Corrosion in Dense Phase CO$_2$ Pipelines – Three Reasons for Concern

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S. Clausen (Gassco AS)
Issues to be addressed

- Motivation for studying corrosion in the pipeline
- State of the Art
- When can we get corrosion
- Experimental work
  - Corrosion, water < 500 ppmw
  - Corrosion in a separate water phase (water ingress)
  - Depressurization and the effect on the corrosivity
Significant reduction in CO₂ emission

Transport and injection of large amounts of CO₂ (2-3x)

Huge amount of pipes

**Emission 2010: 30 Gt CO₂**

- 12” pipelines ~1700
- 36” pipelines ~190

\[ 20\%, \ 1.5 \text{ m/s} \]

Need to define a safe operational window
Dense phase CO\textsubscript{2} transport, State of the Art

- CO\textsubscript{2} injection for EOR > 30 years (USA)
- More than 100 installations, more than 5000 km pipeline
- C-steel: Good experience with clean and dry CO\textsubscript{2}
- Reported corrosion when water accumulates
- CRA: ”Wet” CO\textsubscript{2}, Sleipner, short distance
- Thousands of papers/corrosion studies for pCO\textsubscript{2} < 20 bar
- Few studies for pCO\textsubscript{2} > 50 bar
- Less than 5 publications presenting data with flue gas impurities
- Not much focus on corrosion in the CCS community (GHGT 10)
Will corrosion be a problem?

Good experiences with CO$_2$ transport in USA!

Is CCS different?
Concentrations of impurities in dried CO₂

<table>
<thead>
<tr>
<th></th>
<th>SO₂</th>
<th>NO</th>
<th>H₂S</th>
<th>CO</th>
<th>N₂ /Ar/O₂</th>
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</thead>
<tbody>
<tr>
<td><strong>COAL FIRED PLANTS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Post- combustion capture</td>
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<td>&lt;100</td>
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<td>Pre-combustion capture(IGCC)</td>
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<td>300-</td>
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<td></td>
<td></td>
<td>6 000</td>
<td>4 000</td>
<td>6 000</td>
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<tr>
<td>Oxy-fuel</td>
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<td>0</td>
<td>100</td>
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<tr>
<td>Pre-combustion capture</td>
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<td>0</td>
<td>&lt;100</td>
<td>400</td>
<td>13 000</td>
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<tr>
<td>Oxy-fuel</td>
<td>&lt;100</td>
<td>&lt;100</td>
<td>0</td>
<td>0</td>
<td>41 000</td>
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*Source: Intergovernmental Panel on Climate Change (IPCC)*
## Concentrations of impurities in dried CO₂

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<td>Pre-combustion capture (IGCC)</td>
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<tr>
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Source: Intergovernmental Panel on Climate Change (IPCC)
ppmv vs. ppmw

ppm weigth
ppm mass

ppm vol, ppm mol

DYNAMIS
Kinder Morgan
Corrosion scenarios in dense phase CO$_2$ systems?

- Impurities and low water content
  - O$_2$
  - H$_2$S, S
  - CH$_4$, N$_2$, Ar ++
  - SO$_x$ and NO$_x$, CO
  - MEG, TEG, amines, salt

- Free water phase
  - Insufficient drying, water may condense/precipitate from the CO$_2$ phase
  - Accidental/unforeseen water ingress

- Shut down, depressurization and accumulation
- Re-using existing infrastructure, deposits (UDC)

Affects water solubility, the corrosion mechanisms and the phase properties +++
Autoclave experiments

200 - 550 bar

High pressure filling system

Good mixing

Mobilization of corrosive phase (<$10^{-3}$)
Loop experiments

Alloy C 276
Pressure: 200 bar
Flow: 0.1-3 m/s
Iron counts
Electrochemistry
## Autoclave experiments, 100 bar, 25 °C

<table>
<thead>
<tr>
<th>Exp. No:</th>
<th>IFE 4a</th>
<th>IFE 5a</th>
<th>IFE 5b</th>
<th>IFE 6a</th>
<th>IFE 6b</th>
<th>IFE 6c</th>
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<tbody>
<tr>
<td>H$_2$O, ppm wt</td>
<td>500</td>
<td>200</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>200</td>
</tr>
<tr>
<td>SO$_2$, ppm wt</td>
<td>0</td>
<td>500</td>
<td>500</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO$_2$, ppm wt</td>
<td></td>
<td></td>
<td>500</td>
<td>200</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Exposure, days</td>
<td>18</td>
<td>14</td>
<td>14</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Weight loss Cor. rate, mm/y</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.02</td>
<td>1.6</td>
<td>0.7</td>
<td>0.17</td>
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<tr>
<td>Pitting attack</td>
<td>Y</td>
<td>Y</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

H$_2$O solubility $\sim$ 1200 ppmw
500 ppmw SO$_2$ and H$_2$O

200 ppmw H$_2$O

FeSO$_{4/3}$

200 µm

10 mm

10 µm
500 ppmw NO$_2$ and H$_2$O

Corrosion rate 1.6 mm/y
Free water phase (50 vol%), stagnant conditions

17 mm/year

- Start pH 3-3.2
- High cm²/cm³ ratio
- Fe²⁺ 90-900 ppm
- pH shift
- Film formation
- Duration 2-3 weeks
Free water, flowing conditions, 100 bar
Partitioning

GC: NO$_2$, SO$_2$
Dew meter
Partitioning coefficients (gas/liquid)

<table>
<thead>
<tr>
<th></th>
<th>O₂</th>
<th>H₂S</th>
<th>SO₂</th>
<th>H₂O</th>
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<td>2.5-3</td>
<td>0.6-0.8</td>
<td>0.04-0.06</td>
<td>0.2-0.3</td>
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Concentration in gas phase

Concentration in liquid phase

O₂ concentration / mol %

wt % CO₂ removal
### Partitioning coefficients (gas/liquid)

<table>
<thead>
<tr>
<th></th>
<th>$\text{O}_2$</th>
<th>$\text{H}_2\text{S}$</th>
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![Graph showing concentration of $\text{H}_2\text{S}$ in gas and liquid phases versus wt % CO2 removal](attachment:image.png)
Water accumulation in the liquid CO\textsubscript{2} phase

100 ppm dissolved water, 4 \textdegree}C

![Graph showing water accumulation in liquid CO\textsubscript{2} phase](image-url)
Summary/Conclusion

- Non corrosive when the water content is significantly lower than the solubility limit in pure water and CO₂
- Corrosion can take place at water content less than 200 ppmw when SO₂ and/or NO₂ are present
- The corrosion rate in a free water phase can be huge, 10-50 mm/y
- O₂ destabilized the FeCO₃ film and initiated localized attack
- Corrosivity can increases after depressurization as impurities like H₂O, SO₂, NO₂ accumulate in the remaining liquid CO₂ phase
State of the Art

- Not much focus on corrosion in CCS community
- Less than 5 publications actually reporting corrosion data in dense phase CO₂ with flue gas impurities
- Very little is known about the effect of impurities and particularly about mixed contaminants
- The lack of data makes it difficult to predict corrosion rates and define a safe operation window for transport of dense phase CO₂ originating from different sources with different contaminants
- Corrosion should be given more attention
Acknowledgement

• The authors would like to acknowledge Gassco AS for financial and technical support for parts of the presented work.
Consumption of reactants

- Consumption of H₂O, ppm w
  - 0.7 cm²
  - 2.0 cm²
  - 3.2 cm²

- Consumption of SO₂, ppm w
  - 0.7 cm²
  - 2.0 cm²
  - 3.2 cm²

Corrosion rate, mm/y