More accurate fluid properties enable reductions of CCS costs and risks

Part II of webinar "Research for safe and efficient CO₂ transport and injection"

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2020-12-16
Agenda

• Thermophysical properties
  • What are they
  • Why are they important

• Impurities
  • Impact
  • Data situation

• ECCSEL/SINTEF facilities to address fluid properties
Thermophysical properties – what are they?

• Thermodynamic properties
  *Characteristic features of a system, capable of specifying the system's state.*
  - Derived from equations of state
  - Important examples: Phase equilibria, density, heat capacity, ….

• Transport properties:
  - Viscosity, heat conductivity, and diffusivity
Thermophysical properties – what are they?

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Thermophysical properties – what are they?

- Phase equilibria
- At what temperatures and pressures do we have phase transition?
Influence of impurities on VLE

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  - What are the composition of the phases?

Thermophysical properties – what are they?

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- Density
  - Mass per volume
Thermophysical properties – what are they?

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- Density
  - Mass per volume

- Viscosity
  - "Resistance of a fluid to flow"
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• ECCSEL/SINTEF facilities to address fluid properties
Where are fluid properties important? Some examples

• Capture / conditioning
  • Heat transfer (thermal conductivity, viscosity, phase behavior, …)
  • Optimization of low-temp separation
  • Dimensioning of equipment, e.g. absorption columns

• Transport
  • Pumping
  • Fiscal metering
  • Corrosion
  • Pipeline: Pressure drop / required pipeline thickness
  • Ship transport: Freeze-out

• Injection and storage
  • Well integrity: VLE, thermal conductivity, viscosity
  • Reservoir plugging, eg. brine dry-out and hydrate formation: VL(H)E
  • Reservoir modeling requires prediction of eg viscosity, density, VLE with impurities
Where are fluid properties important? In most CCS processes!

• Capture / conditioning: **Property uncertainty leads to non-ideal processes**
  • Heat transfer (thermal conductivity, viscosity, phase behavior, …)
  • Optimization of low-temp separation
  • Dimensioning of equipment, e.g. absorption columns

• Transport: **Property uncertainty mandates excess margins**
  • Pumping
  • Fiscal metering
  • Corrosion
  • Pipeline: Pressure drop / required pipeline thickness
  • Ship transport: Freeze-out

• Injection/storage **Property uncertainty may lead to unpleasant surprises**
  • Well integrity: VLE, thermal conductivity, viscosity
  • Reservoir plugging, eg. brine dry-out and hydrate formation: Phase equilibria
  • Reservoir modeling requires prediction of eg viscosity, density, VLE with impurities
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There are impurities in CCS......

<table>
<thead>
<tr>
<th>Component</th>
<th>Impurity Concentrations From Capture (IPCC, 2005 / Li et al. 2014)</th>
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<tbody>
<tr>
<td></td>
<td>Min mol%</td>
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<tr>
<td>CO₂</td>
<td>75</td>
</tr>
<tr>
<td>H₂O</td>
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### Proposed Mongstad Transport Spec. Gassnova 2013

- >99.5 mol %
- < 50 ppm
- <0.2 %
- <200 ppm wt
- (implicit <500 ppm mol)
- ? (<500 ppm mol)
- <100 ppm wt
- ? (<500 ppm mol)
- ? (<500 ppm mol)
- ? (<500 ppm mol)
- Trace (?)
- Trace (?)

Conditioning / purification

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**why care?**
### Component Impurity Concentrations

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#### Impurities affect capture/conditioning process

#### Costs?

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<tbody>
<tr>
<td>Gassnova 2013</td>
<td>ppm (mol)</td>
</tr>
<tr>
<td>&gt;99.5 mol %</td>
<td>No explicit spec. *</td>
</tr>
<tr>
<td>&lt; 50 ppm</td>
<td>&lt; 30</td>
</tr>
<tr>
<td>&lt;0.2 %</td>
<td>No explicit spec. *</td>
</tr>
<tr>
<td>&lt;200 ppm wt</td>
<td>&lt;10</td>
</tr>
<tr>
<td>(implicit &lt;500 ppm mol)</td>
<td>No explicit spec. *</td>
</tr>
<tr>
<td>? (&lt;500 ppm mol)</td>
<td>&lt;10</td>
</tr>
<tr>
<td>&lt;100 ppm wt</td>
<td>&lt;9 (H₂S only)</td>
</tr>
<tr>
<td>? (&lt;500 ppm mol)</td>
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</tr>
<tr>
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*NL spec. for non-condensables (N₂, Ar, CH₄...) is the solubility at the capture side terminal, which, in fact, is temperature dependent.
Realistic optimization CCS requires reliable models for impure CO₂. Impurities affect capture/conditioning process, and reliable models require experimental data!

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**Costs?**

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<td>&gt;99.5 mol %</td>
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</tr>
<tr>
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**Why care?**

**Impurities down-stream / in the reservoir?**

**Reliable models require experimental data!**
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• Thermophysical properties
  • What are they
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• Impurities
  • Impact
  • Data situation

• ECCSEL/SINTEF facilities to address fluid properties
Influence of impurities on VLE

Pressure-temperature diagram for CO$_2$-rich mixtures with 5% impurities calculated using the SPUNG EOS

- CH$_4$
- N$_2$
- N$_2$ (50%)
- SO$_2$
- CO$_2$

Introduction

Impact of impurities on viscosity

- High deviations with small amounts of impurity
- Similar situation for other bulk fluid properties, e.g. density

![Graph showing the impact of impurities on viscosity](image)

- Mixture w/ 5 % N\textsubscript{2} vs pure CO\textsubscript{2}
- Visc. Ratio REFPROP\textsuperscript{1}
- Visc. Ratio SINTEF\textsuperscript{2}

\textsuperscript{1}REFPROP\textsuperscript{2}, models Fenghour 1998 and Chichester 2008
\textsuperscript{2}SINTEF tool, using principles of Reichenberg 1979/ data fit & TRAPP
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Phase Eq. Data Situation

System | # Sources | # Points | T (K) | p (MPa) | XCO₂
--- | --- | --- | --- | --- | ---
CO₂-N₂ | 34 | 26 | > 700 | 208–303 | 0.6–21.4 | 0.15–0.999
CO₂-O₂ | 8 | 2 | > 292 | 218–298 | 0.9–14.7 | 0.15–0.999
CO₂-CO₂ | 4 | 2 | ~ 200 | 233–299 | 1.5–14.0 | 0.25–0.999
CO₂- SO₂ | 3 | 0 | > 425 | 293–418 | 2–9.5 | 0.09–0.93
CO₂-H₂S | 8 | 3 | > 270 | 248–365 | 1.0–8.9 | 0.01–0.97
CO₂-H₂O | 1 | 0 | > 100 | 293–307 | 5.3–7.2 | 0.26–0.88
CO₂-NO₂ | 2 | 1 | 26 | 262–328 | 0.17–9.0 | 0.005–0.88
CO₂-N₂O₄ | 3 | 1 | 106 | 223–293 | 0.8–14.2 | 0.20–0.996
CO₂-CO | 8 | 4 | > 400 | 218–303 | 0.9–172 | 0.07–0.999
CO₂-CO₂ > 50 | 19 | 15 | > 180 | 153–320 | 0.68–20 | 0.062–0.99
CO₂-H₂O > 50 | > 1500 | 251–623 | 0.1–350 | 0.08–1.00
CO₂-N₂O₄ | 2 | 0 | > 413–531 | 4.3–81.7 | 0.023–0.33

H₂O-N₂ | 29 | 15 | > 876 | 233–657 | 0.045–270 | 0.01–1.00
H₂O-O₂ | 9 | 5 | 246 | 273–711 | 0.1–280 | 0.00–0.99
H₂O-Ar | 12 | 10 | > 460 | 258–663 | 0.1–340 | 0.00–0.95
H₂O-SO₂ | 30 | 8 | > 756 | 273–423 | 2.10–3.45 | 0.86–0.999
H₂O-H₂S | 17 | 6 | > 700 | 273–589 | 0.01–20.7 | 5.10–0.9997
H₂O-N₂O | 3 | 2 | > 52 | 286–303 | 0.1–7.3 | 0.95–0.9996
H₂O-CO | 2 | 2 | 41 | 304–589 | 1.1–13.8 | 0.001–0.99995
H₂O-H₂ | 6 | 5 | > 25 | 310–713 | 0.34–105 | 6.10–0.999996
H₂O-CH₄ | This system is nominally well covered
H₂O-MEA
H₂O-DEA
H₂O-MDEA
H₂O-NH₃

These systems are nominally relatively well covered

CO₂-N₂O₂ | 3 | 0 | 80 | 218–273 | 5.1–13 | −0.925
CO₂-O₂-N₂ | 1 | 1 | 36 | 253–302 | 2.1–8.7 | 0.95–0.93
CO₂-O₂-H₂ | 1 | 1 | 36 | 233–283 | 2–20 | 0.17–0.98
CO₂-Ar | 2 | 2 | > 100 | 220–293 | 6–10 | 0.27–0.99
CO₂-H₂S | 1 | 0 | 16 | 222–239 | 2.1–4.8 | 0.024–0.78
CO₂-H₂O-CH₄ | 5 | 5 | > 132 | 243–423 | 0.1–100 | 0.001–0.83
CO₂-H₂O-NaCl | 28 | 16 | > 1150 | 278–673 | 0.0–40 | 10⁻⁴–0.998
CO₂-Brines
CO₂-O₂-Ar-N₂ | 1 | 1 | 5 | 252–293 | 7.1–9.0 | 0.892

These systems are nominally relatively well covered
Thermodynamics model maturity ~ data situation

PhD thesis of Stefan Herrig
Ruhr-Universität Bochum 2018

Data and model quality

- Specific departure function
- Generalized departure function
- Adjusted reducing functions
- Lorentz-Berthelot combining rules
- Linear combining rules

Model developed in this work
GS EOS-CG model of Gernert and Span
KW GERG model of Kunz and Wagner
CO$_2$-CO VLE

CO$_2$-CO at 25 °C

Accurate models require data!

Bubble pts
Dew pts
EOS-CG
SRK
New Data
Ke 2001
CO$_2$-Ar VLE

CO$_2$-Ar at 0 °C

Data should always be verified!
**CO₂ + water**

- Technological very important
- Most liquid data on water rich phase
- Little VLE data for CO₂ rich liquid phase

Data: Aasen et al., Fluid phase equilb., 2017
Data situation CO$_2$-rich liquids – viscosity

- Thin data situation pure CO$_2$
- Relevant binary data only on 5 compositions
  - $>7$ °C
  - All from the same PhD thesis, uncertainty analysis limited
- Relevant multicomponent data on 4 compositions published
- All multicomponent and binary data from the same groups
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• ECCSEL/SINTEF facilities to address fluid properties
State of the art phase equilibria measurements

**CO$_2$Mix facility (NO2.4)**
- Designed for CCS
- Up to 200 bar
- -60 to 200 °C
- Typical total uncertainty < 0.1 % in terms of composition
CO$_2$Mix
- Operating work-horse
- < 200 bar, -60 to 200 °C
- Fluid phase and fluids with solids equilibria

HPC-PE
- New cell
- < 1000 bar, -60 to 200 °C
- Fluid phase and fluids with solids equilibria
- Particularly well suited for
  - Water and brines mixtures
  - Liquid-liquid equilibria
- Prepared for additional in-situ analysis
Installation II of CO2Mix: Setup for gravimetric

- Facility for very accurate preparations of gas mixtures
- Buoyancy correction using reference cylinder
- Down to ppm-level accuracy
- Heated lathe available
- 10 l gas cylinders
VLE measurements

Investigated systems:

- CO₂-N₂ (3 isotherms ++)
- CO₂-O₂ (6 isotherms)
- CO₂-Ar (7 isotherms, including solids)
- CO₂-CH₄ (3 high-temp isotherms)
- CO₂-CO (NCCS, 4 isotherms)
- 2018/19: CO₂-N₂-CH₄ (NCCS, 5+ isotherms)
Visc-Dense: Two-Capillary Viscometer and Densimeter

- **Operational Conditions:**
  - Pressure Range: up to 1000 bar
  - \(-50 \, ^\circ\text{C} < T < 200 \, ^\circ\text{C}\)

- **High Accuracy and Stability:**
  - Accuracy <0.1 % (except close to critical point)

- **Density Measurements:**
  - Pressure Range: up to 1000 bar
  - \(-10 \, ^\circ\text{C} < T < 200 \, ^\circ\text{C}\) (-50 °C with lower accuracy)
Measurements lead to ....

Critical pt estimation

Other internal / partner direct utilization

New Data

Cubic models

TREND

Thermodynamic Reference & Engineering Data

Publications
Measurements lead to ....

Low-Cost and Robust CCS

Better engineering tools

Publications

NIST ThermoML DDB ....

Data bases

Third Party Modeling

www.eccsel.org | 34
Acknowlegements

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Video: Phase separation of CO₂-N₂ from critical conditions