# A New Look at Impurities in $CO_2$ for EOR and their Consequences

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# *Presentation Overview*

- Example specifications for Pipeline / EOR $CO_2$

- Technical and economic impacts of several types of impurities that may be found in Pipeline / EOR $CO_2$
  - Water
  - Oxygen
  - Hydrogen Sulfide
  - Nitrogen
  - Hydrocarbons ($CH_4$, $C_2H_6$, $C_3H_8$+)
  - Others (Ar, $H_2$, CO, $NO_x$, $SO_2$, COS, glycol, compressor oil)

- Conclusions

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# Why Do We Need Specifications?

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# *Example Pipeline / EOR Specifications (1 of 2)*

| Component | Example Industrial Pipeline ( Ref. 1) | DOE Pipeline Design Guideline (Ref. 2) | DOE EOR Design Guideline (Ref. 2) |
|---|---|---|---|
| $CO_2$ | ≥ 95 mol. % | ≥ 95 vol. % | ≥ 95 vol. % |
| $H_2O$ | ≤ 30 lb / MMcf (633 ppmv) | ≤ 500 ppmv | ≤ 500 ppmv |
| Oxygen | ≤ 10 ppmw | ≤ 10 ppmv | ≤ 10 ppmv |
| $H_2S$ | ≤ 20 ppmw | ≤ 100 ppmv | ≤ 100 ppmv |
| Total Sulfur | ≤ 35 ppmw | | |
| Nitrogen | ≤ 4 mol. % | ≤ 4 vol. % | ≤ 1 vol. % |
| Hydrocarbons | ≤ 5 mol. % | (next slide) | (next slide) |
| Glycol | ≤ 0.3 gal / MMcf | ≤ 46 ppbv | ≤ 46 ppbv |

Ref 1 – $CO_2$ Transportation, Ken Havens, Kinder-Morgan CO2 Company, June 5, 2008

Ref 2 –  National Energy Technology Laboratory, Quality Guidelines for Energy System Studies, $CO_2$ Impurity Design Parameters, August 2013

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# *Example Pipeline / EOR Specifications (2 of 2)*

| Component | DOE Pipeline Design Guideline (Ref. 2) | DOE EOR Design Guideline (Ref. 2) |
|---|---|---|
| Ar | ≤ 4 vol. % | ≤ 1 vol. % |
| $H_2$ | ≤ 4 vol. % | ≤ 1 vol. % |
| $CH_4$ | ≤ 4 vol. % | ≤ 1 vol. % |
| $C_2H_6$ | ≤ 1 vol. % | ≤ 1 vol. % |
| $C_3+$ | < 1 vol. % | < 1 vol. % |
| CO | ≤ 35 ppmv | ≤ 35 ppmv |
| $NO_x$ | ≤ 100 ppmv | ≤ 100 ppmv |
| $SO_2$ | ≤ 100 ppmv | ≤ 100 ppmv |
| COS | Trace | ≤ 5 ppmv |

Ref 2 – National Energy Technology Laboratory, Quality Guidelines for Energy System Studies, $CO_2$ Impurity Design Parameters, August 2013

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# *Impacts of Water in CO$_2$*

## Corrosion of carbon steel



Corrosion of carbon steel tube sheet placed in wet CO$_2$, water condensing service.

## CO$_2$-H$_2$O Hydrates



Puck of solid CO$_2$ hydrate

http://www.bgs.ac.uk/scienceFacilities/laboratories/research/hydrates.html

# *Saturation Water Content in CO$_2$*

Note that example limit of 30 lb water / MMscf (633 ppmv) is well below saturation limit of CO$_2$ at typical pipeline operating temperatures.
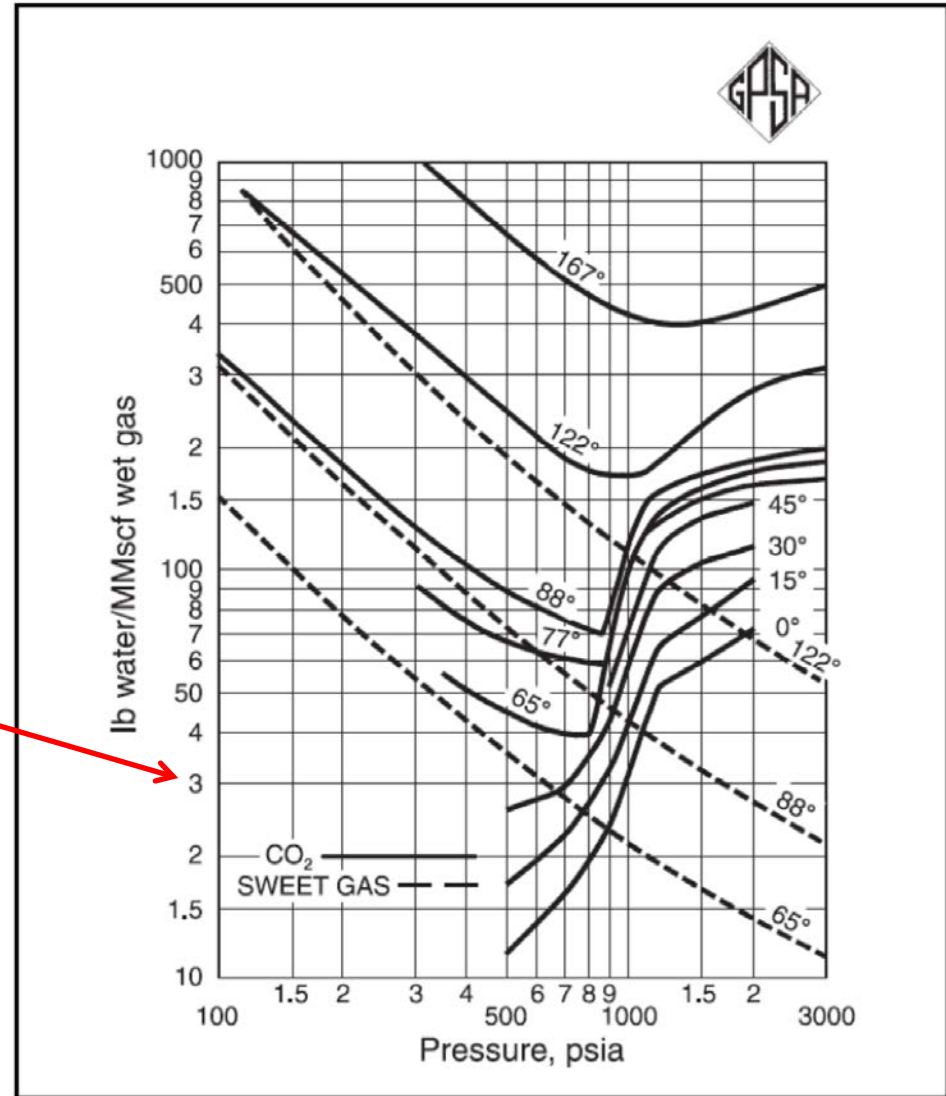


Figure used courtesy of GPSA. Ref 3 - GPSA Engineering Data Book, 12$^{th}$ Ed., Figure 20-6

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7

# *Phase, Pressure, and Temperature – Impacts on Corrosion in $CO_2$ Pipeline and EOR Applications*

- Under normal conditions, a free liquid phase (usually water) has to be present for corrosion to occur in $CO_2$ pipeline and EOR applications

- Higher partial pressure and temperature of $CO_2$ generally increase the corrosion rate
  - Increasing concentration of $CO_2$ increases partial pressure of $CO_2$
  - Increasing total pressure increases partial pressure of $CO_2$

- de Waard-Milliams Equation (Ref 4)

$$\text{Log } V_{corr} = 5.8 - 1710 / (273+t) + 0.67 \log (pCO_2)$$

$V_{corr}$ in mm/year, t is temp in $^o$C, and $pCO_2$ is partial pressure of $CO_2$ in bar

Ref 4 – de Waard C, Lotz U. Prediction of $CO_2$ corrosion of carbon steel.  Corrosion/93 Paper No 69, NACE, Houston, Texas 1993

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# *Impurity Impacts on Corrosion in $CO_2$ Pipeline and EOR Applications*

- At 75% relative saturation, an $O_2$ concentration of 1 mol. % (10,000 ppmv) produced a corrosion rate of 0.37 – 0.40 mils per year (Ref 5)

- At 75% relative saturation, an $H_2S$ concentration of 5 mol. % (50,000 ppmv) produced a corrosion rate of 0.16 mils per year (Ref 5)

  - Rule of thumb is that corrosion rates ≥ 1 mil per year begin to trigger closer monitoring and perhaps efforts to reduce corrosion rates

- Once $CO_2$ containing small amounts (> 10 ppmv) of $O_2$ or $H_2S$ is injected in a formation and contacts water, corrosion and other problems in the injection well, the formation, and the recycle facility may occur

Ref 5 - GPA Research Report RR-222 "Corrosion in Acid Gas Injection Systems", June 2014

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# CO₂ – Water Hydrates

H here stands for Hydrate.  We are concerned about temperatures dropping lower than this line (primarily at pressures in the highlighted region).
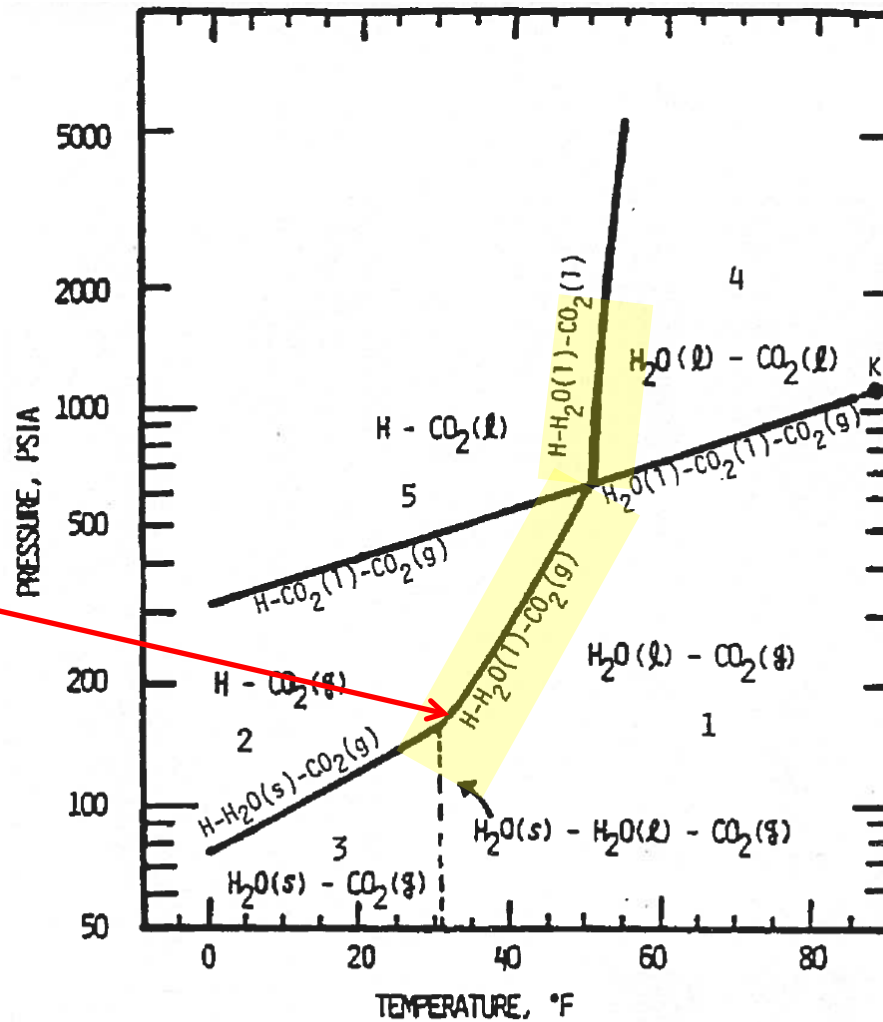


FIGURE 1.  Pressure-Temperature Projection of Univariant Loci for CO₂-Water System.

Figure used courtesy of GPA.  Ref 6 - GPA Research Report RR-99 "The Water Content of CO2 Rich Fluids in Equilibrium with Liquid Water and / or Hydrates", June 1986.

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10

# *Water Removal Costs (1 of 2)*

- TEG (triethylene glycol) absorption-based dehydration is most common
  - Installed equipment costs are on the order of $ 30,000 / MMscfd of treatment capacity (for a nominal 50 MMscfd plant)
  - Installed equipment costs in $ / MMscfd decrease with increasing throughput capacity
  - Operating costs are fairly minimal (fuel gas, glycol)

- If pressure is higher than about 1,000 psig, glycerol is often used instead of TEG
  - TEG solubility in $CO_2$ increases with increasing pressure and losses would be unacceptably high
  - Equipment costs are comparable to TEG
  - Operating costs are slightly higher
    - Water loading is higher at these pressures, so fuel costs for regeneration are higher
    - Glycerol is typically more expensive than TEG

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# *Water Removal Costs (2 of 2)*

- If refrigeration-based processes such as $CO_2$ liquefaction for distillation or Natural Gas Liquids recovery are involved, then adsorption-based processes (molecular sieve) may be required

  – Higher capital and operating costs

  – Installed equipment costs are on the order of $ 50,000 / MMscfd of treatment capacity (for a nominal 60 MMscfd plant)

  – Installed equipment costs in $ / MMscfd decrease with increasing throughput capacity

  – More complex operation

    - Cyclical operation of drying and regenerating beds

    - Monitor performance of media over time (months) and adjust cycle times until it becomes necessary to replace adsorbent media (years)

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# *Impacts of Oxygen*

- Once $CO_2$ containing $O_2$ contacts water, the mixture is more corrosive than $CO_2$ and water in the absence of $O_2$

- Oxygen can lead to biological growth in the formation

- Oxygen can oxidize TEG and glycerol

- Oxygen can react with $H_2S$ under certain conditions to form elemental sulfur, sulfuric acid, and / or other sulfur compounds

- It is difficult to treat a $CO_2$ stream to remove oxygen
  - Liquefaction and distillation have been used in some applications
  - Some catalytic approaches may be applicable in principle
  - Preferred approach is to try and limit the introduction of oxygen at the source

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# *Comparison of $H_2S$ and $CO_2$ Exposure Limits*

| Component | OSHA Ceiling | OSHA PEL | OSHA IDLH |
|---|---|---|---|
| $H_2S$ | 20 ppmv | 50 ppmv for 10 minutes | 100 ppmv |
| $CO_2$ | | 5,000 ppmv for 8 hour shift | 40,000 ppmv |

- Definitions
  - Ceiling - at no time should this exposure limit be exceeded
  - PEL – permissible exposure limit
  - IDLH – immediately dangerous to life or health

- While the toxicity of $H_2S$ is well known in this industry, the toxicity of pipeline / EOR quality $CO_2$ also needs to be understood

- Toxicity risks of $CO_2$ are not the same as the asphyxiation hazard of $CO_2$

For more details, see Tyndall, K., K. McIntush, J. Lundeen, K. Fisher, C. Beitler, "When is $CO_2$ more hazardous than $H_2S$", Hydrocarbon Processing, January 2011, Vol. 90, No. 1, pp. 45-48.

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# *Impacts of Hydrogen Sulfide (1 of 2)*

- Limits on the order of 10 ppmv are often specified for these reasons:
  - Concerns with toxicity and odor
  - Avoid monitoring and public hearing requirements for Texas RR Comm. Rule 36 when $H_2S$ > 100 ppmv and similar rules in other states
  - May avoid designing to meet NACE MR0175 requirements to prevent sulfide stress corrosion cracking

- Presence of $H_2S$ in $CO_2$ EOR is common in West Texas, but > 10 ppmv in other areas can be a concern because concentrations could increase with recycle and $H_2S$ accumulates in in low pressure steps (flash and storage)

- $H_2S$ can react with $O_2$ or $SO_2$ under certain conditions to form elemental sulfur, sulfuric acid, and / or other sulfur compounds

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# *Impacts of Hydrogen Sulfide (2 of 2)*

- $H_2S$ lowers the minimum miscibility pressure, which is a benefit to EOR operations

- Trace amounts (10's of ppmv) can usually be treated economically with scavengers
  - Order of magnitude costs are $ 5 to $ 20 / lb of $H_2S$ removed
  - As an example, annual operating costs to treat 8 MMscfd of $CO_2$ to lower $H_2S$ from 440 to 4 ppmv are on the order of $ 750,000

- Higher levels (% levels) require liquid redox or absorption processes
  - Higher capital costs than scavengers
  - Lower operating costs than scavengers

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# Impurities Impact Operating Costs

- Example Scenario
  - 100 MMscfd, 100 mile, 12-inch pipeline, 2,000 psig pipeline inlet pressure, booster pump at end of pipeline to get back to 2,000 psig injection pressure

| Individual Impurity | Booster Pump Inlet Pressure for 2 vol. % Impurity (psig) | Additional Power Cost for 2 vol. % Impurity at $ 0.07/kW-hr ($/yr) and (%) | | Booster Pump Inlet Pressure for 4 vol. % Impurity (psig) | Additional Power Cost for 4 vol. % Impurity at $ 0.07/kW-hr ($/yr) and (%) | |
|---|---|---|---|---|---|---|
| None | 1,590 | | | 1,590 | | |
| Ar | 1,583 | $ 6,404 | 4 % | 1,574 | $ 15,096 | 9 % |
| $H_2$ | 1,587 | $ 6,404 | 4 % | 1,581 | $ 16,468 | 10 % |
| $N_2$ | 1,585 | $ 5,489 | 3 % | 1,579 | $ 12,351 | 8 % |
| $CH_4$ | 1,589 | $ 3,202 | 2 % | 1,587 | $ 7,319 | 4 % |
| $C_2H_6$ | 1,586 | $ 4,117 | 3 % | 1,582 | $ 8,691 | 5 % |
| $C_3H_8$ | 1,583 | $ 5,032 | 3 % | 1,575 | $ 10,979 | 7 % |

# *Impacts of Nitrogen*

- $N_2$ will increase the minimum miscibility pressure and raise the critical pressure, which increase operating costs and are detrimental for oil production

- $N_2$ will decrease the saturation water content of $CO_2$

- $N_2$ will increase the potential for hydrate formation

- Presence of $N_2$ can require increased transport pipe strength due to ductility issues (Ref 2)

- Some operators place a limit on the total "light gases", "non-condensables", or "inerts" in the range of 2 vol. % to 4 vol. %

Ref 2 – National Energy Technology Laboratory, Quality Guidelines for Energy System Studies, CO2 Impurity Design Parameters, August 2013

# Impacts of Hydrogen

- $H_2$ will increase the minimum miscibility pressure and raise the critical pressure, which increase operating costs and are detrimental for oil production

- Presence of $H_2$ can require increased transport pipe strength due to ductility issues (Ref 2)

- Some operators place a limit on the total "light gases", "non-condensables", or "inerts" in the range of 2 vol. % to 4 vol. %

- $H_2$ is valuable and would likely be lowered to far less than 4 vol. % in a $CO_2$ stream under normal operating conditions

Ref 2 – National Energy Technology Laboratory, Quality Guidelines for Energy System Studies, CO2 Impurity Design Parameters, August 2013

# *Impacts of Methane*

- $CH_4$ will increase the minimum miscibility pressure and raise the critical pressure, which increase operating costs and are detrimental for oil production

- $CH_4$ will decrease the saturation water content of $CO_2$

- $CH_4$ will increase the potential for hydrate formation

- Hydrocarbons accumulate in recycle $CO_2$ over time in facilities without NGL recovery
  - Changes the viscosity of the oil by stripping away lighter components
  - Takes up pore space, which is detrimental to $CO_2$ EOR

- Some operators place a limit in the range of 0.3 vol. % to 1 vol. % on $CH_4$

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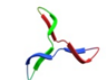
# *Impacts of Other Hydrocarbons*

- $C_2H_6$, $C_3H_8$, and heavier hydrocarbons will decrease the minimum miscibility pressure, which is beneficial for oil production

- Hydrocarbons accumulate in recycle $CO_2$ over time in facilities without NGL recovery
    - Change the viscosity of the oil by stripping away lighter components
    - Take up pore space, which is detrimental to $CO_2$ EOR

- Some operators place a limit in the range of 3 vol. % to 5 vol. % on total hydrocarbons

- Hydrocarbon removal (including $CH_4$) is typically done with membranes or via liquefaction and distillation
    - Capital intensive process on the order of $ 80 MM for a 200 MMscfd facility
    - Capital and operating costs may be offset by NGL and sales gas revenue

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# *Impacts of CO, NO$_x$, SO$_2$, and COS*

- Limits on CO, NO$_x$, and SO$_2$ are largely driven by health and safety related exposure limits

- COS is a concern for the following reasons:
  - COS can hydrolyze to H$_2$S in the presence of free water, which means that pipeline CO$_2$ that starts with COS may come back as CO$_2$ with H$_2$S in the recycle stream
  - COS is unacceptable in food and beverage CO$_2$ product and removal costs are significant

- As more manmade CO$_2$ sources are transported in pipelines and used for EOR, the impacts of these types of impurities will become better understood and current proposed limits may be revised

# *Impacts of Glycol and Compressor Oil*

- In addition to concentration limits, specifications may require that no glycol can be present in a liquid state at the pressure and temperature conditions of the pipeline

- Excess glycol carryover can cause damage to seals and other components (Ref 2)

- Use of mineral oil for $CO_2$ compressor cylinder lubricant has led to asphaltene plugging issues in injection wells requiring acid treatments

- Use of higher cost synthetic oil avoids this problem, but it is important to keep mineral oil and synthetic oil separate because they can form a gel when mixed together

Ref 2 – National Energy Technology Laboratory, Quality Guidelines for Energy System Studies, CO2 Impurity Design Parameters, August 2013

# *Conclusions*

- Limiting impurities in $CO_2$ transported in pipelines and used for EOR is necessary to ensure reliable operation and to protect health, safety, and the environment

- Specification limits must be determined on a case by case basis considering the source of the $CO_2$ and the use of the $CO_2$

- As more manmade $CO_2$ is transported in pipelines and used for EOR, impacts of newer types of impurities will be become better understood and proposed limits may be revised

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