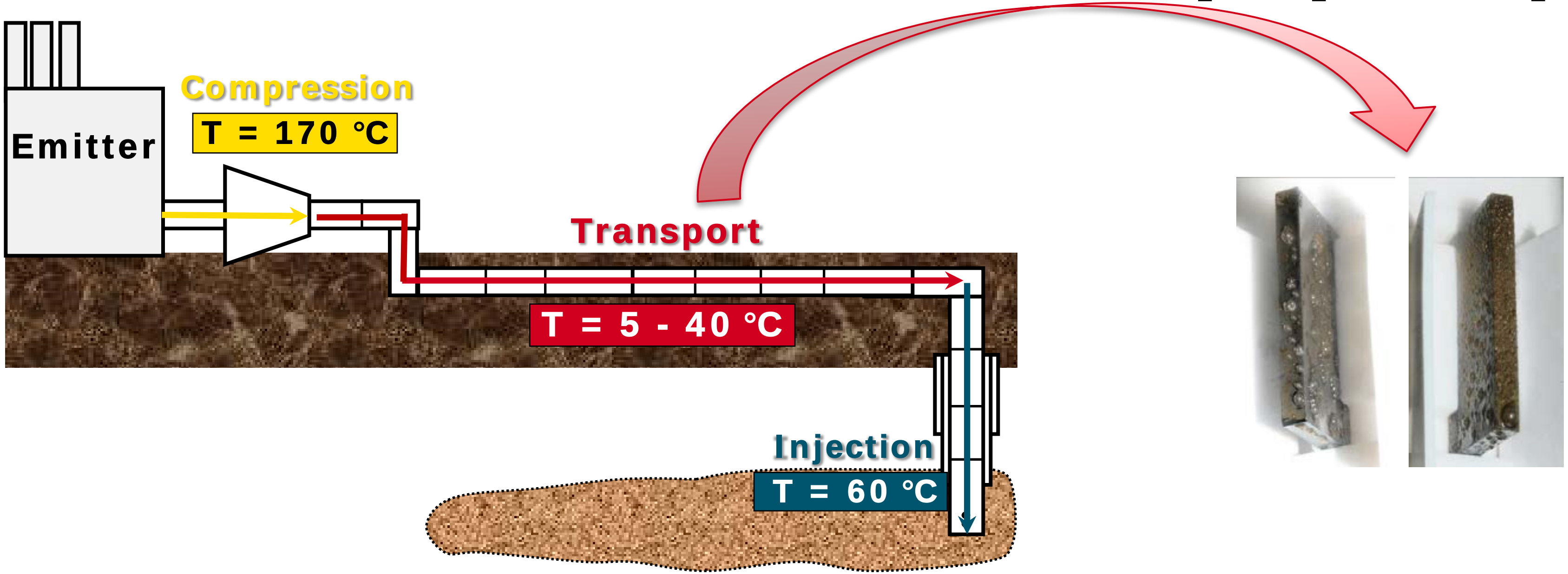
$\Rightarrow$ **How will reducing impurities modify these interactions?**

$2\ SO_2 + O_2 \rightarrow 2\ SO_3$ (very slow)
$SO_2 + NO_2 \rightarrow SO_3 + NO$ (faster alternative)
$SO_2 + H_2O \rightarrow H_2SO_3$
$SO_3 + H_2O \rightarrow H_2SO_4$

Corrosion Investigations

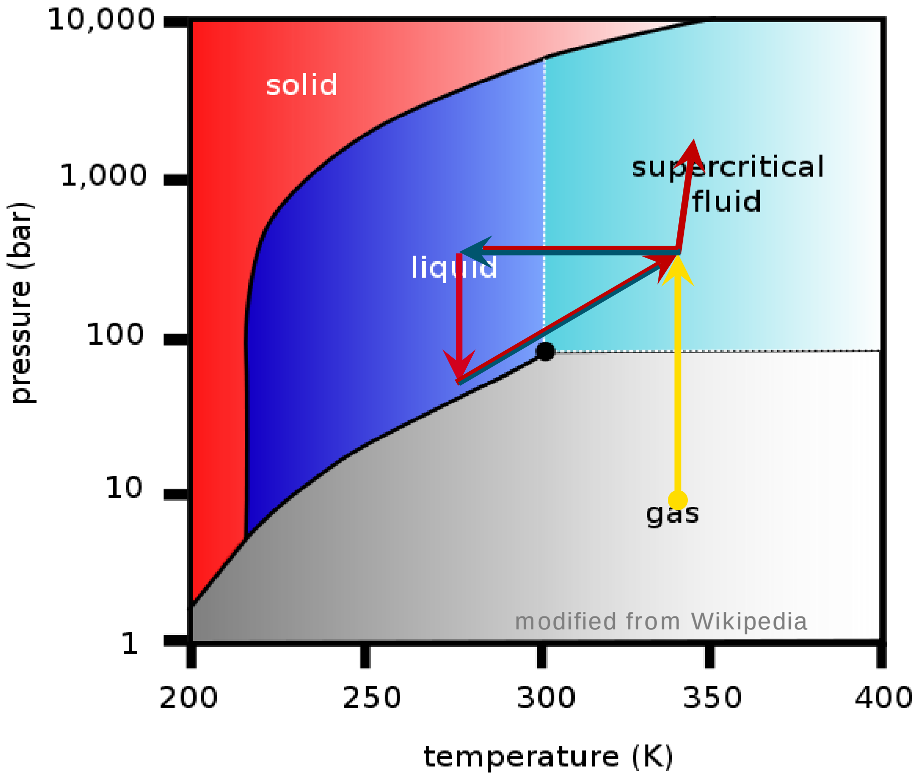
Approach

CO_2 with O_2, NO_x, SO_x,
CO, H_2S, H_2, …and H_2O



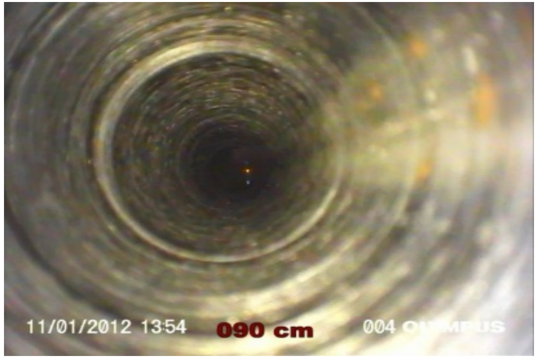
Corrosion Investigations

Phase Diagram CO_2



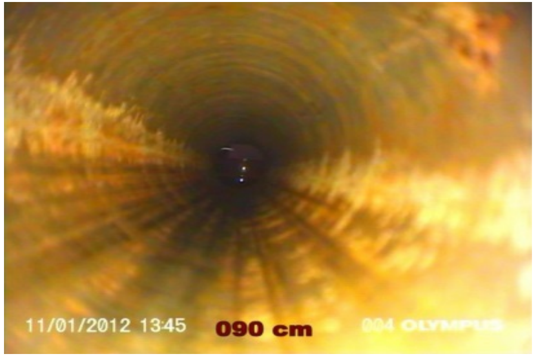
Corrosion Investigations

First Pipeline Tests

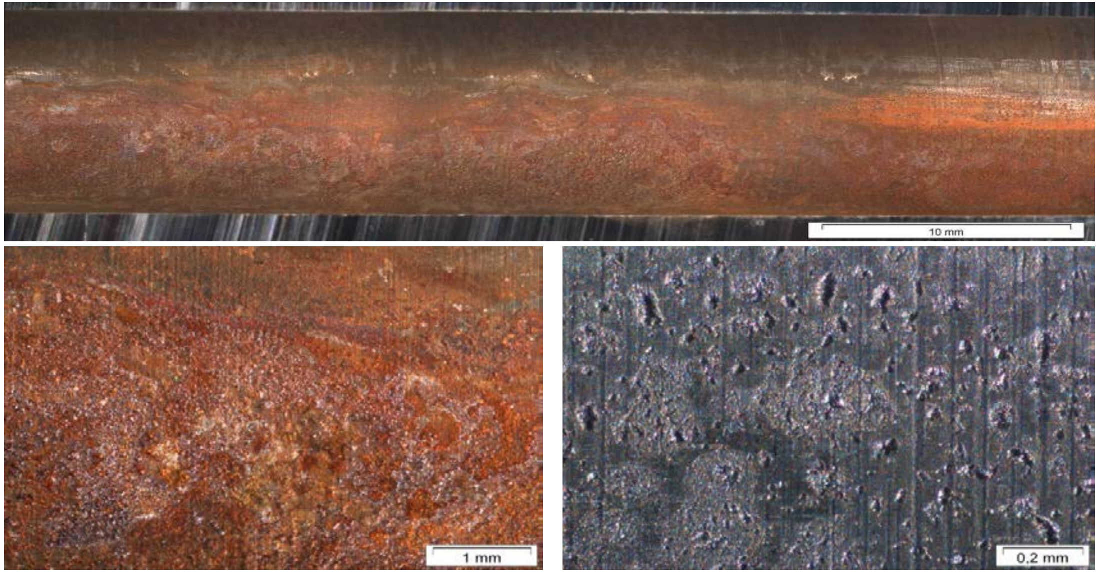


before

after



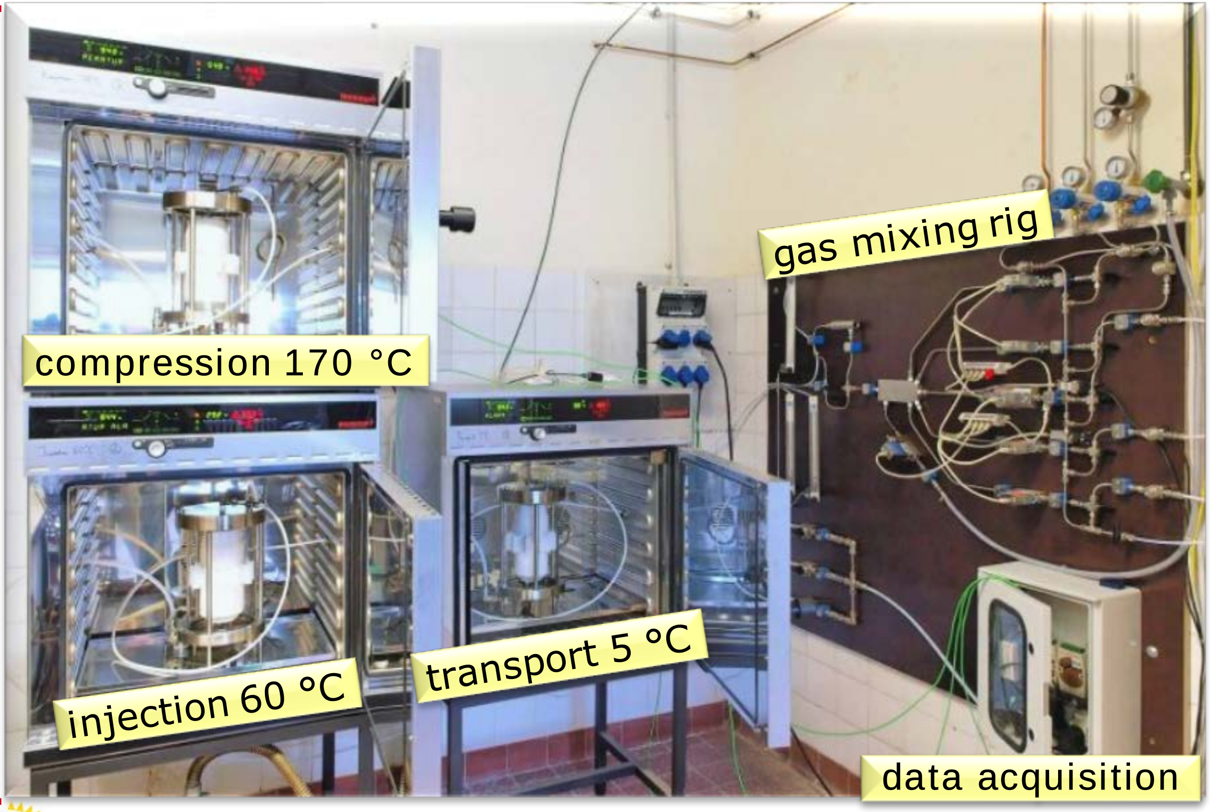
1000 h, 50 °C, 150 bar, 2 m/s CO_2,
25 ppm H_2O, 25 ppm SO_2, 0.8 % O_2



Despite of very low water content clear corrosion effects

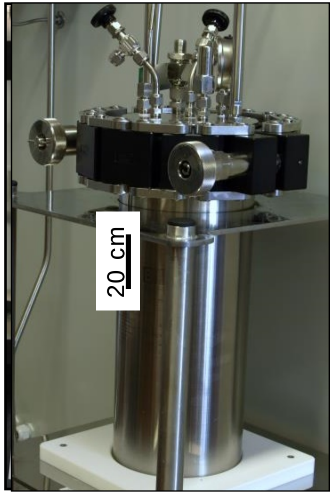
Corrosion Investigations

Lab Setup



High pressure

100 bar / 5...40 °C



circulating flow

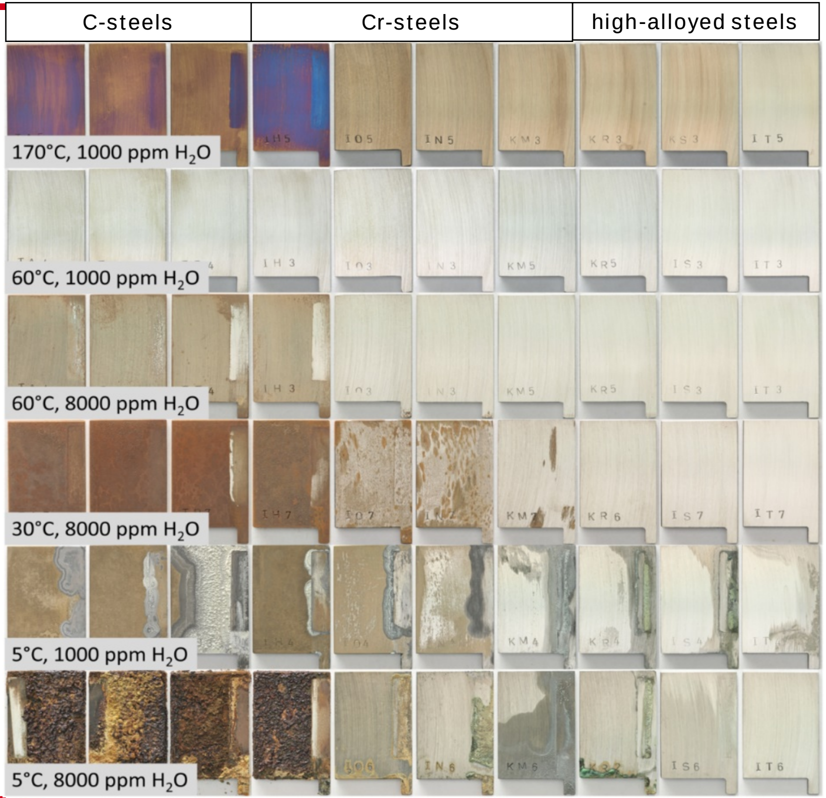
Corrosion Investigations

Materials

	Material
Compression	**X3CrNiMo13-4 (S41500)**
	X5CrNiCuNb16-4 (S17400)
	X12Cr13 (S41000)
	Ti-Al6-V4 (R56400)
	X1NiCrMoCu32-28-7 (N08031)
Transport	L290NB
	L360NB
	L485MB
	„Soft Iron“
Injection	X2CrMnNiN22-5-2 (S32101)
	X1NiCrMoCu32-28-7 (N08031)
	X5CrNiCuNb16-4 (S17400)
	X46Cr13 (S42000)
	42CrMo4 (G41400)
	X20Cr13 (S42000)

Corrosion Investigations

Results, Normal Pressure



– 600 h / 1.8 % O_2,
– 750 ppm_v CO,
– 1000 ppm_v NO_2,
– 220 ppm_v SO_2

– recommendation given for max. 50 to 100 ppm water

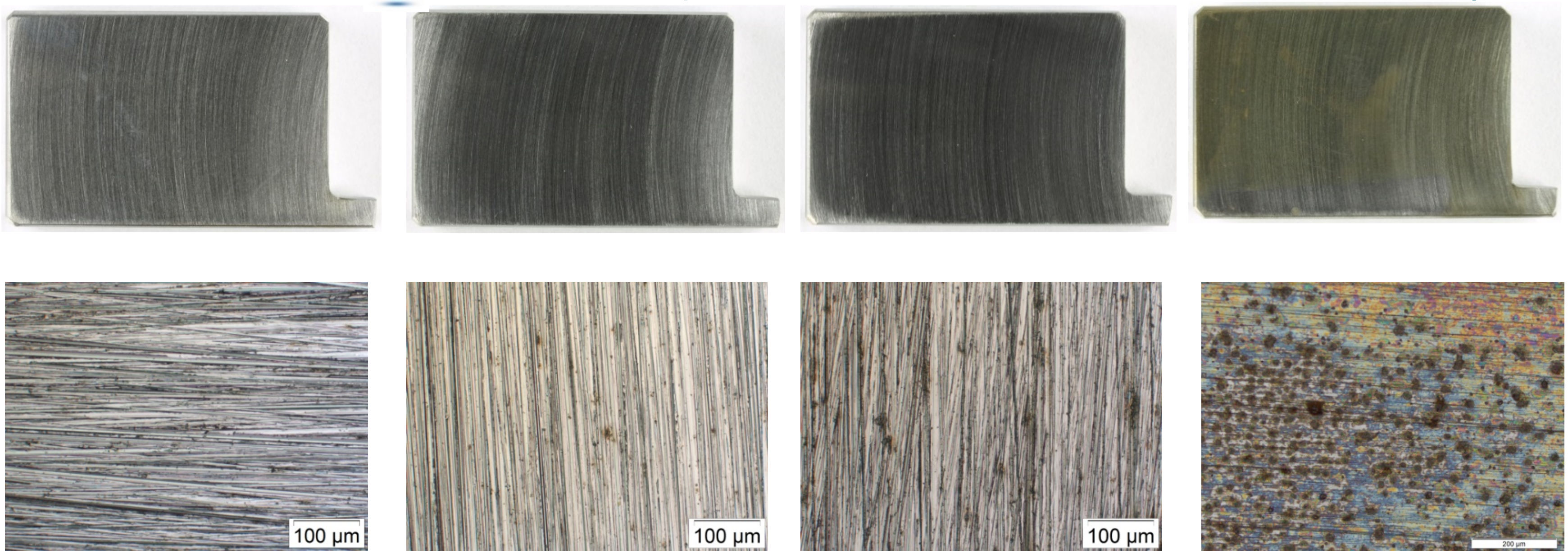
A. S. Ruhl, A. Kranzmann (2012)

Corrosion Investigations

Results – Water Content Effect, 2 Days, 5 °C, Carbon Steel

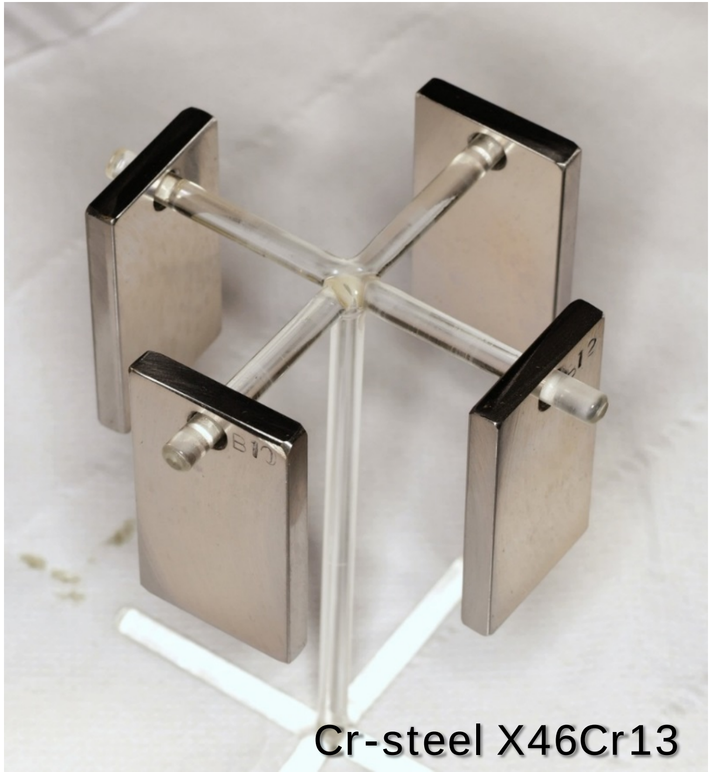
CO_2 + 100 ppm_v NO_2 + 70 ppm_v SO_2 6.700 ppm_v O_2 (48 h)

original | + 50 ppm_v | + 500 ppm_v | + 5000 ppm_v



Corrosion Investigations

Results – „Worst Case Mixture", 186 Days



Corrosion Investigations

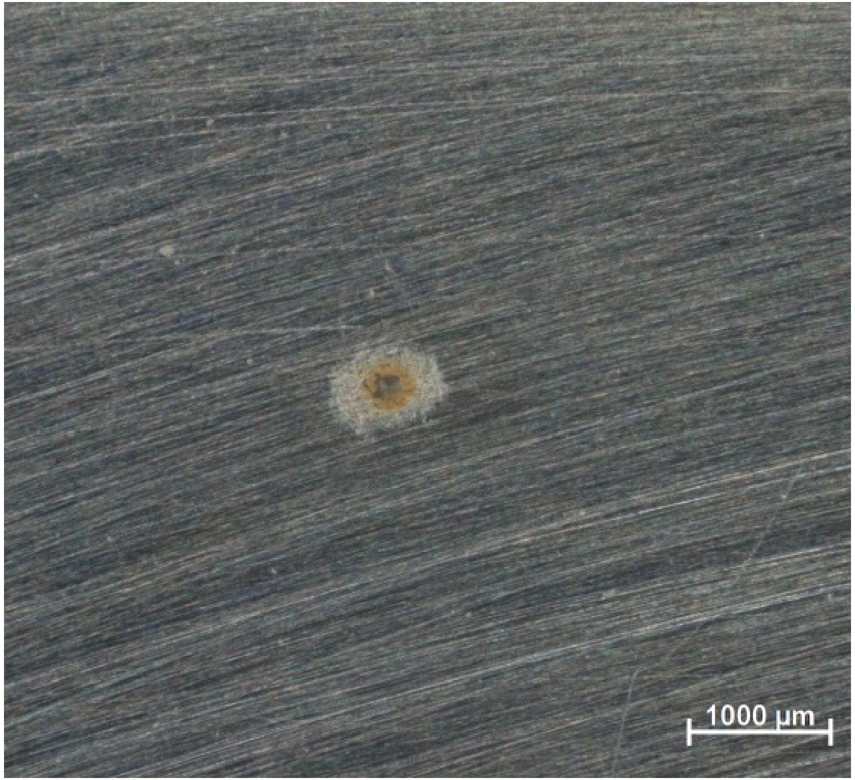
Results – „Worst Case Mixture“, 186 Days

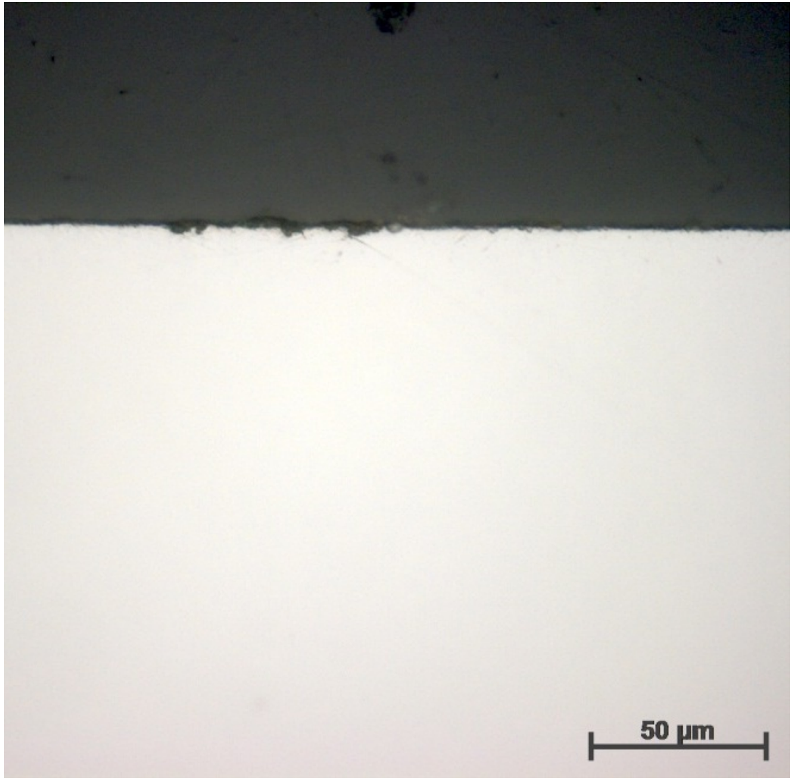
Carbon Steel:
- uniform corrosion
- 0.0025 mm/a

Cr-Steel:
- localized corrosion
- shallow pit depth
  < 10 µm

Corrosion Investigations

Results – Cr-Steel, Details

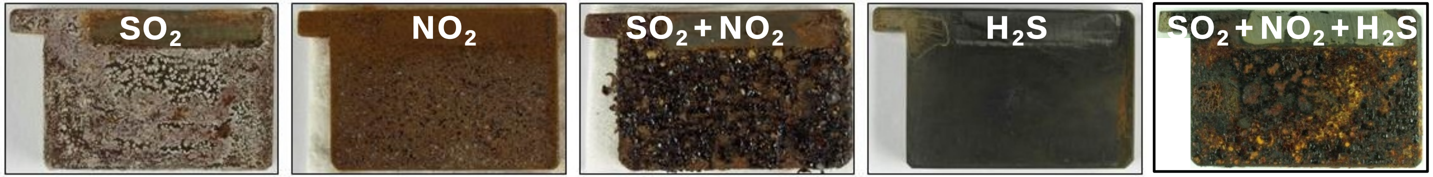




Corrosion Investigations

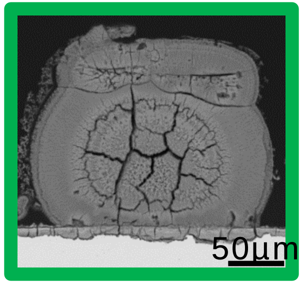
Ambient Pressure, 5 °C, Acid Condensation

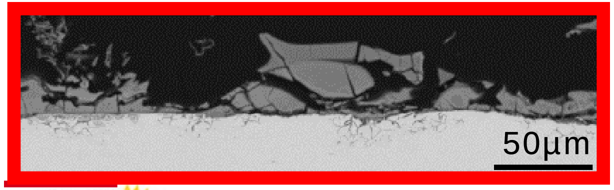
C-steel

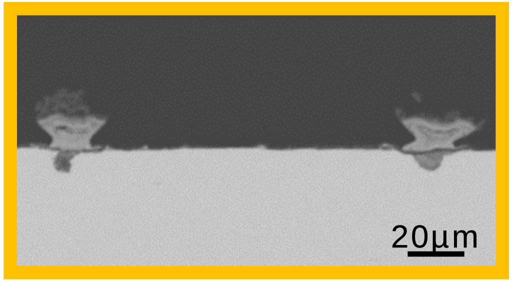


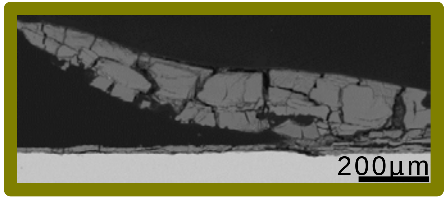
8000 ppm

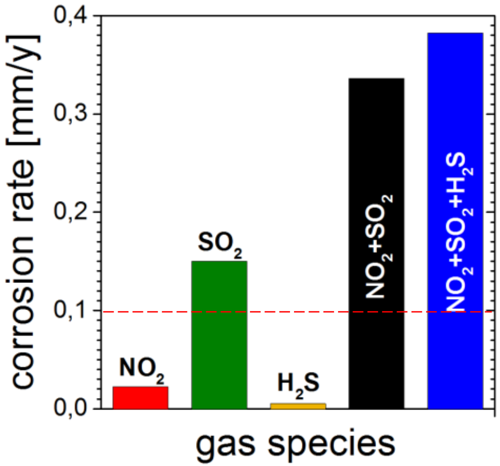
Sulfates | **Oxides** | **Sulfates** | **Sulfates / Sulfide** | **Sulfates**









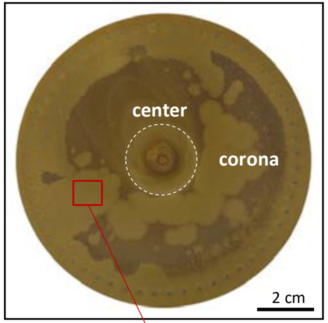


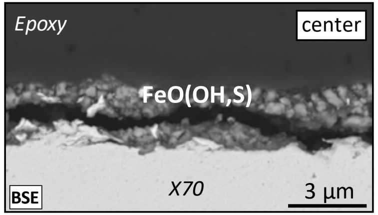
Corrosion Investigations

Results on C-Steel at High Pressure

High Pressure - 10 MPa | 5°C | 50 ppm | 300 h | *X70*

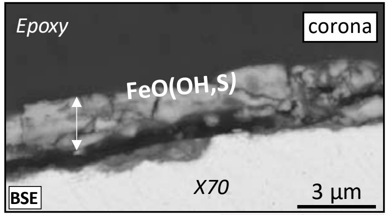
Red + Oxi





XRD: FeO(OH)

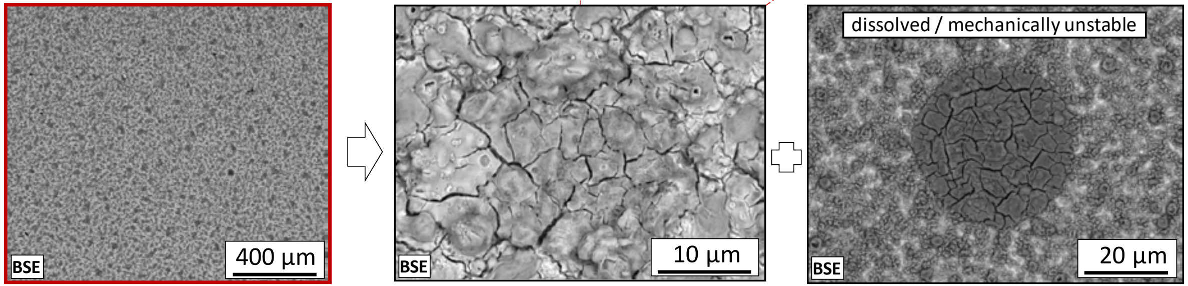
Fe[at%]	28-34
O [at%]	60-66
S [at%]	4-6



Fe[at%]	29-34
O [at%]	58-63
S [at%]	3-5

uniform shallow pitting / v_{CR} ≤0.07 mm/a

OH^-: 152 pm
S^{2-} : 170 pm



Kratzig et al.: Eurocorr 2017

Corrosion Investigations

High Pressure - 10 MPa

5…40°C | 50 ppm | 300 h

Oxi (70 ppm SO_2; 100 ppm NO_2; 6700 ppm O_2) **Red** (50 ppm H_2S, 10 000 ppm H_2) **Mixed**

C-steel - X70

- considerable corrosion only at 5 °C (Oxi; Oxi+Red)
- powdery, easily removable 2-layer system: ***Fe-Hydroxide*** (2-3 µm) + outgrowth (≤ 10 µm)
- ***uniform/shallow pitting*** => linearly extrapolated $v_{CR} \leq 0.07$ ***mm/a***

Safe concentrations for carbon steel

Low Pressure - 0.1 MPa

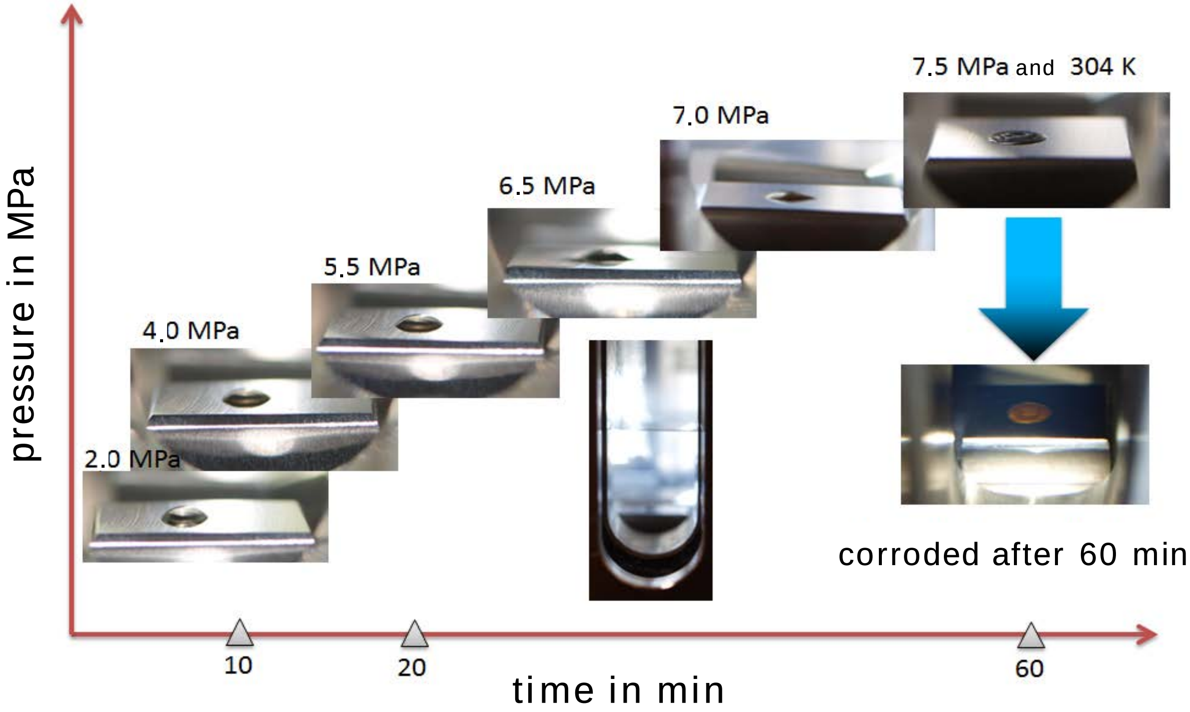
5°C | 8000 ppm | 168 h

- Oxi ≈ Mixed → uniform/shallow pitting …v_{CR} = ***0.4 - 0.5 mm/a*** …Fe-Hydro-Sulfates
- Red → pitting corrosion …$v_{CR} \leq 0.01$ ***mm/a*** …Fe-Sulfides

Kratzig et al: Eurocorr 2017

Corrosion Investigations

Results – Droplet, C-Steel



- 220 ppm$_v$ SO_2,
- 6700 ppm$_v$ O_2

5 µL H_2O as droplet

Corrosion Investigations

Results in Supercritical and Gaseous CO_2

In supercritical impure CO_2 (worst case scenario), from 7 up to 186 exposure days:

- Corrosion rate decreases by longer exposure times
- Carbon steels tend to general corrosion with low corrosion rates (< 0.1 mm/a)
- High alloyed steels tend to localized corrosion
- Corrosion rate increases by increasing water content, however 1000 ppm_v seems to be a limit
- Droplet formation due to condensation can cause localized acidic attack

Corrosion Investigations

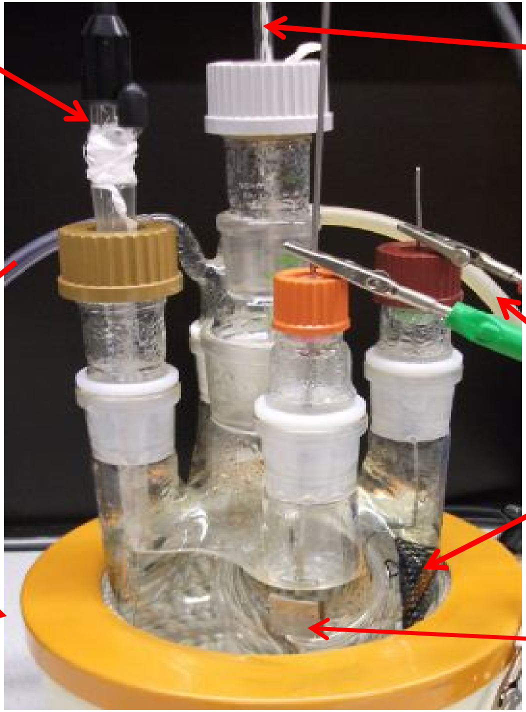
More Results in Supercritical and Gaseous CO_2

- **1 bar & 5 °C** (168 h, 8000 ppm_v H_2O, Oxi/Red/Mix)
  - no/minimal corrosion on high alloyed steels but clearly on pipeline steel
  - amorphous/weak crystallinity of corrosion layers
  - thin corrosion layer and initial pit formation already at 50 ppm_v H_2O and 48 h (Oxy)
  - SO_2, H_2S, SO_2+NO_2, SO_2+NO_2+H_2S → sulfates or NO_2 → oxides
  - Corrosion type: H_2S → pitting, NO_2 → intergran., rest → shallow/uniform
- **100 bar & 40 °C** (300 h, 50 ppm_v H_2O, Oxi/Red/Mix)
  - no acid condensation observable
  - minimal corrosion (3 sections) → thin film and cavities visible
- **Acid Condensation**
  - NO_2 promotes the formation of H_2SO_4

Corrosion Investigations

Set Up – Injection Conditions

Reference electrode



Temperature controller

CO_2 out

CO_2 in

Counter electrode

Heater

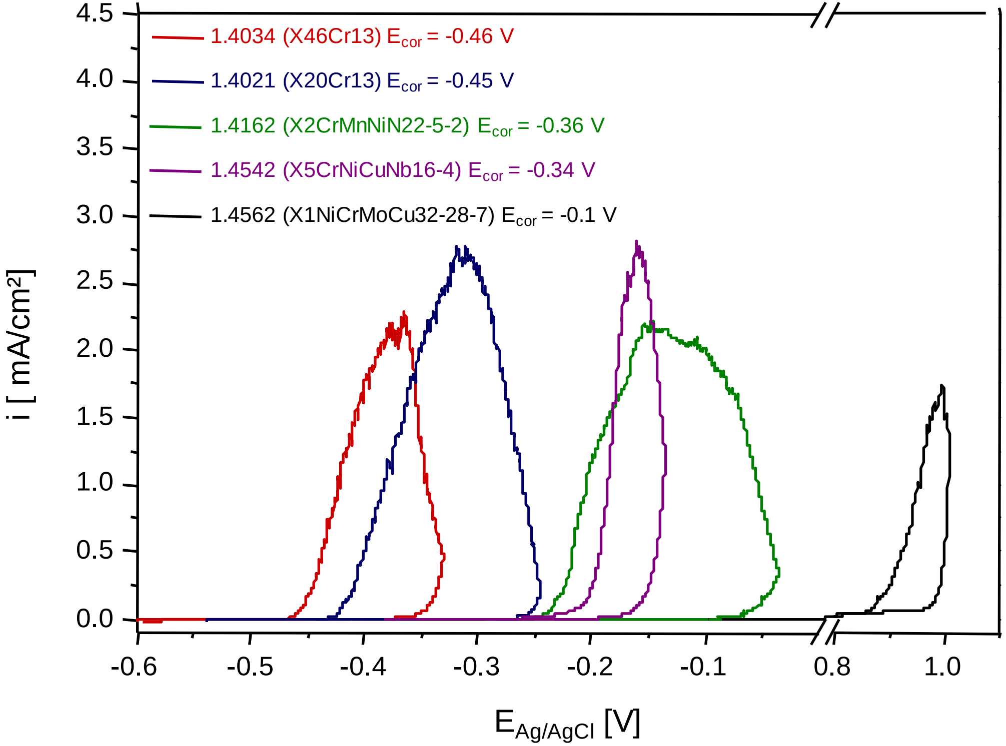
WE=Test specimen

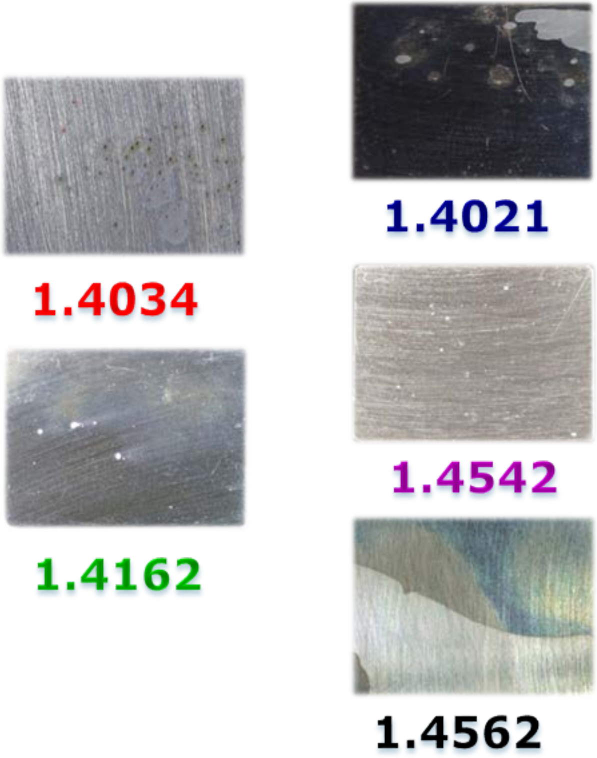
Brine composition			
Cations	**mg L^{-1}**	**Anions**	**mg L^{-1}**
Ca^{2+}	1760	Cl^-	143300
K^+	430	SO_4^{2-}	3600
Mg^{2+}	1270	HCO_3^-	40
Na^+	90100		

T = 60 °C
CO_2 flow 3 - 5 L/h
pH = 5.8 - 6.0

Corrosion Investigations

Results – Electrochemistry; Cyclovoltametrie, 60 °C





Corrosion Investigations

Results – Electrochemistry

- **in CO_2–saturated, artificial saline water**
  - C- and Cr-Steels are **not pitting corrosion resistant**
  - high alloyed materials are **pitting corrosion resistant**
- **chloride concentration determines corrosion kinetics**

Results

Survey

	Material	CO_2-stream, normal pressure, "worst case", 170 °C, 5 °C, 60 °C, max. 4 weeks	CO_2-stream, normal pressure, "condensated" at 5 °C, ≥ 1000 ppm H_2O, max. 4 weeks	brine, CO_2-saturated, normal pressure, 60 °C, 2 weeks	condensate H_2SO_4+HNO_3+CO_2, normal pressure, 5 °C, 2 weeks	CO_2 supercritical, worst case, 60 °C, 10 MPa, 1000 ppm H_2O 7 days	CO_2-stream supercritical, laminar, "worst case", 60 °C, 10 MPa, 6 month	CO_2-stream supercritical, turbulent, "worst case", 60 °C, 10 MPa, 5 days	Final Evaluation
compression	X3CrNiMo13-4	+	-, P			+			+ *
	X5CrNiCuNb16-4	+	-, P	-, P		-, P			-
	X12Cr13	+	-, P	-, P					-
	Ti-Al6-V4	+	+						+
	X1NiCrMoCu32-28-7	+	+	+					+
transport	L290NB	+	-, U, 1.02 mm/a			U, 16 µm/a			+ *
	L360NB	+	-, U 1.31 mm/a		-, L, 1.5 mm/a	U, 25 µm/a	U, 6 µm/a		+ *
	L485MB	+	-, U 1.29 mm/a			U, 36 µm/a		+ *	+ *
	Soft Iron	+	-, U 0.98 mm/a			U, 8 µm/a			+ *
injection	X2CrMnNiN22-5-2	+	+ *	+ **		+***			+**,'+***
	X1NiCrMoCu32-28-7	+	+	+	-, L , 0.6 mm/a	+			+ *
	X5CrNiCuNb16-4	+	-, P	-, P					-
	X46Cr13	+	-, L, 0.70 mm/a	-, P	-, U, 1.6 mm/a	+***	+***, L, 20 µm/a	+	-
	42CrMo4	+	-, U 1.14 mm/a	-, U, 2 mm/a		U, 24 µm/a		+	-
	X20Cr13	+	-, L, 0.52 mm/a	-, P		+***		+	-

+ - resistant max. 0,1 mm/a
- - not resistant
L - localized (shallow pitting) corrosion
P - pitting corrosion
U - uniform corrosion

+ *: resistant, as long as no acid induced corrosion occurs
+ **: susceptible to crevice corrosion
+***: suscetible to shallow pitting, depth less than 0,1 mm/a

Results

General Summary

- CO_2 quality specifications are **not** only a matter of CO_2 purity (i.e. CO_2 content).
- The "rest" also matters, in particular contents of reactive impurities affecting material corrosion (and rock alteration).
- Also chemical reactions in CO_2 stream needs to be considered, in particular when combining CO_2 streams of different compositions.

Results

Summary – Pipeline Steels

- Within "worst case" mixture (600 ppm_v H_2O and 100 ppm_v each NO_2 and SO_2) no significant corrosion occurred at ambient pressure

- At more than 600 ppm_v H_2O and "worst case" mixture
  → no corrosion of pipeline steels at temperatures ≥ 60 °C

- At 30 °C corrosion on pipeline steels only at water contents ≥ 8000 ppm_v.

- Due to acid condensation at 5 °C,
  corrosion when water content ≥ 2000 ppm_v.

- At all temperatures slight corrosion,
  when SO_2 ≥ 600 ppm_v and water content ≥ 2000 ppm_v.

Results

Summary (Autoclave Experiments)

Pressure only

- Mobility of potential acids is very different.
- HNO_3 selective and quickly corrosive
- H_2SO_4 immobile and hygroscopic

Pressure and load (bending frame)

- no SCC on pipeline steel detected
- corrosive conditions result in intergranular corrosion

Pressure, load and turbulent flow (bending frame, circulation)

- significant effects within the zone of turbulent impact
- condensation effects at joints within the circuit

Results

Consequences for CCUS Applications

- Commercially available carbon steels are suitable for compression and pipelines as long as moisture content and impurities are limited. (water 50 to 100 ppm_v, SO_2 and NO_2 ca. 100 ppm_v)
- Corrosion rates increase with increasing water content. (0.2 – 20 mm/a)
- Condensation of acids and therefore droplet formation is always possible, even at low water contents.
- A low SO_2 content within the CO_2-stream might be more important than a low water content.

Results

Consequences for CCUS Applications (cont.)

- Cr13-steels showed a general susceptibility to shallow pitting and pitting. So, they seem to be not suitable for CCUS applications.
- Low alloyed steels showed better corrosion behavior. (predictable uniform corrosion)
- For direct contact with saline aquifer fluids only high alloyed steels shall be used.

Results

Knowledge Gaps

- Reaction kinetics of highly diluted gases in CO_2 (i.e.: oxidation of SO_2 to H_2SO_4, effect of particles)
- Condensation kinetics of highly dissolved impurities in CO_2 on pipeline steel
- Effective removal of highly dissolved impurities from CO_2
- Influence of impurities on parameters of equation of state (compare to Gernert, J. and R. Span 2016)
- Behavior of HAZ and welding material on welded CO_2-pipelines
- Behavior of sealings and sealing materials at changing CO_2-pressure
- Implementation of a demo pipeline within EU and Norway

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COORAL

Federal Ministry for Economic Affairs and Energy

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Any questions, comments, remarks?