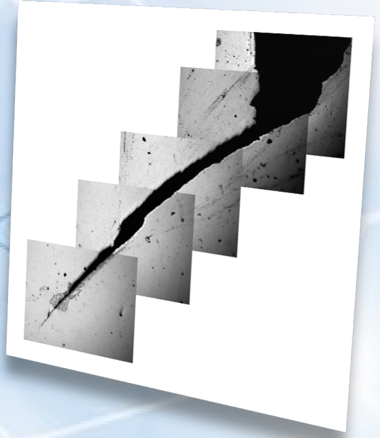
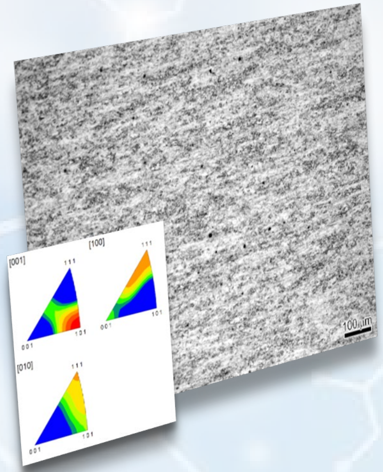
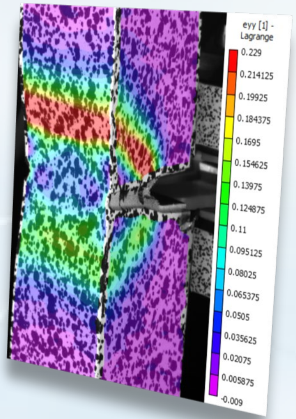
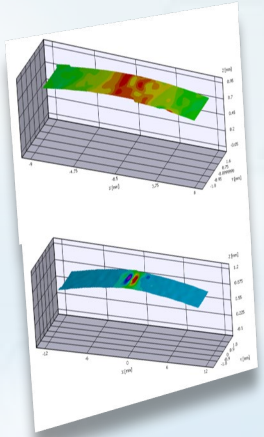
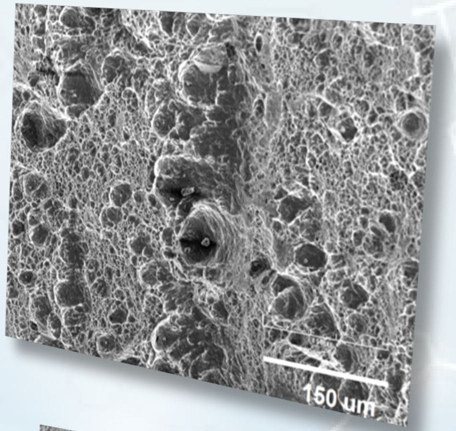
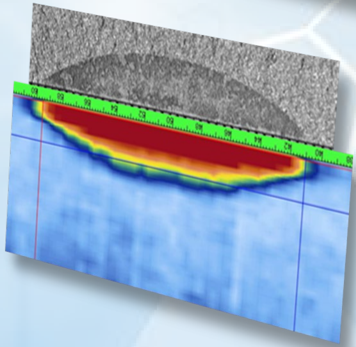












Pipeline Safety

NIST CAPABILITIES AND CONSIDERATIONS FOR CO_2 INFRASTRUCTURE

Dash Weeks

Contributors: Andrew Slifka, May Martin, Ross Rentz, Damian Lauria, Brandi Clark (Fatigue and Fracture)
Allan Harvey, Mark McLinden, Marcia Huber (Thermophysical Properties)
Pam Chu (MML - Carbon Accounting and Decarbonization Program)

NIST
National Institute of Standards and Technology
U.S. Department of Commerce

MATERIAL MEASUREMENT LABORATORY

DOT/PHMSA Pipeline Safety R&D Forum, October 31, 2023, Washington, DC

EXPANDING THE CO_2 INFRASTRUCTURE

- The state of the CO_2 equation of state
- Effects of impurities on thermodynamics
- Erosion/corrosion implications
- In-situ mechanical material properties
- NIST involvement overview

EXPANDING THE CO_2 INFRASTRUCTURE

$$f(p, V, T) = 0$$

Ideal Gas Law

$$pV = RT$$

1834

Non-Ideal Gases (multiple cubic equations)

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$ van der Waals 1873

$$p = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m(V_m + b)}$$ Soave-Redlich-Kwong 1972

$$p = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m^2 + 2bV_m - b^2}$$ Peng-Robinson 1976

There are many more versions and modifications but the most recent EOS are adequate for many engineering purposes.

STATE OF THE CO_2 EOS

Need:

- Accurate Pressure-Volume-Temperature, enthalpy behavior, and phase equilibria is essential for design.
- Better accuracy than simple cubic equations especially near phase boundaries and critical points.
- Viscosity and thermal conductivity correlations, which require calculating density as a function of temperature and pressure.

Solution:

Current Reference EOS: Span and Wagner (1996)

- Experimentally educated
- Multi-parameter
- Substance-specific and at liquid-like densities

Incorporated in NIST's REFPROP

The Span and Wagner EOS has 42 terms of different types. It is computationally complex and too slow for some applications. There are numerical problems in mixture models and near critical points.

NIST CO_2 EOS EVOLUTION

- New experimental data is available since 1996; the speed of sound is more accurate than heat capacity which reduces uncertainty.
- We have a better understanding of theoretical constraints, and the model is a better representation of super-critical and high-temperature behavior.
- Can now perform state-of-the-art molecular modelling and calculations for heat capacity, thermal conductivity, and viscosity.
- The latest EOS optimization techniques retain high accuracy with fewer terms and improved computational efficiency (factor 1.5 – 2)

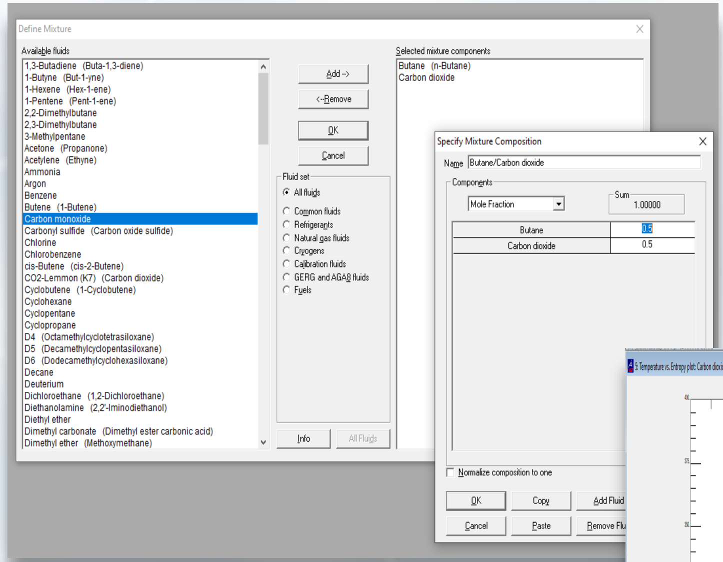
RUHR UNIVERSITÄT BOCHUM

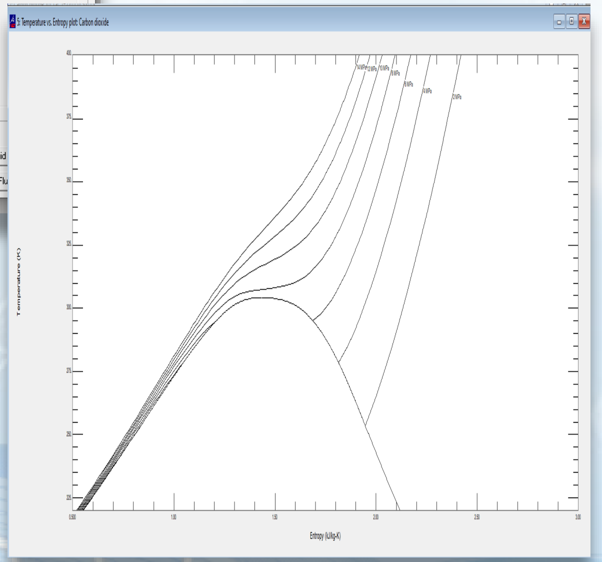
This work is part of an international collaboration with Ruhr University in Bochum Germany. The collaborators are:

- E.W. Lemmon, A.H. Harvey, and I.H. Bell, Applied Chemicals and Materials Division, NIST
- T. Eckermann, R. Span, and M. Thol, Ruhr University Bochum.

REFPROP

REFerence Fluid Thermodynamic and Transport PROPerties (NIST23)





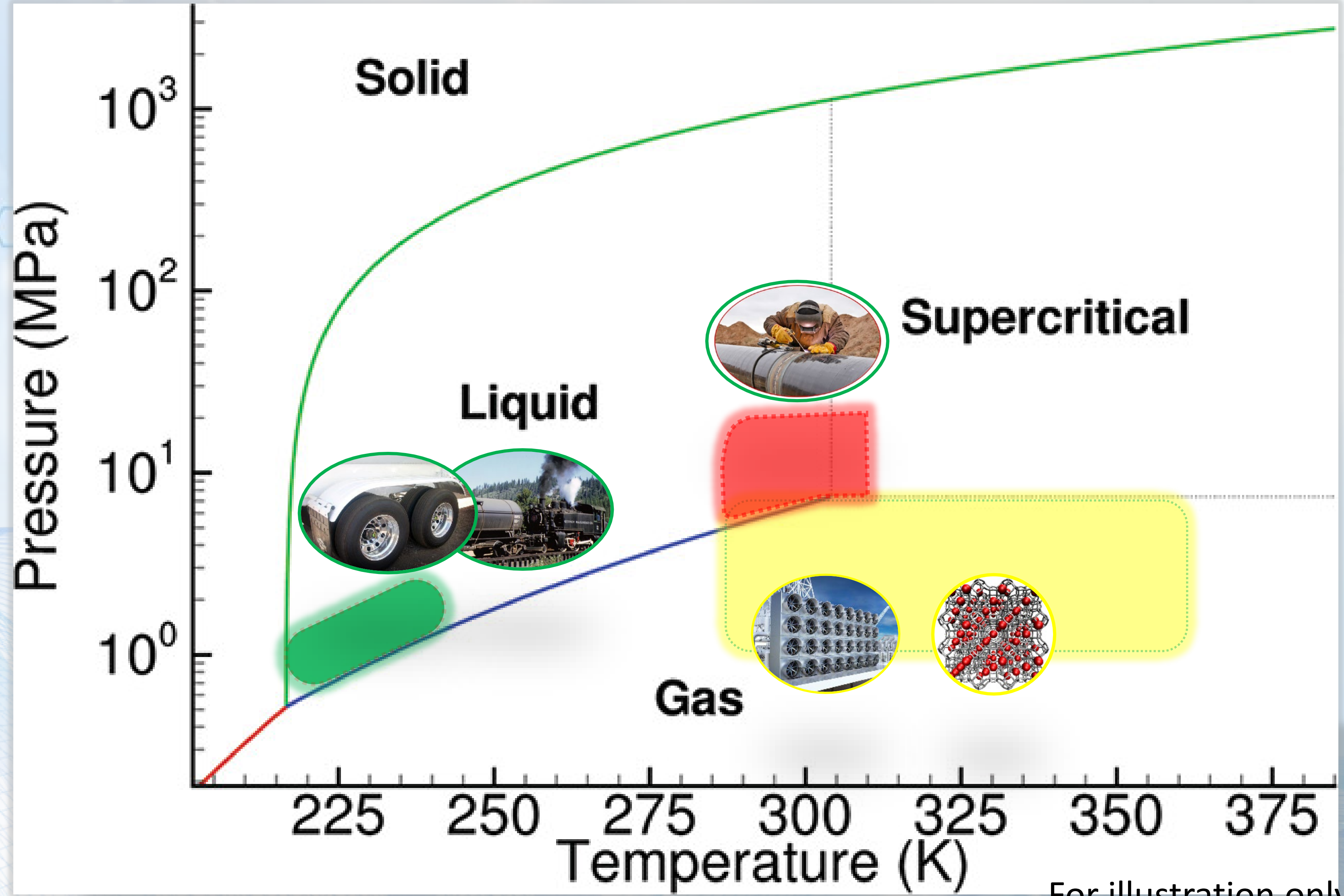
Simple Workflow and GUI

- Select Fluid/Mixture
- Select Units & Properties
- Select calculation(s)
- Plot/Export

- REFPROP is a computer program that can provide the thermophysical properties of common industrial fluids and their mixtures, including CO_2 and CO_2 mixtures.
- Computer program sold by NIST Standard Reference Data
  https://www.nist.gov/srd/refprop
- It may be used on a Windows machine with the graphical user interface (GUI) or one can interface the program with 3rd party software and programs such as Python, Excel, Matlab, Mathematica, etc. using the supplied DLL.

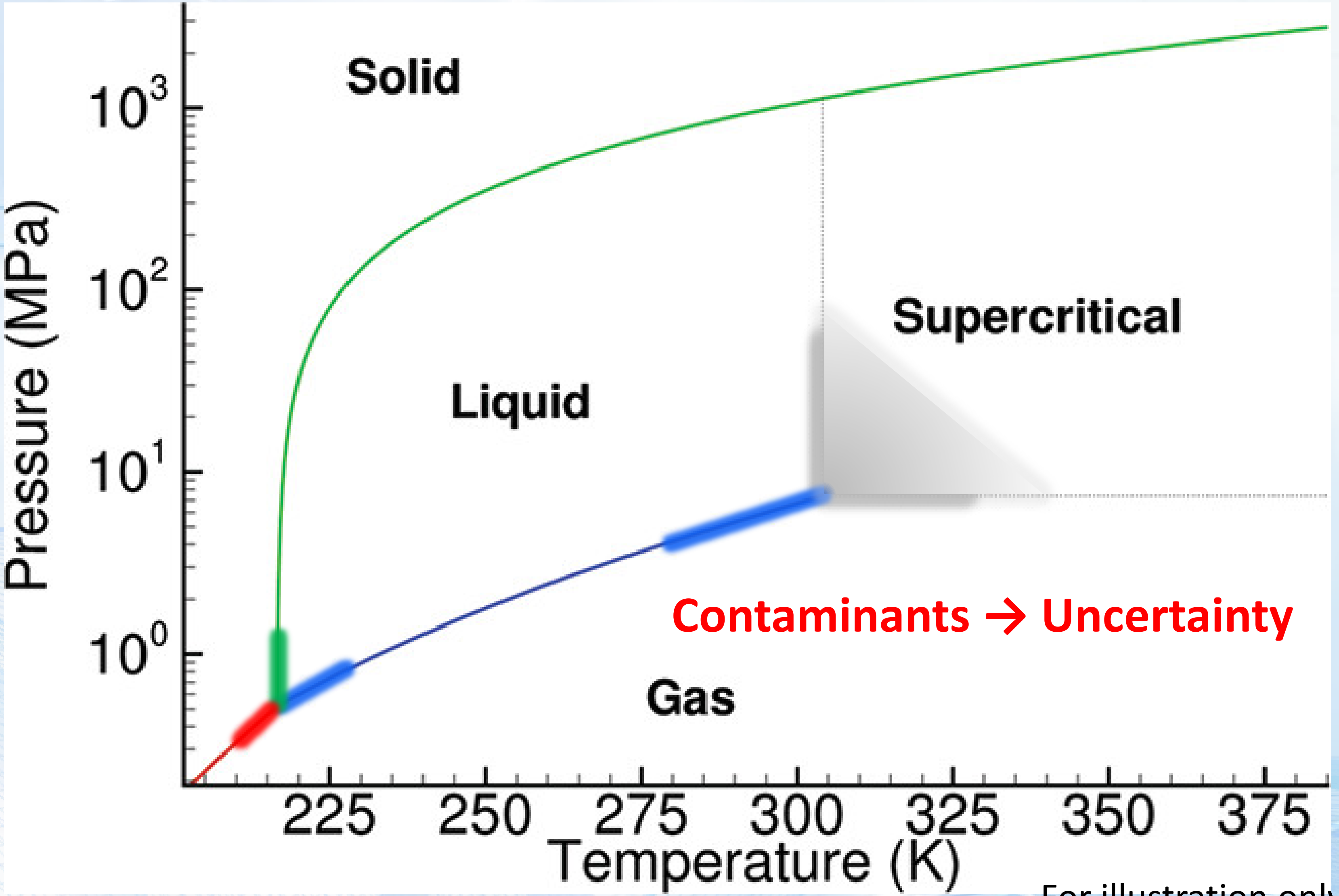
"The NIST REFPROP Database for Highly Accurate Properties of Industrially Important Fluids", Marcia L. Huber, Eric W. Lemmon, Ian H. Bell, and Mark O. McLinden, Ind. Eng. Chem. Res. 2022, 61, 42, 15449-15472 https://doi.org/10.1021/acs.iecr.2c01427

CO_2 PHASE DIAGRAM



For illustration only

CO_2 PHASE DIAGRAM UNCERTAINTY



For illustration only

MIXTURE OR CONTAMINANT (?)

Small concentrations result in small changes in thermodynamic properties

1. What is a significant concentration (change)?
2. What are the limits of detectability?
3. How accurately can we measure concentration?

CO_2 Measurements and Reference Materials

https://www.nist.gov/programs-projects/carbon-dioxide-measurements-and-reference-materials

Contaminants also impact:

Mechanical Material Properties

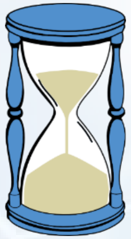
Corrosion/Erosion

Health & Safety

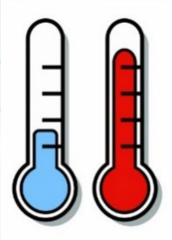
Operations

What are acceptable levels of contaminants to maintain pipeline integrity and public safety?

RANGE OF CONDITIONS IN THE LITERATURE



Duration
hours →1 year



Temperature
12 °C – 265 °C

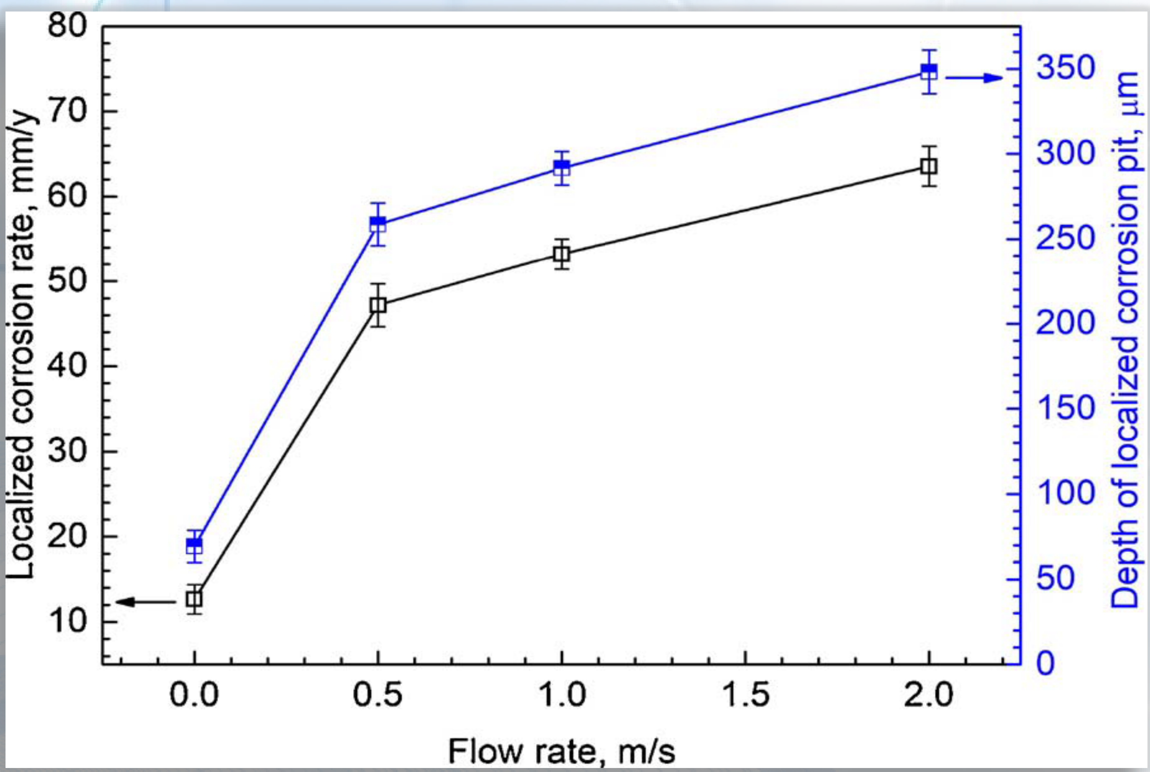
Pressure
80 – 240 bar

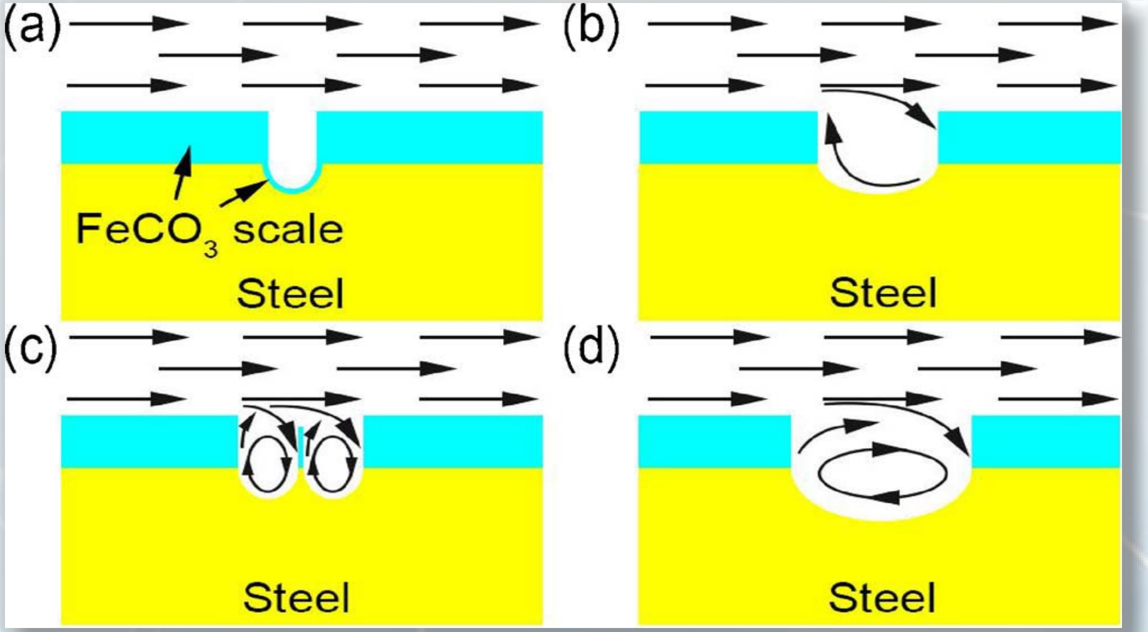
Flow Rate
many static, a few with flow

Contaminants
H_2O, H_2S, O_2, NO_2, SO_2
(often in combination)

Result: Reported corrosion rates **vary** over **four orders of magnitude** (0.01 – 100 mm/year).

IMPORTANCE OF FLOW RATE





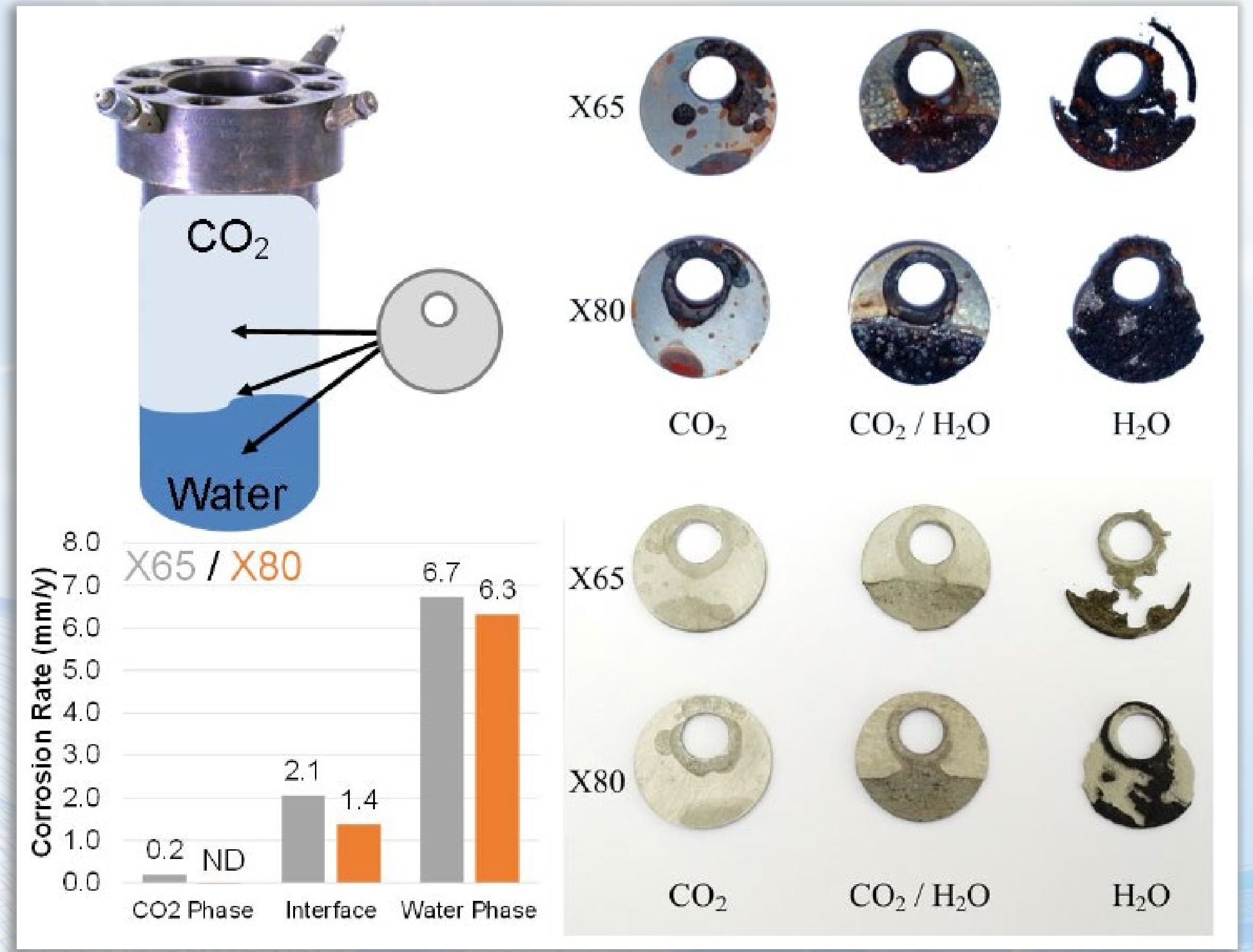
L. Wei, X. Panga, K. Gaoa, Effect of flow rate on localized corrosion of X70 steel in supercritical CO2 environments, Corr. Sci. ***136*** *(2018)*

NIST CO_2 TEST FACILITY

- State-of-the-art test facility for $SCCO_2$ environmental testing within a walk-in fume hood for H_2S testing capability with remote monitoring and continuous data-logging.
- Static and dynamic test applications to evaluate flow-induced damage on multiple alloys simultaneously.
- Multiple autoclaves up to 206 bar and 500 °C
- IGS Analyzer (FTIR) for constituent monitoring

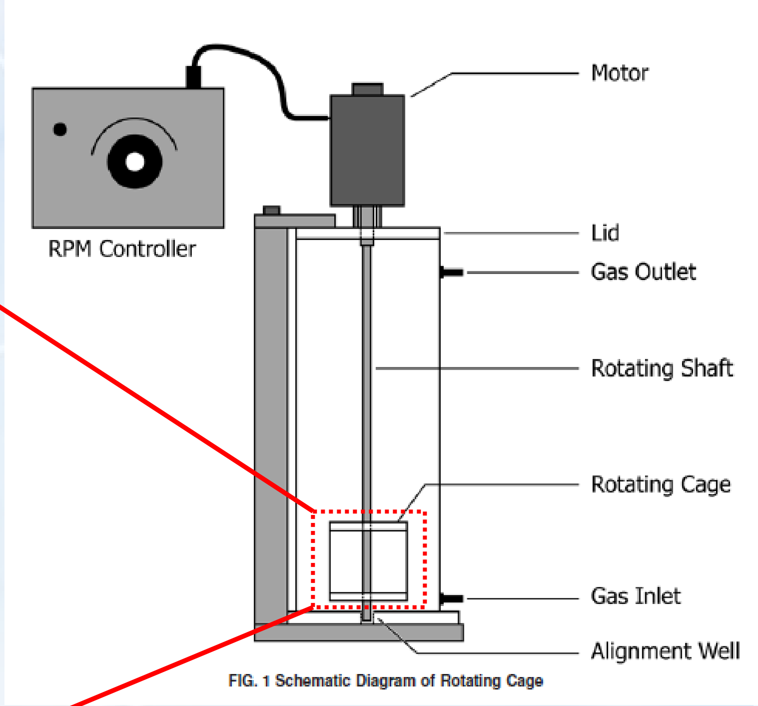
Real conditions include turbulent mixing and contaminants are replenished (locally).
Lab conditions have little to no mixing and a limited contaminant supply (locally).

NIST CO_2 CORROSION TESTS



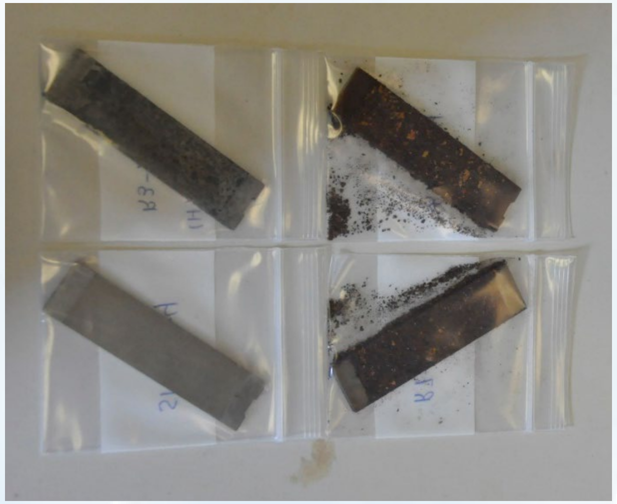
NACE TM0169
ASTM G31

NIST CO_2 FLOW Simulations

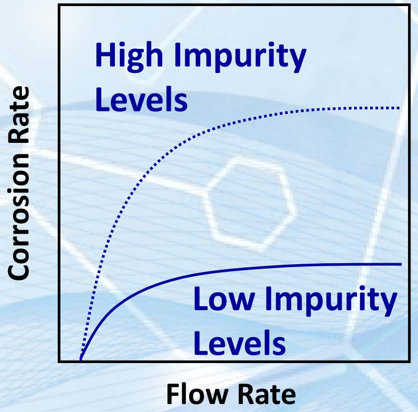


ASTM G184

Concept modified for use in an autoclave with a magnetic drive.



Test coupons are 75 x 19 mm and 3 mm thick



Higher impurity levels are expected to produce thicker corrosion products which could lead to spallation and erosion-corrosion.

NIST CO_2 IN-SITU MECHANICAL TESTS

ASTM E1681

NACE TM0177
Method B

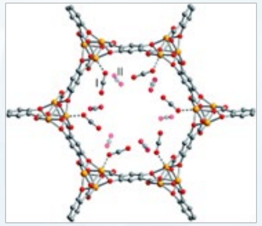
Advancing Carbon Dioxide Removal

pamela.chu@nist.gov

Examples of focus areas include:
- Direct Air Capture Sorbent Materials Characterization
- Low Carbon Cements and Concretes Consortium
- Next Generation Seawater CO_2 Reference Materials
- CO_2 Measurements and Reference Materials
- Ocean Color Satellite Calibration
- Standards to Underpin MRV
- Standards for Carbon Markets and Accounting
- CO_2 Pipeline Material Reliability
- Convergence with
    - GHG Measurements
    - Circular Economy

- NIST collaborates with industry, academia, standards, and government organizations on a broad array of **research, measurements, and standards** to advance CDR, carbon accounting, and decarbonization.

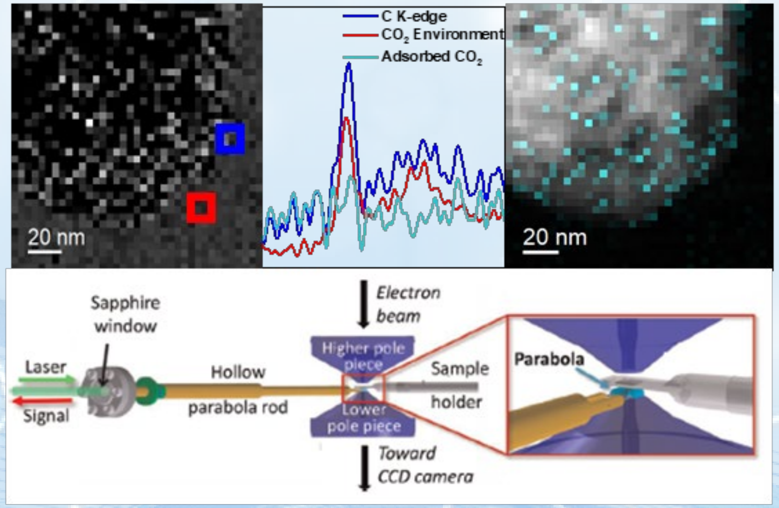
Direct Air Capture Sorbent Materials Characterization



CO_2–MOFs Structure

Crystal structures nanosececond dynamics via neutron scattering

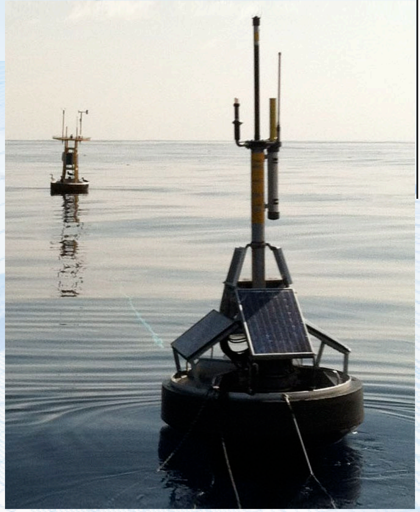
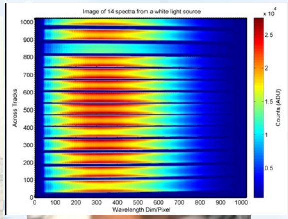
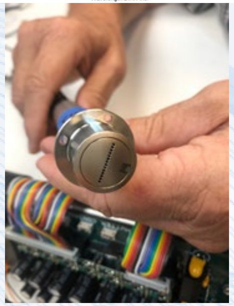
CO_2 adsorption via in-situ STEM-EELS imaging



US Patent US9431211B2 Hybrid electron microscope; Ultramicroscopy 150, 10 (2015), Nature Materials 18 (6), 614–619 (2019) Microscopy and Microanalysis 27 (S1), 800-801 (2021)

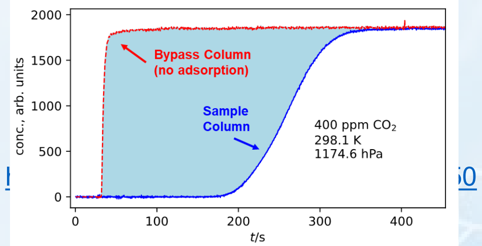
NIST’s Mission is to promote U.S. innovation and industrial competitiveness by advancing measurement science, standards, and technology in ways that enhance economic security and improve our quality of life.

Technology

Develop critical measurement science to accelerate innovation, scalability, & **reduce uncertainties**

Benchmark Measurements Data & Materials



Facilitate **rigor and reproducibility** across measurement ecosystems

Documentary Standards

Support industry and Federal use of **voluntary consensus standards**