Corrosion Aspects of Materials Selection for CO2 Transport and Storage

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Contents

- COORAL Joint Research Project
- Materials and Gas Selection
- Experiments under CO\(_2\) stream
- EC Experiments under Aquifer and CO\(_2\)
- Conclusions
- Outlook
COORAL Main Goals

- COORAL: CO$_2$ Purity for Sequestration and Storing
  (CO$_2$-Reinheit für Abscheidung und Lagerung)
- Funding by
  - German Ministry of Economics (50 %)
  - E.ON, Vattenfall, ENBW, VNG, Alstom (50 %)
- Scheduled term 42 months, start date 01.04.2009
- Objectives:
  - Limits of impurities
  - Developing phases in the CO$_2$ stream
  - Corrosion of compressor and tube materials
  - Geochemical reactions
  - Safety issues
  - Cost effectiveness
CCS Transport Chain

- BAM Fields of Interest:
  - Compression
  - Transport
  - Injection
## Materials Selection

<table>
<thead>
<tr>
<th>Number</th>
<th>Name</th>
<th>Short Sign</th>
<th>Treatment</th>
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<tbody>
<tr>
<td>1.4006</td>
<td>X12Cr13</td>
<td>KM</td>
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<td>1.4313</td>
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<td>KR</td>
<td>QT650</td>
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<td>1.4542</td>
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<td>KS</td>
<td>P930</td>
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<td>1.4562</td>
<td>X1NiCrMoCu32-28-7</td>
<td>KU</td>
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<tr>
<td>3.7165</td>
<td>Ti-Al6-V4</td>
<td>KX</td>
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<td>1.1018</td>
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<td>TA</td>
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<td>L360NB</td>
<td>TC</td>
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<td>1.8977</td>
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<td>TD</td>
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<td>42CrMo4</td>
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<td></td>
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<td>X20Cr13</td>
<td>IN</td>
<td></td>
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<td>X46Cr13</td>
<td>IO</td>
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<td>P930</td>
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<tr>
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<td>X2CrMnNiN22-5-2</td>
<td>IT</td>
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<td>1.4562</td>
<td>X1NiCrMoCu32-28-7</td>
<td>IU</td>
<td></td>
</tr>
</tbody>
</table>

- **Compression**: $T = 170 \, ^\circ C$
- **Transport**: $T = 5 \, ^\circ C$
- **Injection**: $T = 60 \, ^\circ C$
Gas Selection

Estimated CO2 stream compositions

**Oxyfuel**

<table>
<thead>
<tr>
<th></th>
<th>CO2</th>
<th>O2</th>
<th>N2</th>
<th>Ar</th>
<th>NOx</th>
<th>SOx</th>
<th>H2O</th>
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<tbody>
<tr>
<td>++</td>
<td>99.95%</td>
<td>0.01%</td>
<td>0.01%</td>
<td>0.01%</td>
<td>50 ppm</td>
<td>50 ppm</td>
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<tr>
<td>+</td>
<td>98.00%</td>
<td>0.67%</td>
<td>0.71%</td>
<td>0.59%</td>
<td>0.01%</td>
<td>0.01%</td>
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<tr>
<td>-</td>
<td>96.00%</td>
<td>1.34%</td>
<td>1.38%</td>
<td>1.25%</td>
<td>0.01%</td>
<td>0.01%</td>
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</tr>
<tr>
<td>--</td>
<td>85.00%</td>
<td>4.70%</td>
<td>5.80%</td>
<td>4.57%</td>
<td>0.01%</td>
<td>0.01%</td>
<td>0.01%</td>
</tr>
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</table>

**Post-Combustion**

<table>
<thead>
<tr>
<th></th>
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<th>O2</th>
<th>N2</th>
<th>NOx</th>
<th>SOx</th>
<th>H2O</th>
<th>Amin</th>
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<tr>
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<td>99.80%</td>
<td>0.02%</td>
<td>0.02%</td>
<td>0.02%</td>
<td>0.02%</td>
<td>0.02%</td>
<td>0.02%</td>
</tr>
<tr>
<td>-</td>
<td>99.40%</td>
<td>0.01%</td>
<td>0.01%</td>
<td>0.01%</td>
<td>0.01%</td>
<td>0.01%</td>
<td>0.01%</td>
</tr>
</tbody>
</table>

A. Kather, TUHH

So called „Worst Case Composition“ to start with:

\[
\text{CO}_2 - 2\% \ O_2 - 750 \ \text{ppm} \ \text{CO} - 600 \ \text{ppm} \ H_2O - 70 \ \text{ppm} \ SO_x - 100 \ NO_x
\]

Variation of amounts of the impurities to determine their influence
Gas Reactions (without intermediates)

- $\text{SO}_2 + 7 \text{H}_2\text{O} \Rightarrow \text{H}_2\text{SO}_4 (\text{H}_2\text{O})_6$; liquid sulphuric acid forms up to 120 °C
- $\text{CO} + \text{O}_2 \Rightarrow \text{CO}_2 + \frac{1}{2}\text{O}_2$; CO and O$_2$ are consumed
- $\text{NO}_2 + \text{CO} \Rightarrow \text{CO}_2 + \frac{1}{2}\text{N}_2 + \frac{1}{2}\text{O}_2$; N$_2$ is formed
- $\text{H}_2\text{O} + 2\text{NO}_2 \Rightarrow \text{HNO}_3 + \text{HNO}_2$, gaseous nitric acid and nitrous acid are formed to low amounts
- $\text{SO}_2 + \frac{1}{2}\text{O}_2 \Rightarrow \text{SO}_3$; is formed at > 60°C
Screening Experiments under Ambient Pressure

- 3 Chamber Furnaces
- Compression 170 °C
- Gas Mixing
- Transport 5 °C
- Data Akquisition
- Injection 60 °C
Screening Experiments

60 °C, 600 hours, 600 H₂O – 70 SO₂ – 100 NO₂ – 750 CO – 8000 O₂ (in ppm)
Screening Experiments

5 °C, 600 hours, 600 H₂O – 70 SO₂ – 100 NO₂ – 750 CO – 8.000 O₂

• Very slight uniform corrosion of pipeline materials
Phase Analysis Using XRD

- Amorphous or very fine grained layer
Screening Experiments

170 °C, 600 hours, 600 ppm H₂O – 70 ppm SO₂ – 100 ppm NO₂ – 750 ppm CO – 8,000 ppm O₂

Compressor materials

- Ti 1.4562
- X12Cr13 1.4313
- 1.4542
- Ti

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Screening Experiments

170 °C, 600 hours, 600 ppm H₂O – 220 ppm SO₂ – 1.000 ppm NO₂ – 750 ppm CO – 8.000 ppm O₂

From here, the amount of impurities was increased beyond „worst case“
Screening Experiments

60°C, 240 hours, 8.000 ppm H₂O, 220 ppm SO₂, 1.000 ppm NO₂

Amount of H₂O was increased beyound “worst case”
Screening Experiments

30°C, 120 hours, 8,000 ppm H₂O, 220 ppm SO₂, 1,000 ppm NO₂
Screening Experiments

5°C, 8.000 ppm H₂O, 220 ppm SO₂, 1000 ppm NO₂

Acid condensation under extreme conditions
Screening Experiments

5°C, 8.000 ppm H$_2$O, 220 ppm SO$_2$, 1000 ppm NO$_2$

Acid condensation under extreme conditions
L290NB, Experiments over 120 h at 5°C
Thickness Measurement L290NB

5 °C, 2 % H$_2$O, 650 ppm SO$_2$

=> condensating acid

approx. 0.7 .. 1.0 mm loss/year
Conclusions Screening Experiments

Pipeline Steels under Ambient Pressure
• At temperatures of 60°C and higher no corrosion observed under the described conditions
• At 30°C corrosion only under very high H₂O content ≥ 8.000 ppm due to acid condensation
• At 5 °C corrosion only under high water content ≥ 2.000 ppm due to acid condensation

Injection and Compression
• „Compressor materials“ without corrosion
• High alloyed „injection materials“ without corrosion
• 42CrMo4 and X46Cr13 behave similar to pipeline steels
Electro Chemical Experiments on Injection Materials

Conditions:

• Wet CO$_2$ stream
• High temperature, high pressure
• Aquifer water ("brine") with high Cl$^-$ content
• Aquifer water can rise in the pipeline to the injection point during the downtime
Experimental

### Chemical composition of the steels, %

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<thead>
<tr>
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<th></th>
<th></th>
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<tbody>
<tr>
<td>1.4162</td>
<td>0.04</td>
<td>21-22</td>
<td>0.1-0.8</td>
<td>4-6</td>
<td>0.03</td>
<td>1.3-1.7</td>
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<td>0.04</td>
<td>0.1-0.8</td>
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<tr>
<td>1.4021</td>
<td>0.25</td>
<td>12-14</td>
<td>1.5</td>
<td>0.015</td>
<td>1</td>
<td>0.035</td>
<td>0.4</td>
<td>0.04</td>
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<tr>
<td>1.7225</td>
<td>0.45</td>
<td>0.9-1.2</td>
<td>0.15-0.3</td>
<td>0.6-0.9</td>
<td>0.035</td>
<td>0.4</td>
<td>0.035</td>
<td></td>
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</tr>
</tbody>
</table>

Simulation of the “real conditions” in the lab:

- Artificial brine similar to onshore CCS-site in Germany
- Brine saturation with CO₂
- Continues CO₂ flow
- Temperature 60 °C known as critical for CO₂ corrosion
Experimental setup

**Brine composition**

<table>
<thead>
<tr>
<th>Cations</th>
<th>mg L⁻¹</th>
<th>Anions</th>
<th>mg L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca²⁺</td>
<td>1760</td>
<td>Cl⁻</td>
<td>143300</td>
</tr>
<tr>
<td>K⁺</td>
<td>430</td>
<td>SO₄²⁻</td>
<td>3600</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>1270</td>
<td>HCO₃⁻</td>
<td>40</td>
</tr>
<tr>
<td>Na⁺</td>
<td>90100</td>
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</tr>
</tbody>
</table>

T = 333 K
CO₂ flow 3-5 L/h
pH = 5.8-6.0
Theoretical background

**CO₂ corrosion:**

\[ \text{H₂O} + \text{CO₂} + \text{Fe} = \text{FeCO₃} + \text{H₂} \]

\[ \text{CO₂} + \text{H₂O} \leftrightarrow \text{H₂CO₃} \]

**Anodic:**

\[ \text{Fe} \rightarrow \text{Fe}^{++} + 2\text{e}^- \]

**Cathodic:**

\[ 2\text{HCO}_3^- + 2\text{e}^- \rightarrow 2\text{CO}_3^{2-} + \text{H₂} \]

\[ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H₂} \]

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Maurice V., Marcus P. in *Modern Aspects of Electrochemistry*, 2009
1.4021 (X20Cr13) in CO2 saturated saline brine

\[ R_{\text{pol}} \, \text{k}\Omega \cdot \text{cm}^2 \]

\[ t, \text{days} \]

\[ E_{\text{Ag/AgCl}} \, \text{V} \]
1.4021 (X20Cr13) in CO2 saturated saline brine

-350 mV

-380 mV

-390 mV

-400 mV

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Folie 26
1.7225 (42CrMo4) in CO2 saturated saline brine

Corrosion rate 1.9 mm/a
1.7225 (42CrMo4) in CO2 saturated saline brine
1.4162 (X2CrMnNiN22-5-2) in CO2 saturated saline brine

Graph showing the change in $R_{\text{pol}}$ $\Omega \cdot \text{cm}^2$ and $E_{\text{Ag/AgCl}}$ mV over time, days. The graph indicates no pitting corrosion.
1.4162 (X2CrMnNiN22-5-2) in CO2 saturated saline brine

-190 mV  -170 mV  E, $V_{Ag/AgCl}$  -160 mV  -150 mV
Conclusions EC Experiments

- In CO₂ saturated saline brine material 1.4021 is not resistant to pitting corrosion, 1.7225 shows uniform corrosion, alloy 1.4162 is resistant to pitting corrosion

- Cl⁻ ions concentration controls the corrosion kinetics

Outlook

- Corrosion of piping steels in a circulating supercritical impure CO₂ environment
Outlook: High Pressure Tests

Laminary Flow
- Autoclaves with CO$_2$ circuit, max. 120 bar, max. 200 °C
- Installed, first experiments launched

Turbulent Flow
- Max. 200 bar, 200 °C, Turbulent gas stream, max. 10 m/s
- Mechanical stress (ball on ring)
- To be assembled