

Corrosion of Carbon Steel in Dense Phase CO_2 with Impurities

CO_2 Transport and Storage MYRP (1025033)

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FECM/NETL Carbon Management Research Project Review

August 5-9, 2024



U.S. DEPARTMENT OF
ENERGY



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Acknowledgements

This work is performed in support of the U.S. Department of Energy's (DOE) Office of Fossil Energy and Carbon Management's Carbon Transport and Storage Program and executed through NETL Research and Innovation Center's Carbon Transport and Storage MYRP (MYRP#1025033).

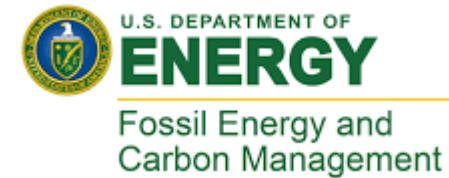
Team



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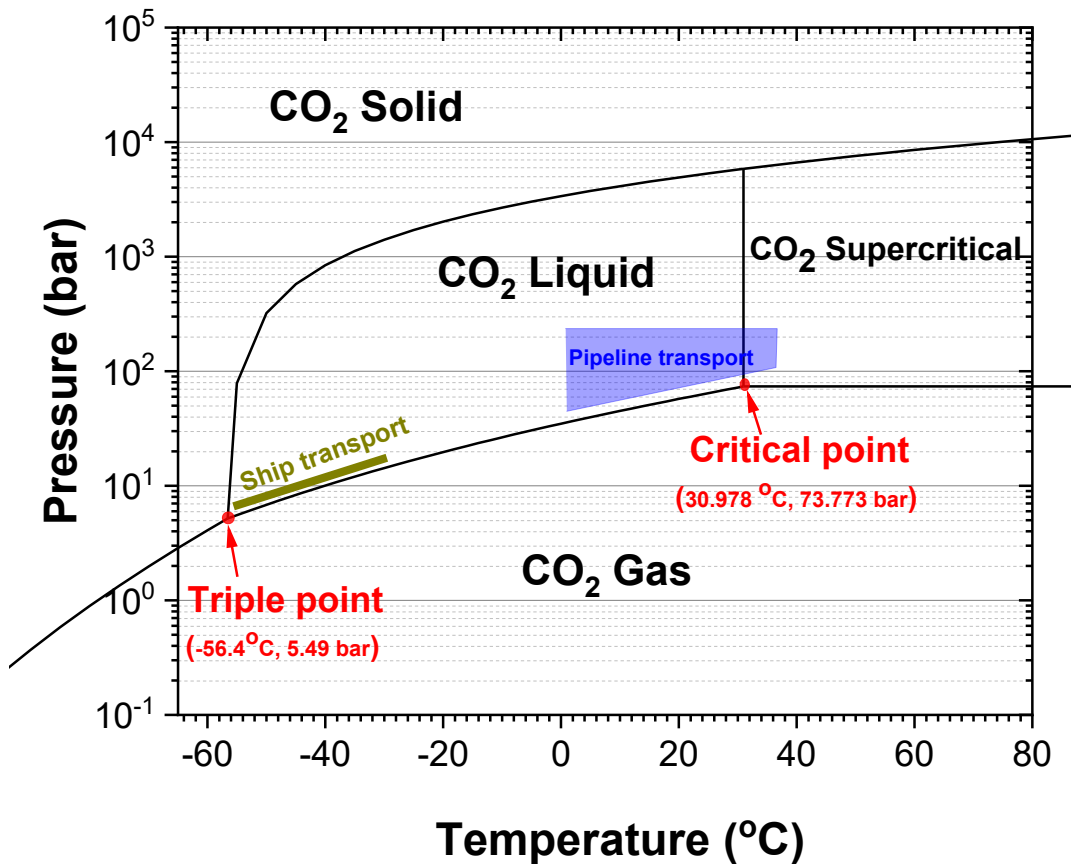
- Bob Smith, Program Manager
- Kevin Dooley, Program Manager



CO₂ Phase Diagram

These pipelines operate in the “dense phase” mode at ambient temperature and high pressure.

Pure CO₂ pressure-temperature diagram



However, impurities in the CO₂ stream can alter the phase diagram depending on the concentration and environmental factors.



if the critical temperature of the impurities is above that of CO₂ (e.g., H₂S and NO₂), the 2-phase region will be found below the critical temperature of the pure CO₂ and vice versa.



The presence of impurities will affect the solubility limit of water



Therefore, the corrosion behavior of carbon steel

Impurities in CO₂ streams

Recommended Composition Limits for CO₂ Streams

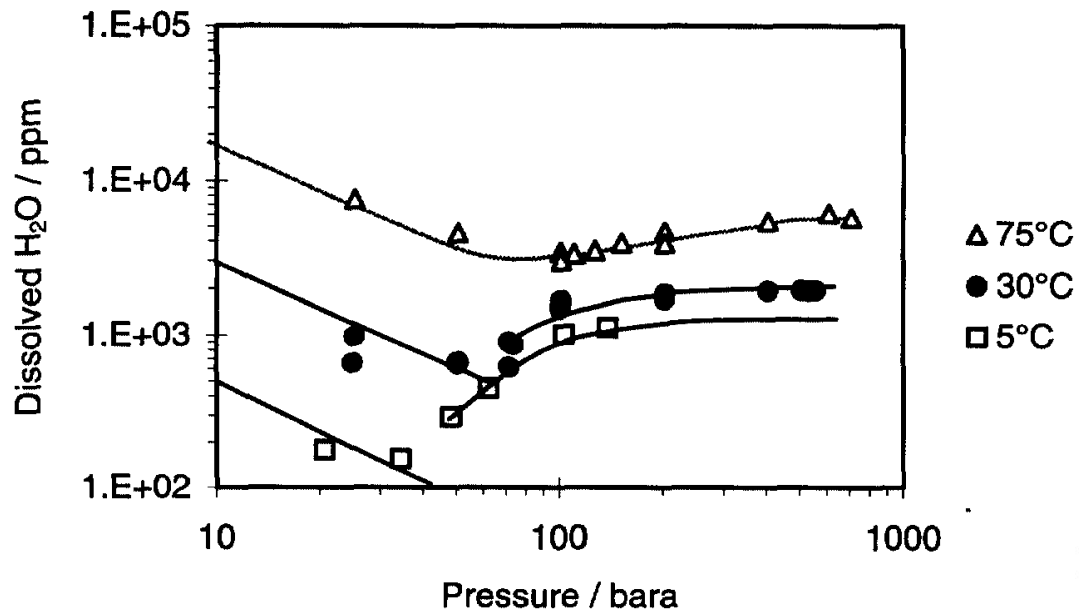
Component	Unit ^a	Carbon Steel Pipeline		EOR		Saline Reservoir Sequestration		Saline CO ₂ and H ₂ S Cosequestration	
		Concept	Literature Range	Concept	Literature Range	Concept	Literature Range	Concept	Literature Range
CO ₂	vol%	95	90–99.8	95	90–99.8	95	90–99.8	95	20–99.0
H ₂ O	ppmw ^c	300	20–650	300	20–650	300	20–650	300	20–650
N ₂	vol%	4	0.01–7	1	0.02–2	4	0.01–7	4	0.01–7
O ₂	vol%	4	0.01–4	0.01	0.001–1.3	4	0.01–4	4	0.01–4
Ar	vol%	4	0.01–4	1	0.01–1	4	0.01–4	4	0.01–4
CH ₄	vol%	4	0.01–4	1	0.01–2	4	0.01–4	4	0.01–4
H ₂	vol%	4	0.01–4	1	0.01–1	4	0.01–4	4	0.01–4
CO	ppmv ^d	35	10–5000	35	10–5000	35	10–5000	35	10–5000
H ₂ S	vol%	0.01	0.002–1.3	0.01	0.002–1.3	0.01	0.002–1.3	75	10–77
SO ₂	ppmv	100	10–50,000	100	10–50,000	100	10–50,000	100	10–50,000
NO _x	ppmv	100	20–2500	100	20–2500	100	20–2500	100	20–2500
NH ₃	ppmv	50	0–50	50	0–50	50	0–50	50	0–50

^a Maximum unless otherwise noted.
^b Immediately dangerous to life and health.
^c Parts per million by weight.
^d Parts per million by volume.
^e Not enough information.

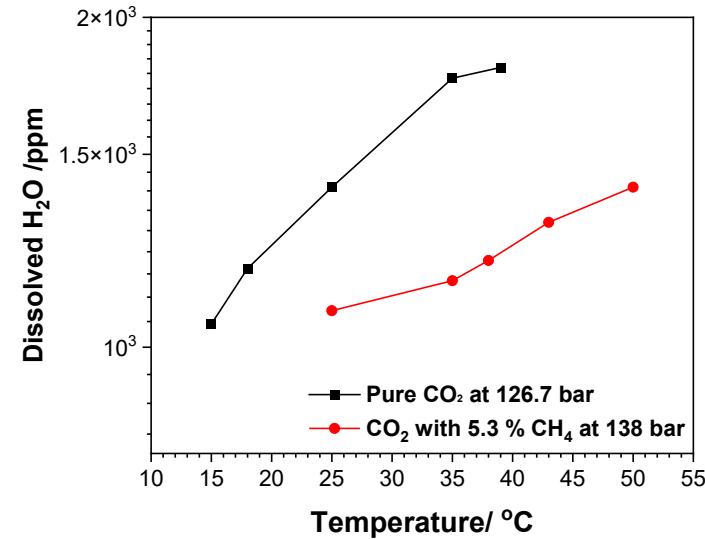
Shirley, Pamela, and Myles, Paul. *Quality Guidelines for Energy System Studies: CO₂ Impurity Design Parameters*. United States: N. p., 2019. Web. doi:10.2172/1566771.

Water solubility in CO₂

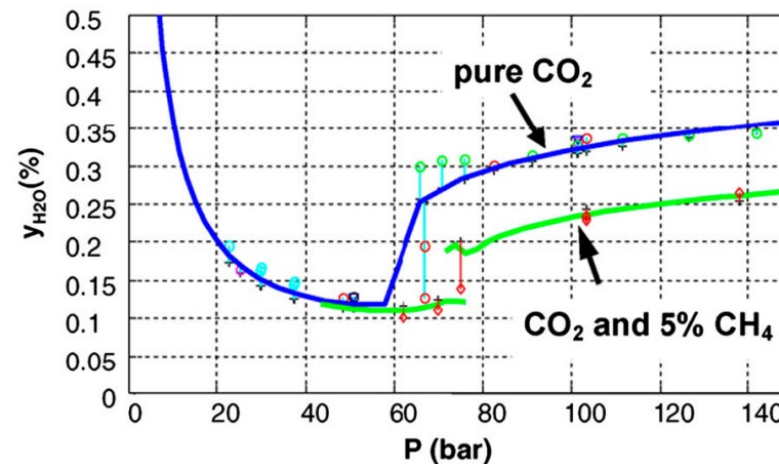
Amount of water that can be contained in CO₂ as a function of pressure and temperature



R. Wiebe, J. Gaddy, J. Am. Chem. Soc. 3, (1941):p. 475.
 K.Y. Song, SPE Paper No. 18583 (Houston, TX: SPE International, 1988)



K.Y. Song, R. Kobayashi, SPE Formation Evaluation (1987) :p. 500.
 M. B. King, A. Mubarak, J. D. Kim, T. R. Bott, J. Supercrit. Fluids 5, (1992) :p. 296

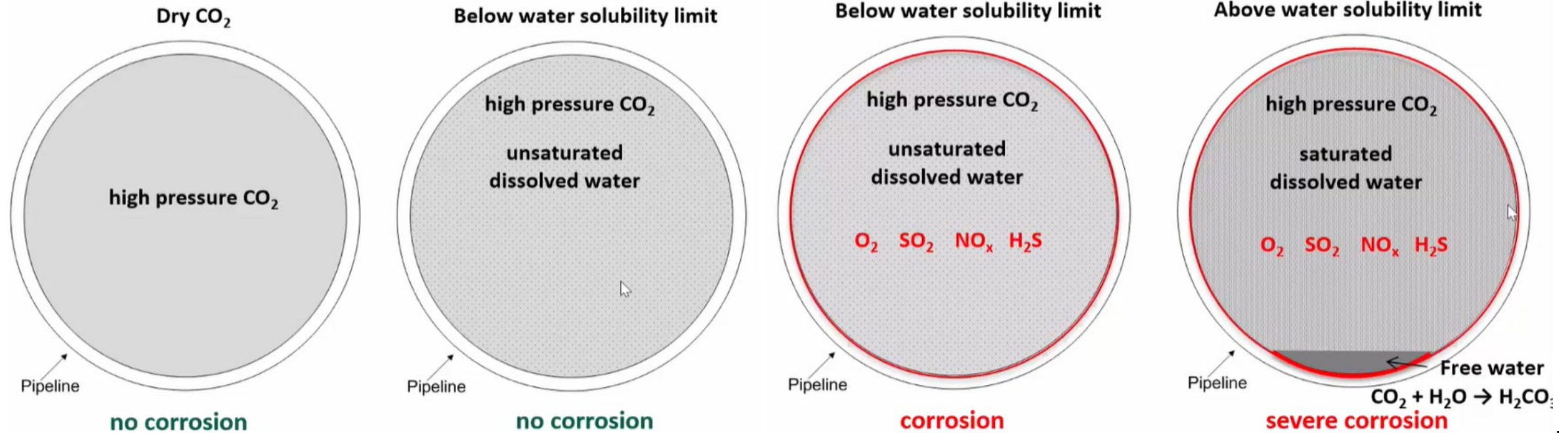


Water solubility in pure CO₂ and in a CO₂-CH₄ mixture at 25°C

Xiang et al., State-of-the-art overview of pipeline steel corrosion in impure dense CO₂ for CCS transportation: mechanisms and models, Corrosion Engineering, Science and Technology, 52:7, 485-509,

Internal corrosion of pipeline steel

Impact of impurities on phase boundaries and reactions in CO₂ and corrosion of carbon steel

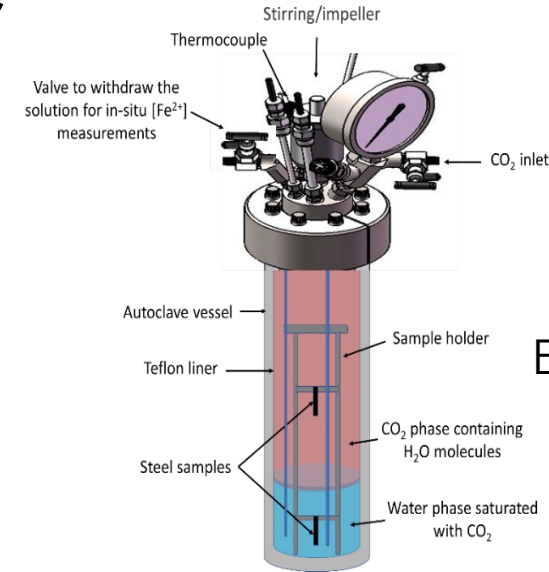


Nesic et al. Ohio University

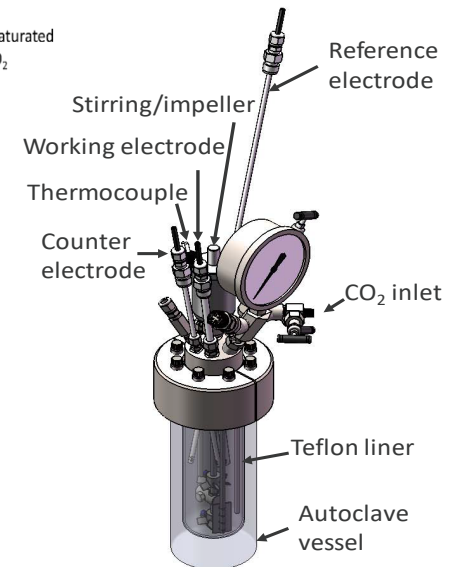
Corrosion in dense phase CO₂ in the presence of water and other impurities

- Investigate the effect of impurities (e.g., CO, O₂, H₂, NO_x, SO_x) on the corrosion of pipeline carbon steel under dense phase CO₂ in electrochemical and immersion autoclaves using weight loss and electrochemical methods.
- The team will investigate improving the test setup by adding capabilities to continuously or periodically measure impurity content in the autoclaves, injecting impurities to replenish those consumed in corrosion reactions, and detecting acid dropout.
- The post-exposure analysis of the coupons will characterize corrosion mechanisms, including localized corrosion and corrosion products, using SEM, EDS, XRD, and Kelvin probe.

Immersion Autoclaves

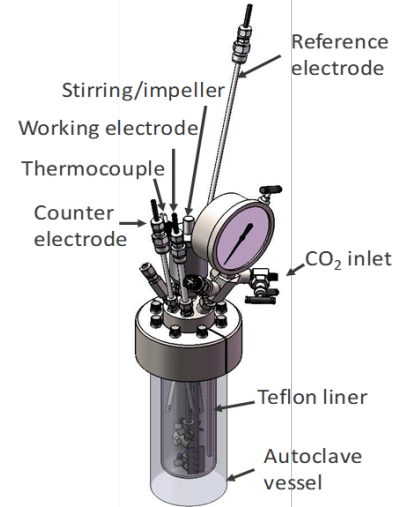


Electrochemical Autoclaves



Corrosion studies in dense phase CO₂ with impurities

Electrochemical reaction autoclaves

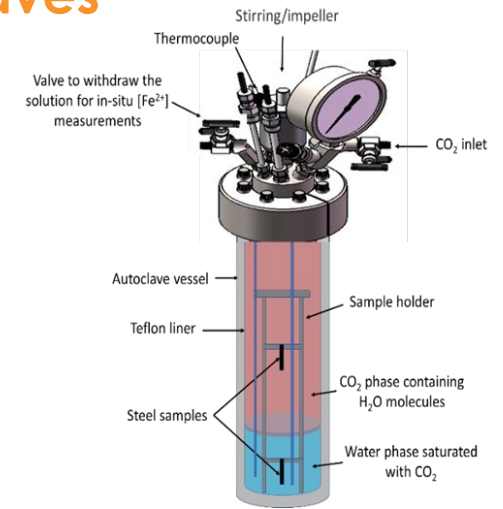


Operational conditions

Autoclave made of Hastelloy 276 with 3 electrode configuration.

- For up to 5000 psi
- Temperature: 25°C to 300°C
- Available gases:
 - SO₂ 12%+O₂ 23.5%+CO₂ ; SO₂ 12%+CO₂ ; H₂S 4%+CO₂
 - CO₂; O₂+CO₂
 - H₂, N₂, Ar
- Rotation speed up to 600 rpm (1.25 m/s, Re=15611 at 40°C)
- High-temperature and high-pressure pH probe
 - High Pressure ZrO₂-based pH probe (85 To 250 °C; for up to 4000 psi)
 - High Pressure Glass-based pH Probe (2 To 80 °C ; 0 to 3000 psi)

Immersion autoclaves



Operational conditions

- Autoclave made of Hastelloy 276; Ni alloys; Stainless steel.
- For up to 5000 psi
- Temperature: 25°C to 250°C
- Available gases:
 - SO₂ 12%+O₂ 23.5%+CO₂ ; SO₂ 12%+CO₂ ; H₂S 4%+CO₂
 - CO₂; O₂+CO₂
 - N₂, Ar
- Rotation speed up to 600 rpm (1.25 m/s, Re=15611 at 40°C)
- In-situ measurements of ions concentration (Fe²⁺, Cr²⁺, ...)
- Gas and liquid phase sample holders



- advanced characterization and microanalysis of selected samples
- donate carbon steel materials for corrosion testing at NETL
- contribute to the discussion of experiments design/conditions and share any relevant experience and corrosion testing results with NETL
- conduct complementary autoclave corrosion tests of dense phase CO₂ with impurities



- perform corrosion tests under varying conditions to characterize the effect of water drop out during operational upsets
- investigate the impact of deposits, left on the steel surface after water dissolution in sCO₂, on the ability to retain water and sustain corrosion under hygroscopic conditions

Project Timeline

Evaluation of the risk of corrosion in dense phase CO₂ in the presence of aqueous/acid phase (continuous or droplets) and other impurities

Tasks	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Literature review	█											
Establish test methodologies and obtain steel samples	█											
Determine general corrosion rates of carbon steel in aqueous/acid phase with SO _x and NO _x	█	█	█	█	█							
Determine general corrosion rates of carbon steel in aqueous/acid phase with additional impurities					█	█	█	█				
Corrosion mechanisms of select steels	█	█	█	█	█	█	█	█	█	█	█	█
Project kick-off and progress meetings	█		█		█		█		█			█

Project Kick-off: June 14, 2024

Any Questions?

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