Effect of Alternate Fuels and CO_2 on Pipelines

Status and Gaps

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July 18, 2012

Alternate fuels

- Bioalcohols
- Biodiesel
- Drop-in hydrocarbons
- Biogas
- Hydrogen
- Shale gas

Biofuels

Status and Challenges

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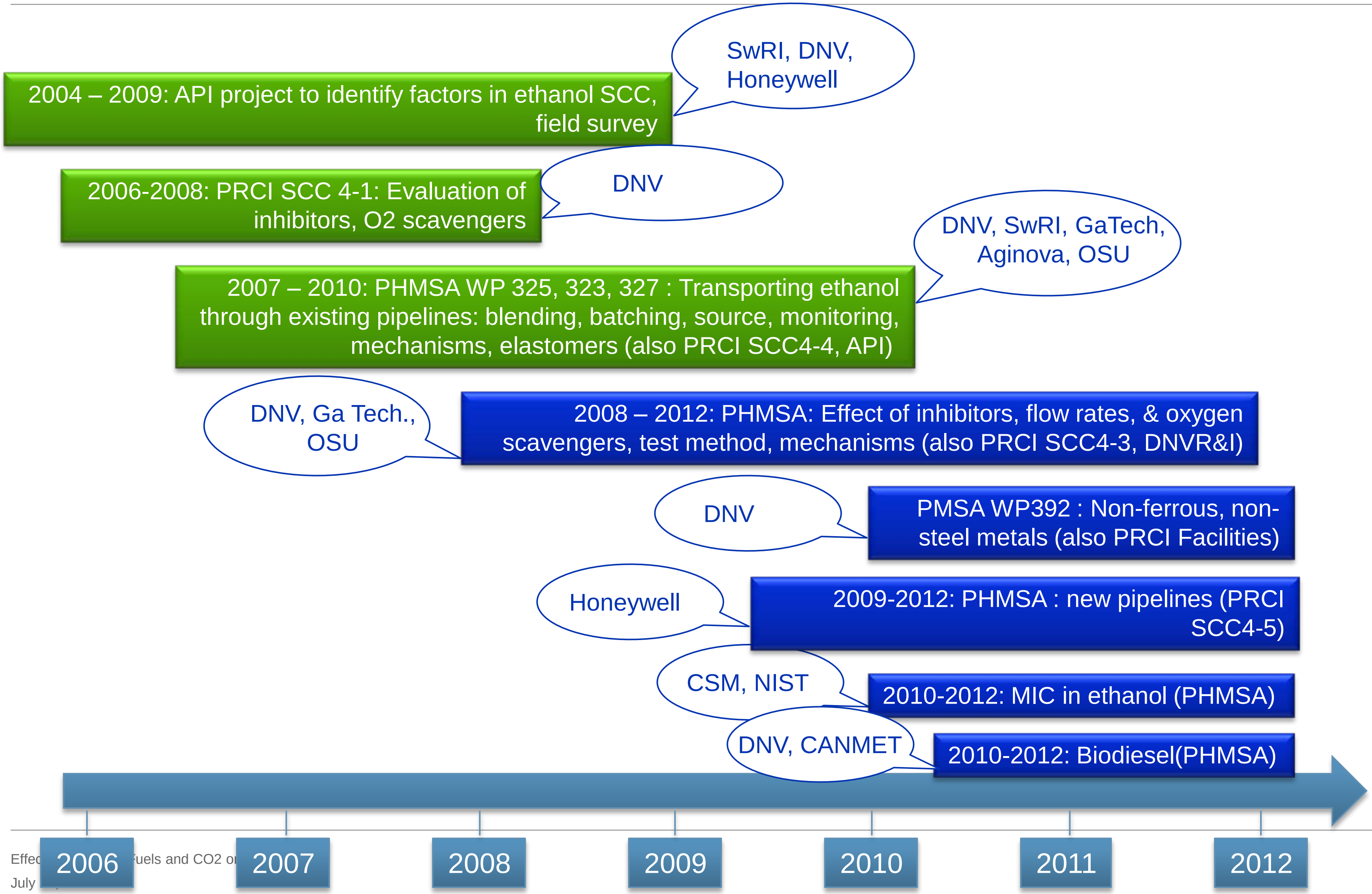
Biofuels materials compatibility program

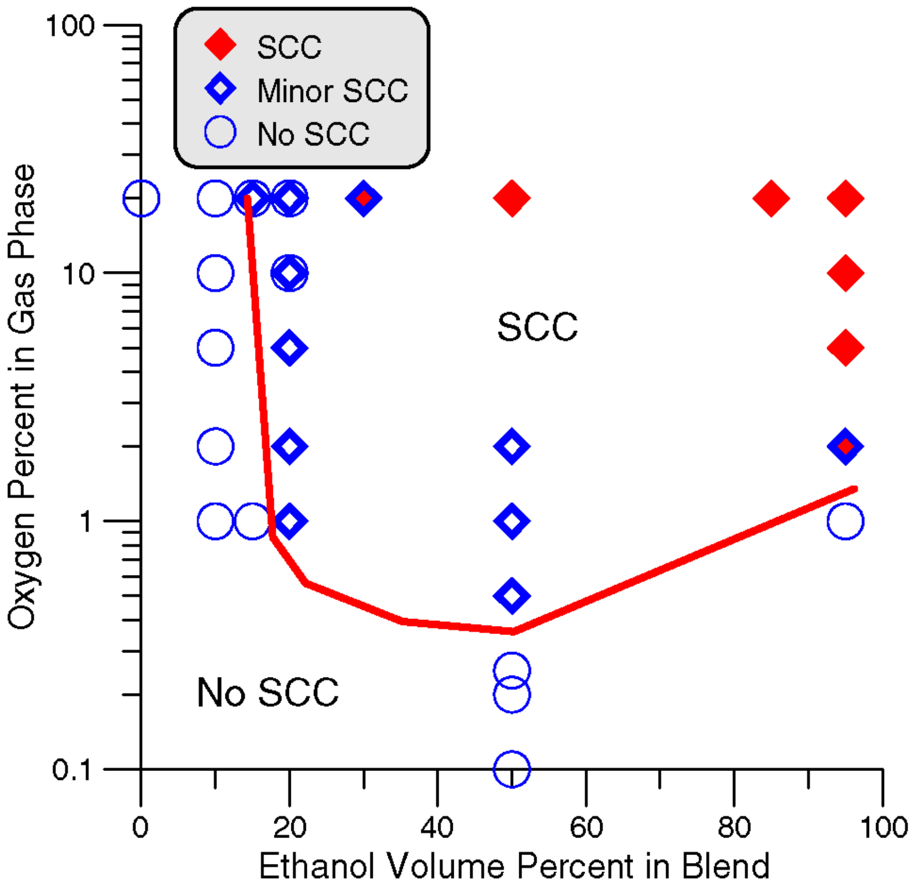


New threats to equipment integrity

Added Integrity Threats	Ethanol	Butanol	Biodiesel	Biogas
Corrosion	Yellow	Yellow	Red	Red
Stress corrosion cracking	Red	Yellow	Green	Green
Delamination	Yellow	Yellow	Yellow	Green
Swelling	Red	Yellow	Yellow	Green
Softening	Red	Yellow	Yellow	Green
Permanent Set	Red	Yellow	Yellow	Green
Soap formation	Green	Green	Yellow	Green
Effect on Product quality	Yellow	Yellow	Green	Green
Permeation	Yellow	Yellow	Yellow	Yellow

Red	Known Threat
Yellow	Possible threat
Green	Unlikely

Key Factors Influencing SCC Susceptibility in ethanol

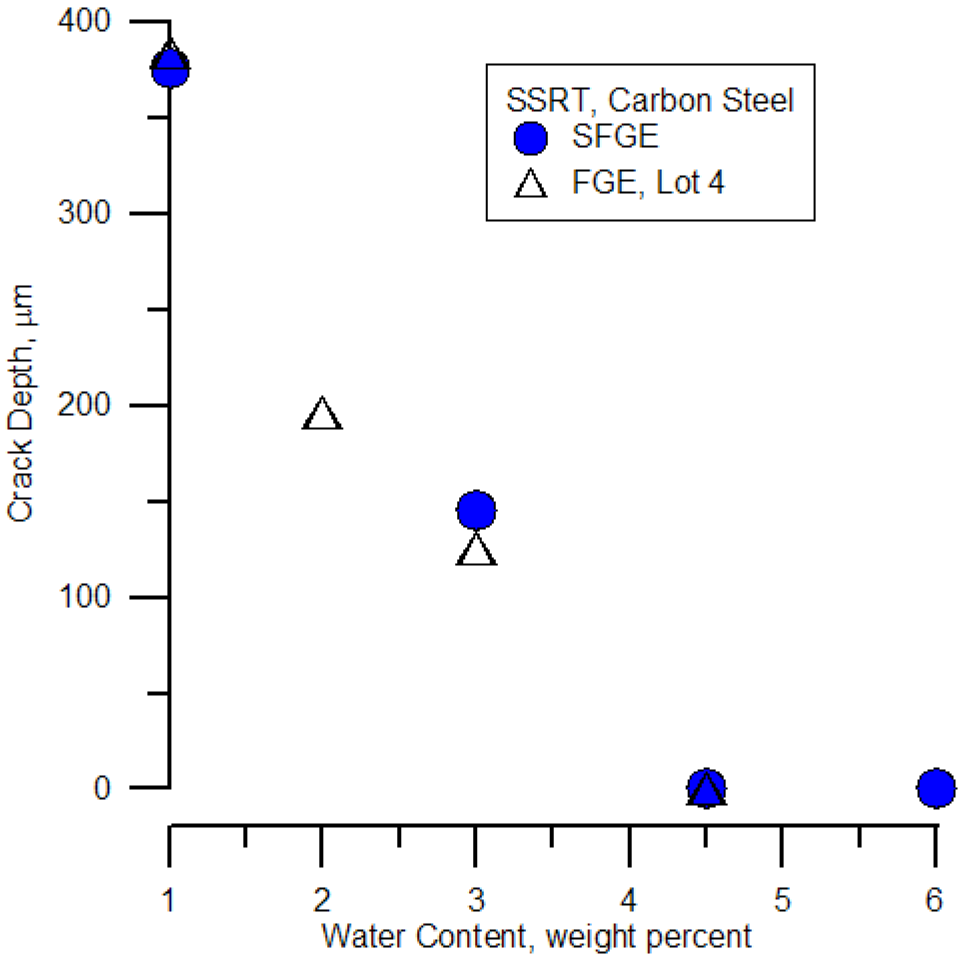


Dissolved oxygen is the most important factor in SCC

No SCC below E-15

E-50 could be the worst

Effect of water on SCC in ethanol

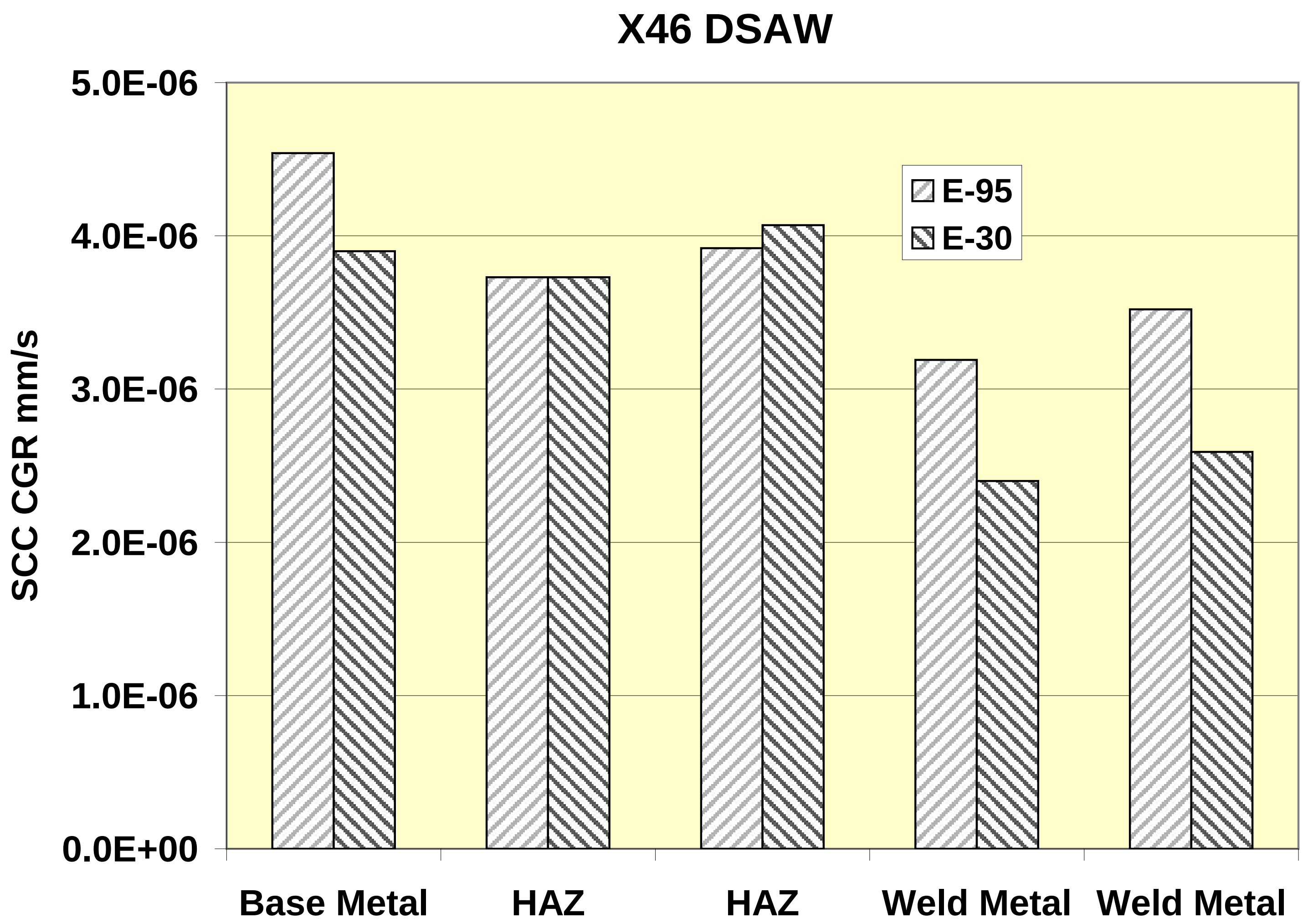


Hydrous ethanol will not cause SCC

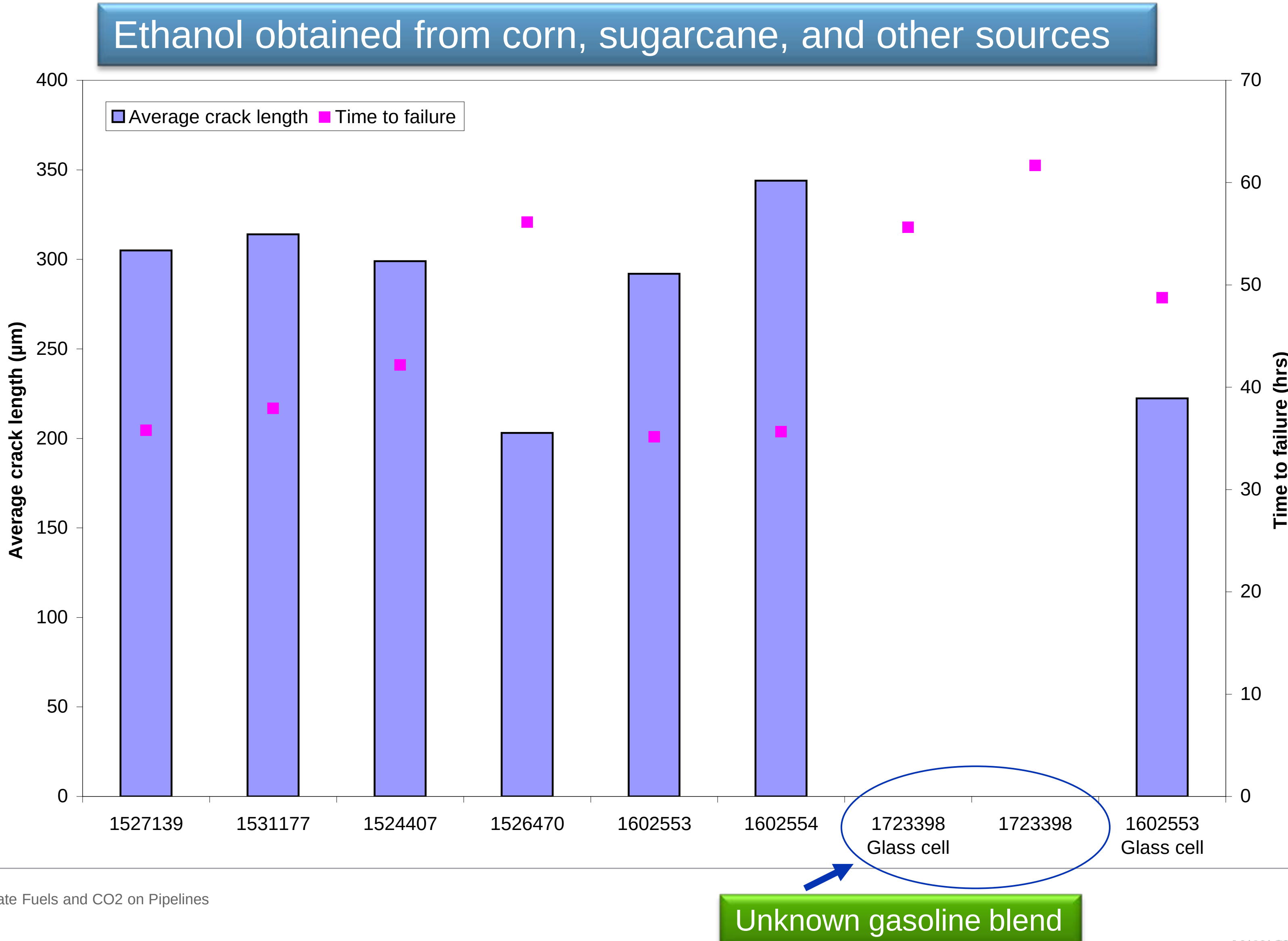
Ammonia requires about 3000 ppm water to inhibit SCC

Methanol requires about 0.5% water to inhibit SCC

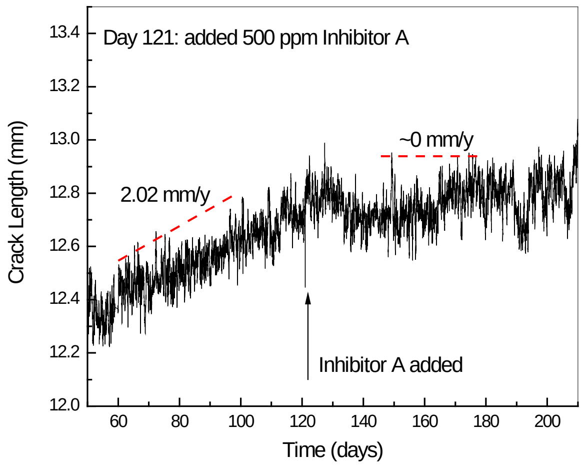
Steel microstructure is not very important for SCC

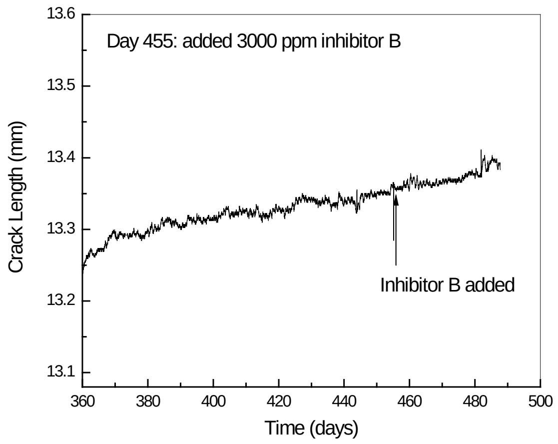


Effect of ethanol chemistry – no smoking gun

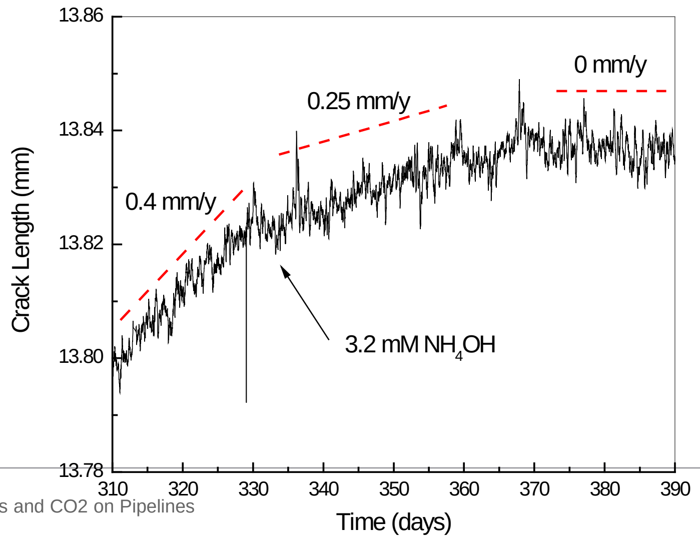


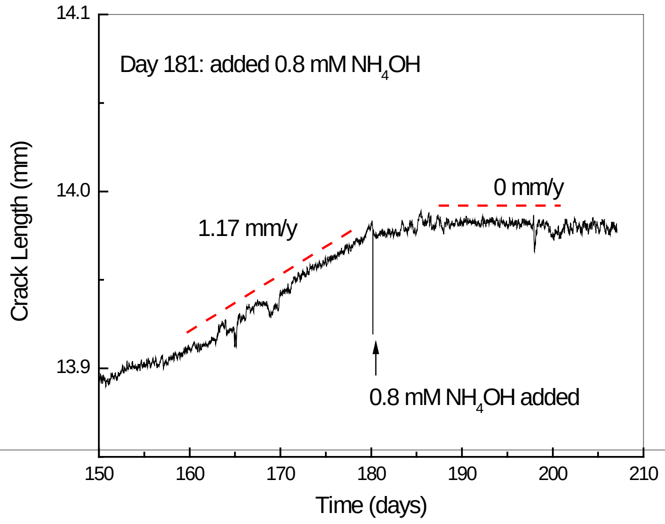
Some Inhibitors are effective in mitigating SCC





But ammonium hydroxide is the best by far





Biodiesel

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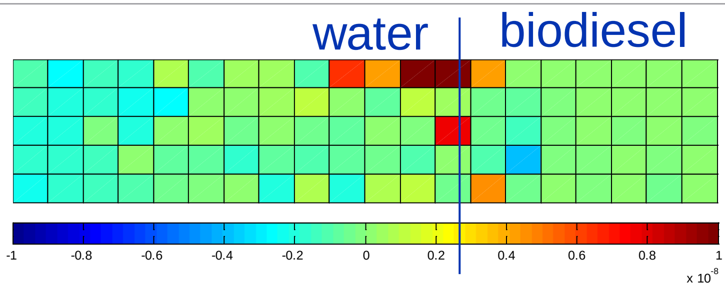
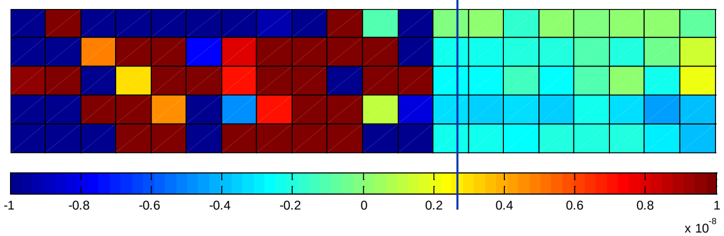
Issues

- Corrosion
- High electrical resistivity – electrochemical measurements difficult
- Current ASTM fuel corrosivity test is useless for pipelines
- Corrosion rates in emulsions negligibly low – phase separation important

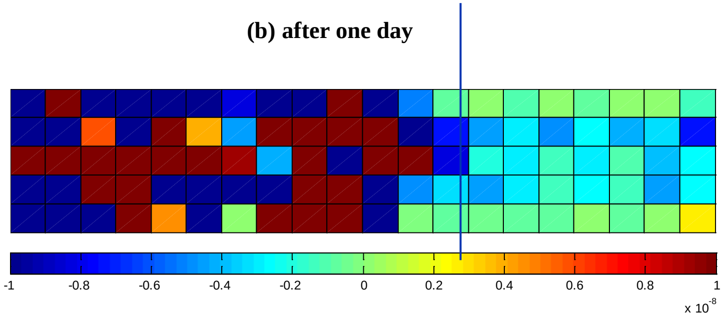
Measuring corrosion in biodiesel/water mixture – Multielectrode Array Technique



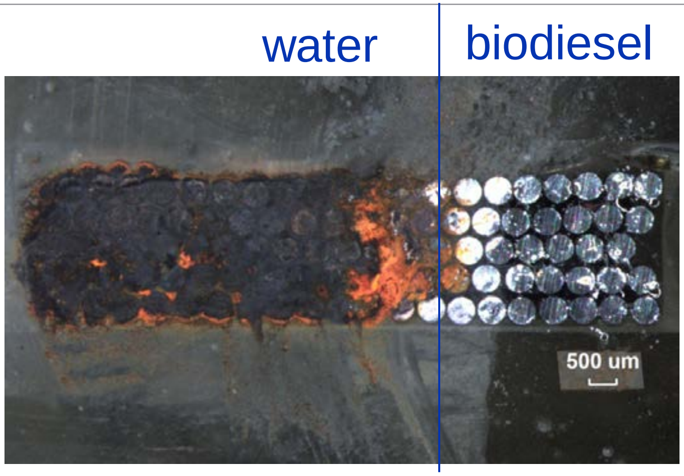
(a) Shortly after immersion;



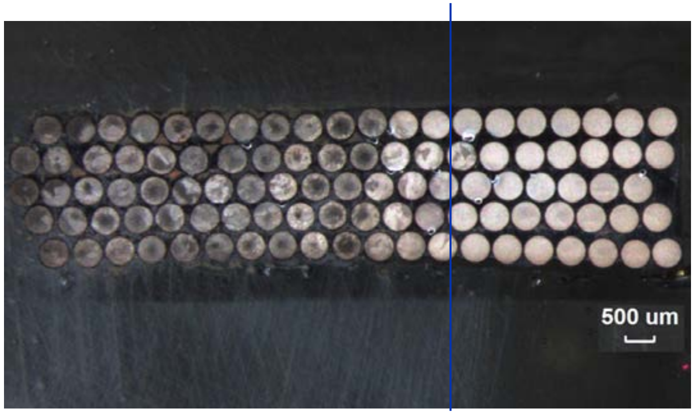
(b) after one day



(c) after two week

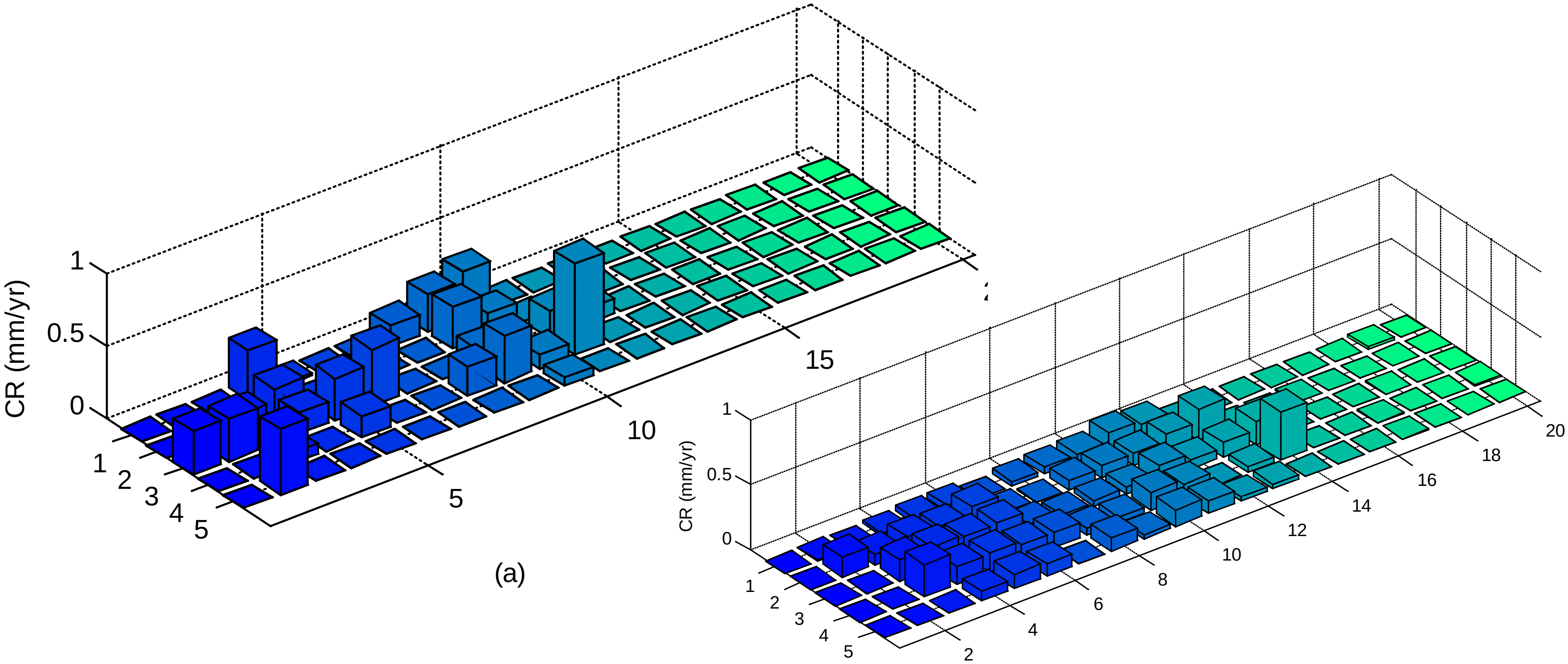


(a) before cleaning



(b) after cleaning

Corrosion rate comparison



(b)

(a): biodiesel/water mixture
(b):ULSD/water mixture

Gaps and challenges for biofuel pipelines

- SCC is still observed in terminals and storage tanks (and possibly pipelines)
- SCC control in ethanol
  - Ammonium hydroxide seems to be the best, but unknown downstream effects
  - SCC monitoring tool
- Corrosion control in biodiesel
  - How does biodiesel influence water corrosivity?
  - Appropriate corrosion test methods
  - Monitoring methods
- Other materials
  - Non-ferrous alloys in ethanol and biodiesel
  - Elastomer behavior in alcohol fuels
- Integrity assessment

CO_2 Pipelines

Status and challenges

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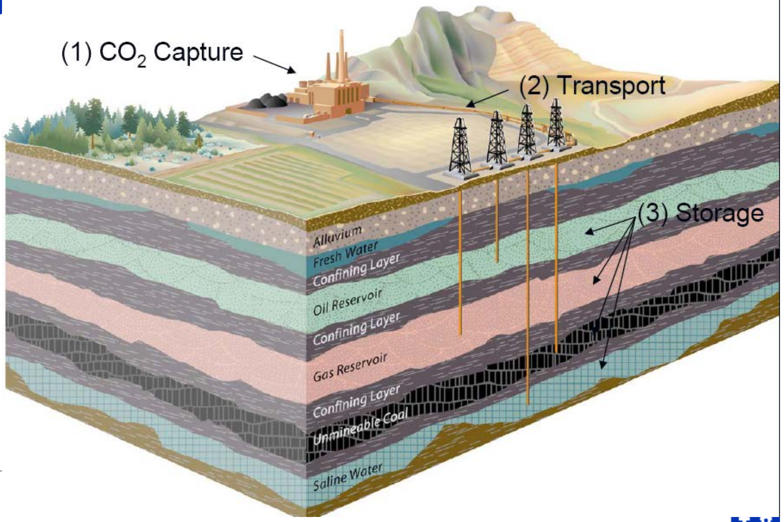
Three Strategies to Reducing CO_2 in Atmosphere

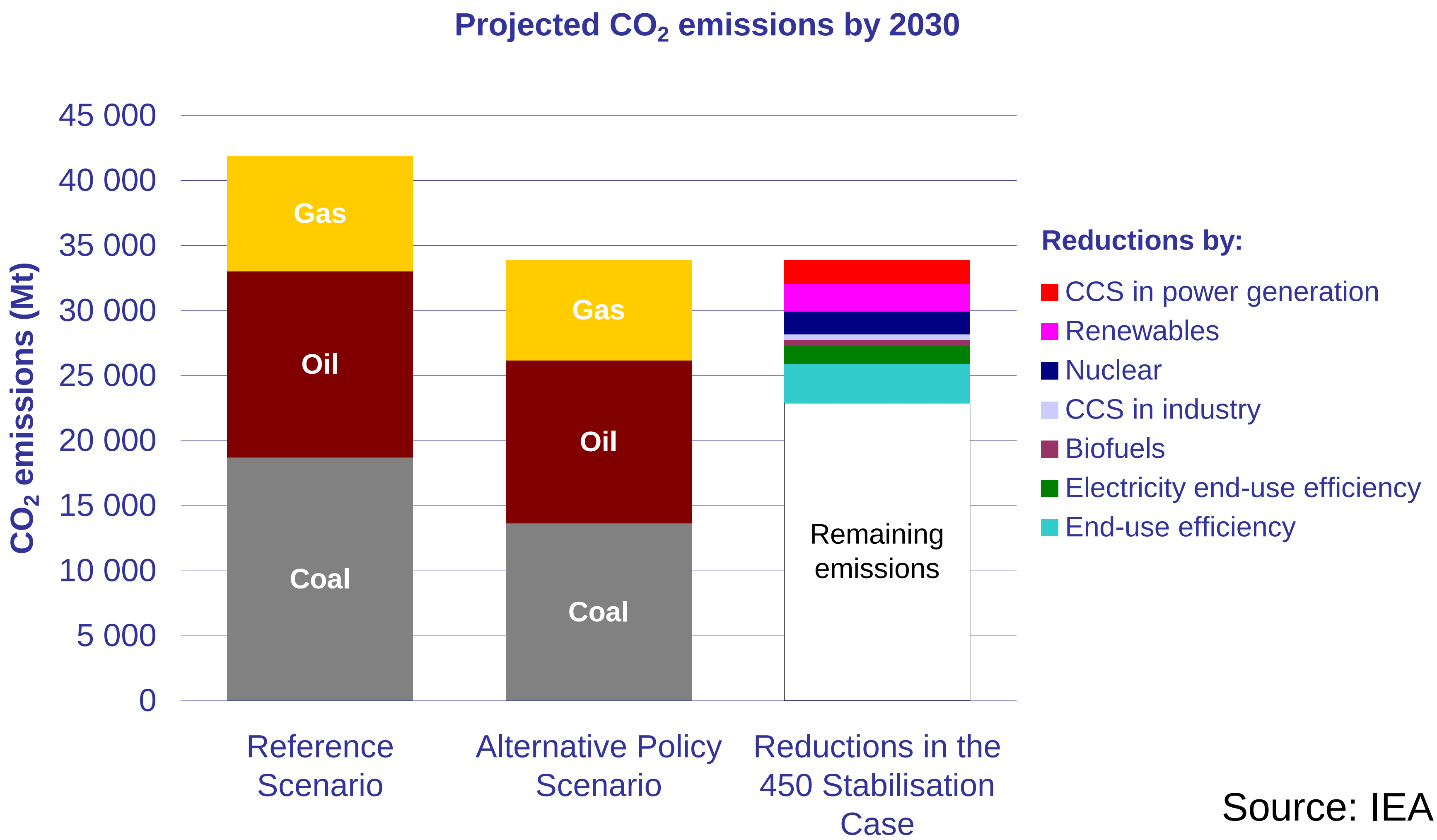
Reduce emissions - Improved efficiency or non-carbon energy sources

Once-through Disposal - CCS



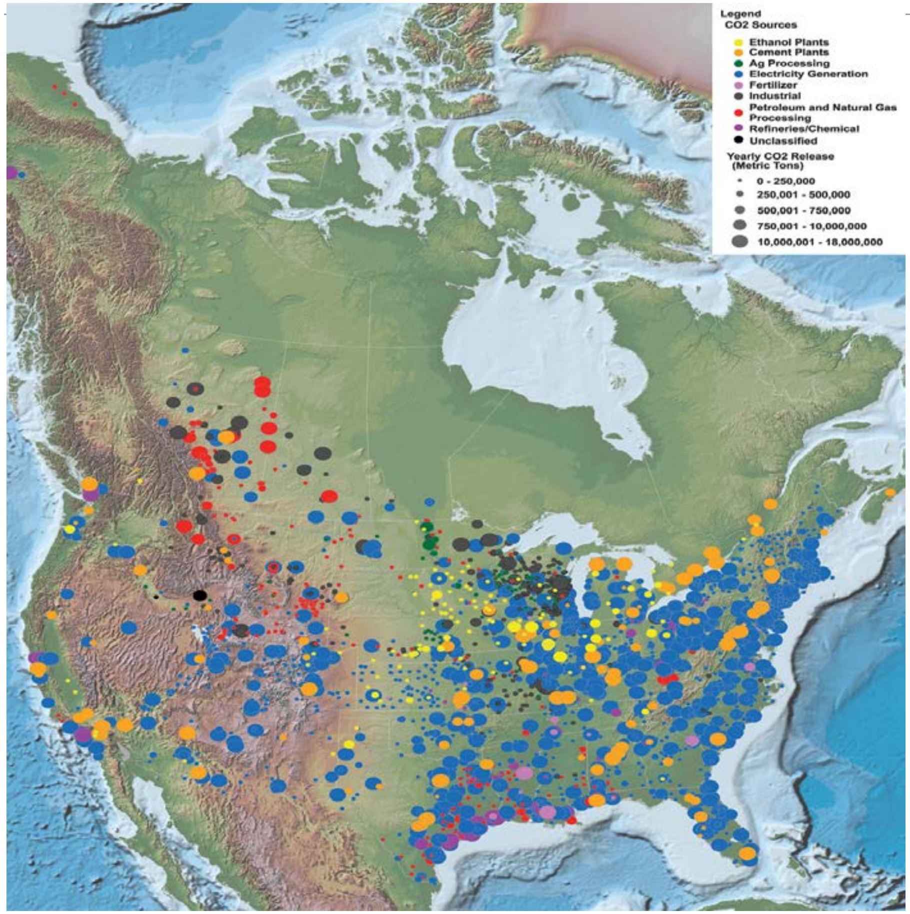
CO2 Recycling into useful products

The future for clean energy markets (IEA)



Source: IEA

Why Transport of Super Critical CO_2 Important?



The CO_2 generation and storage sources are not all in geographical proximity.

Transporting the CO_2 will be a critical challenge in the CCS world.

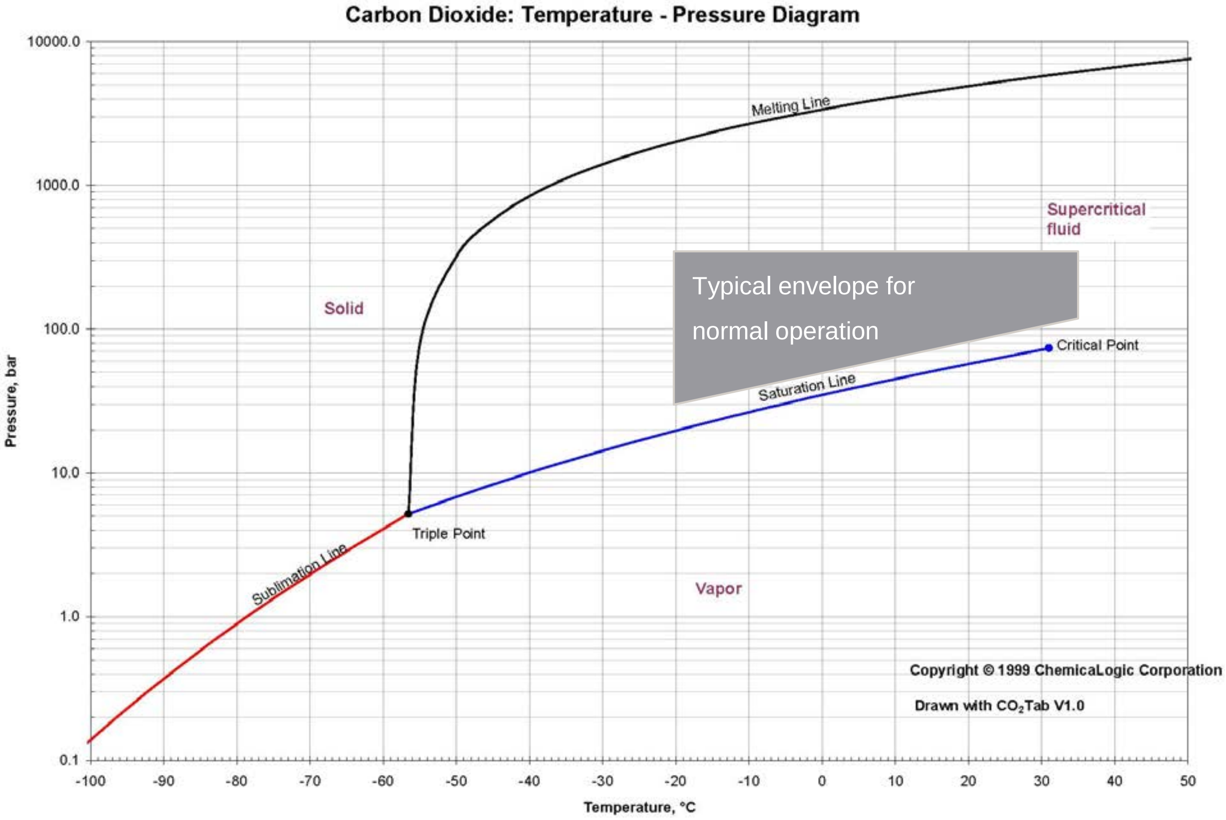
ISK

Major safety issues in CO_2 pipeline transportation

- Running ductile fracture
- Release and depressurization effects on pipeline
- Corrosion (gas quality specification, co-mingling effects)
- Seals/gaskets (rapid depressurization, swelling, plasticizing)
- Liners
- Non-ferrous metals (valves, pumps, measuring devices, etc.)

§2 Specific properties of CO2 - Physical properties

Property	Unit	Value
Molecular Weight	g/mol	44.01
Critical Pressure	bara	73.8
Critical Temperature	ºC	31.1
Triple point pressure	bara	5.18
Triple point temperature	ºC	-56.6
Aqueous solubility at 25˚C, 1 bar	g/L	1.45
Standard (gas) density	kg/m^3	1.98
Density at critical point	kg/m^3	467
Liquid density at 0˚C, 70bar	kg/m^3	995
Sublimation temp, 1bara	ºC	-79
Solid density at freezing point	kg/m^3	1562
Colour	-	None



Impurities in Supercritical CO_2

- Aggressive species :

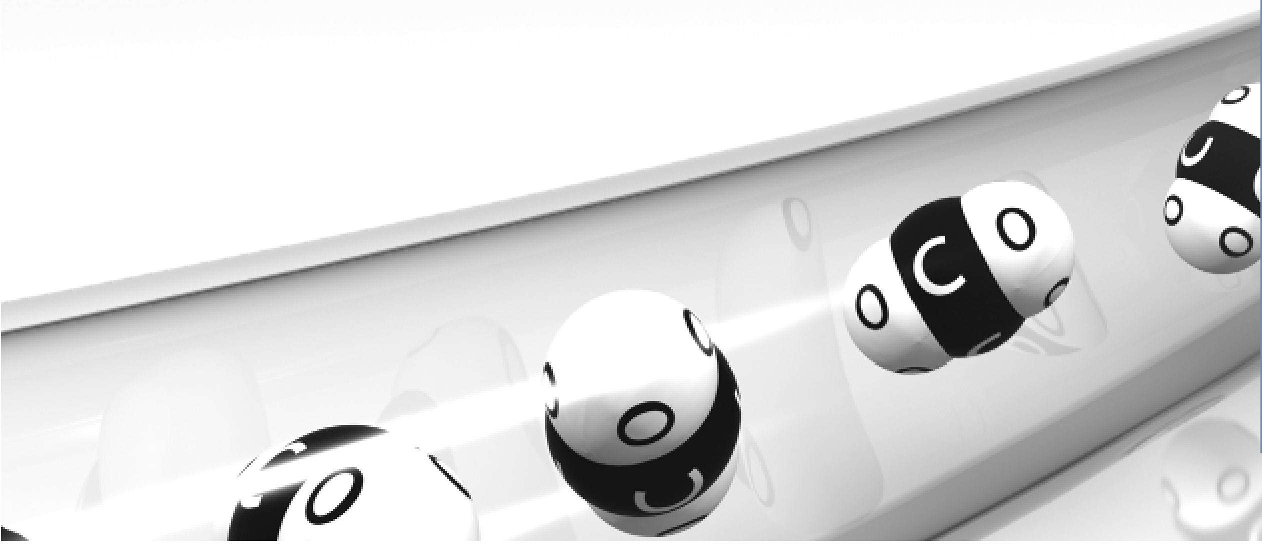
  - -Water
  - -O_2
  - -SO_2
  - -NO_2
  - -H_2S
  - -HCl

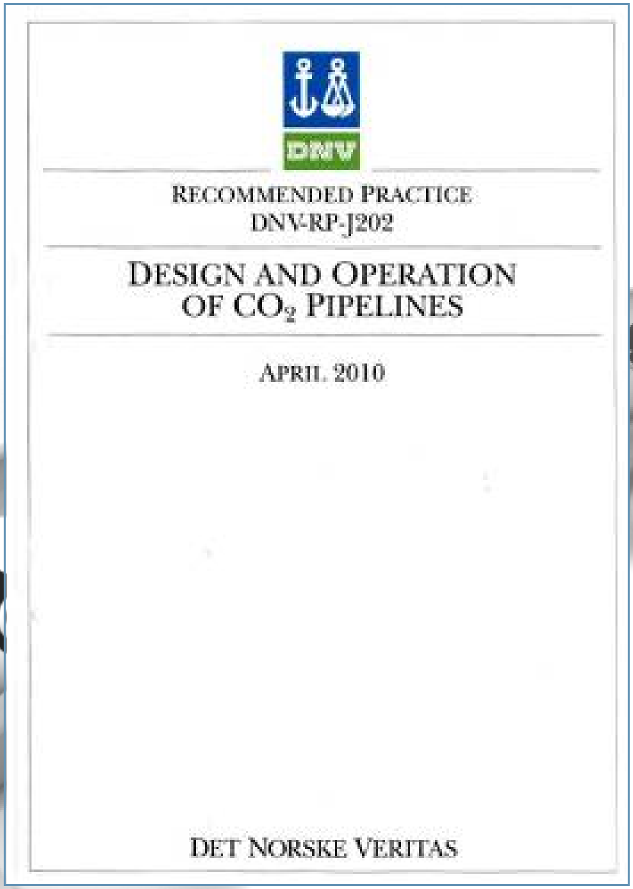
- Inhibitive species:

  - -Amine
  - -NaOH
  - -Other organics

Overall objective of DNV JIP - CO2PIPETRANS

- To provide guidance on *safe, reliable and cost efficient design, construction and operation* of CO_2 pipelines
- Two phased approach:
  - Phase 1: Gather existing knowledge into a guidance document
  - Phase 2: Close the found knowledge gaps to a adequate confidence level





DNV

RECOMMENDED PRACTICE
DNV-RP-J202

DESIGN AND OPERATION OF CO_2 PIPELINES

APRIL 2010

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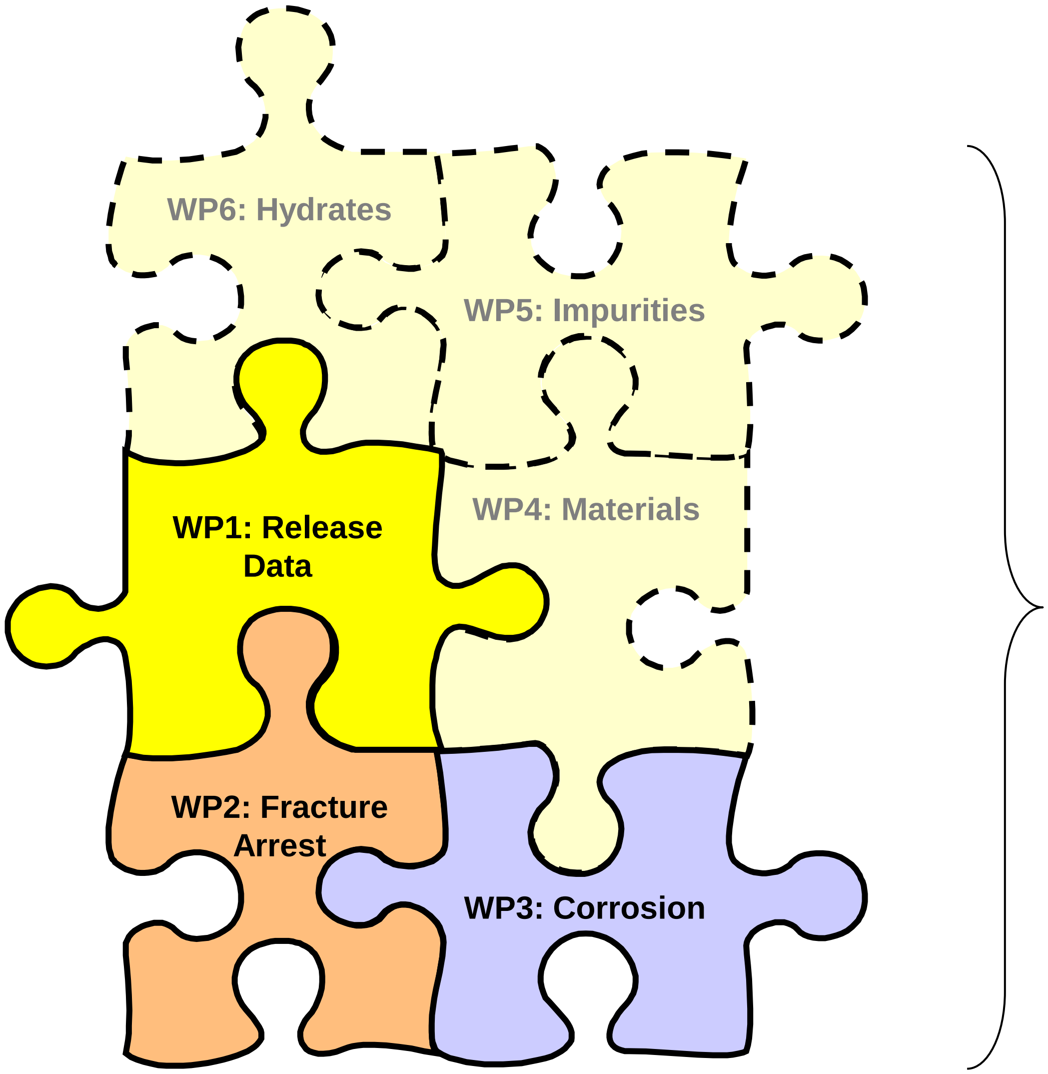
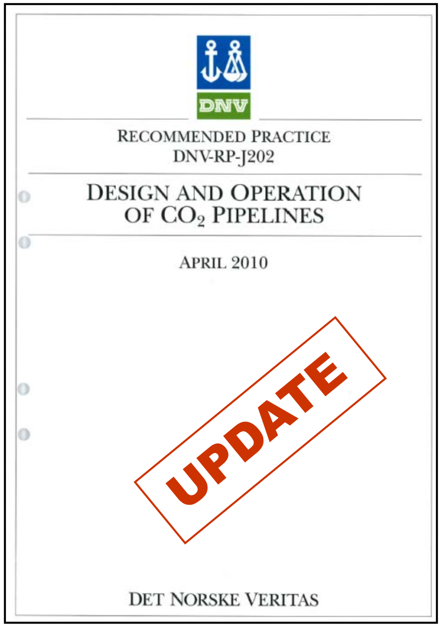
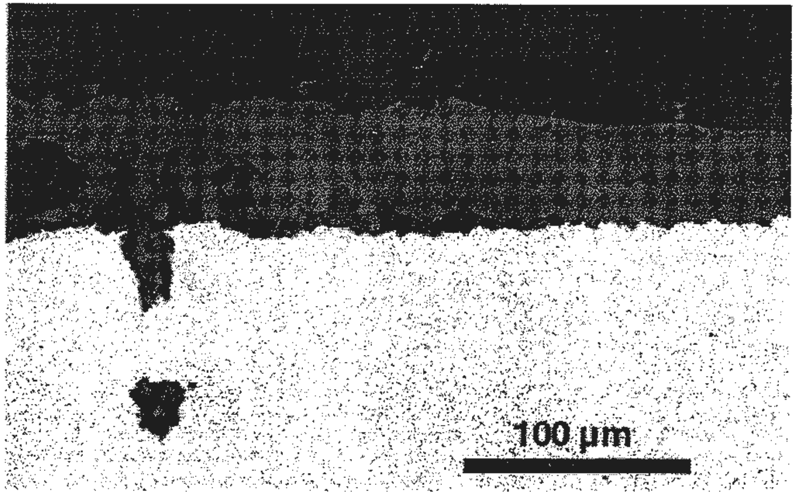
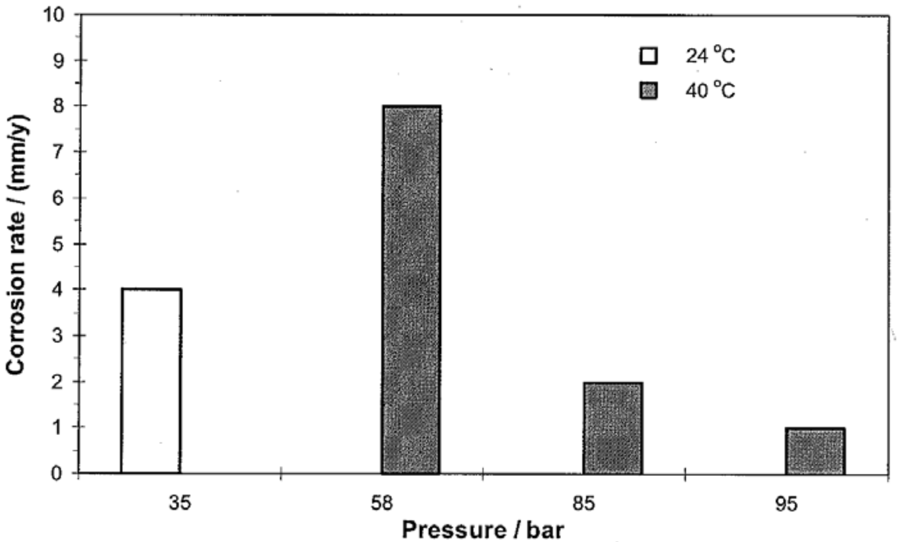
CO2PIPETRANS Phase 2





Current Knowledge of CO_2 Corrosion





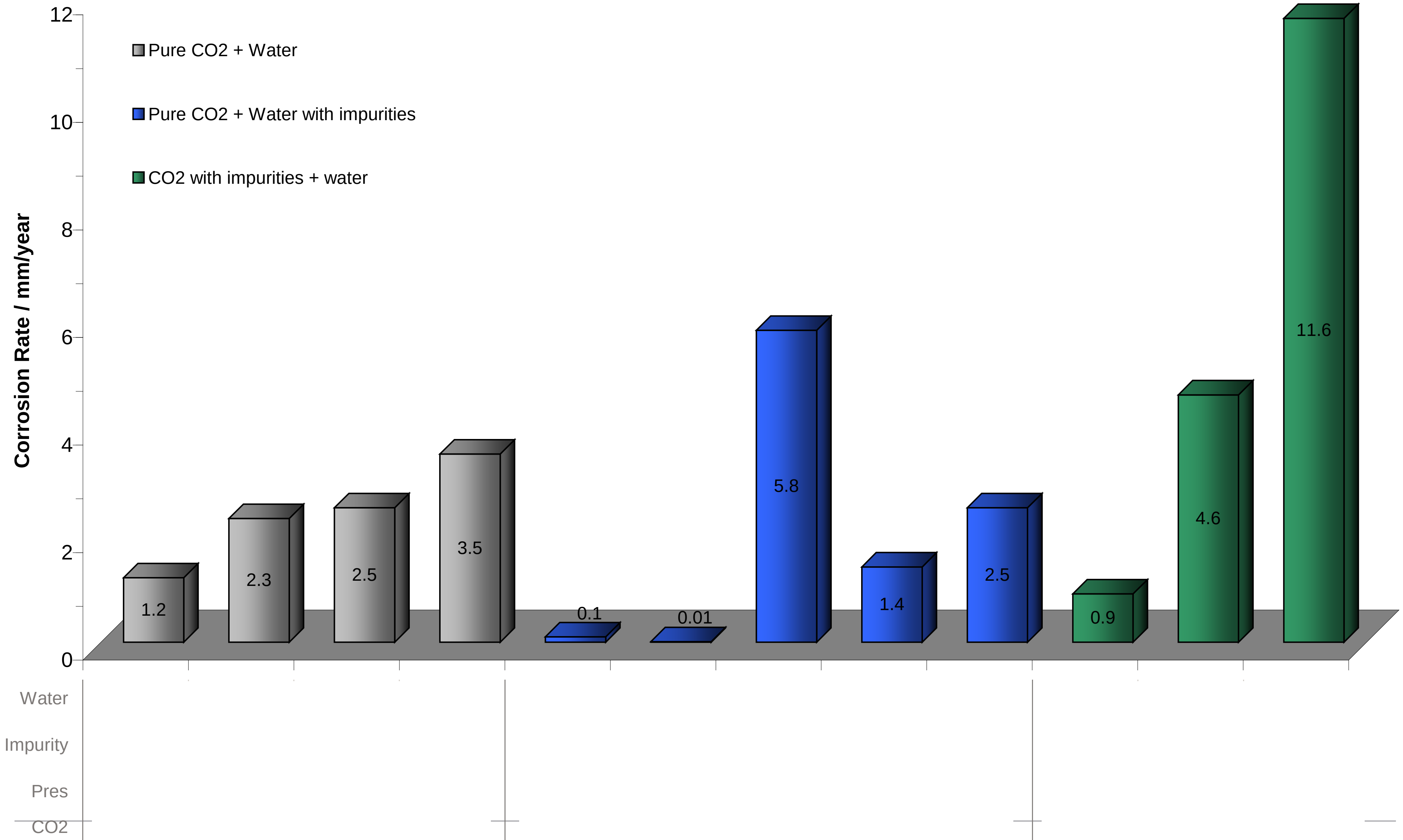
40°C, pCO_2 = 40 bar, 170h

Srdjan Nesic et. al.

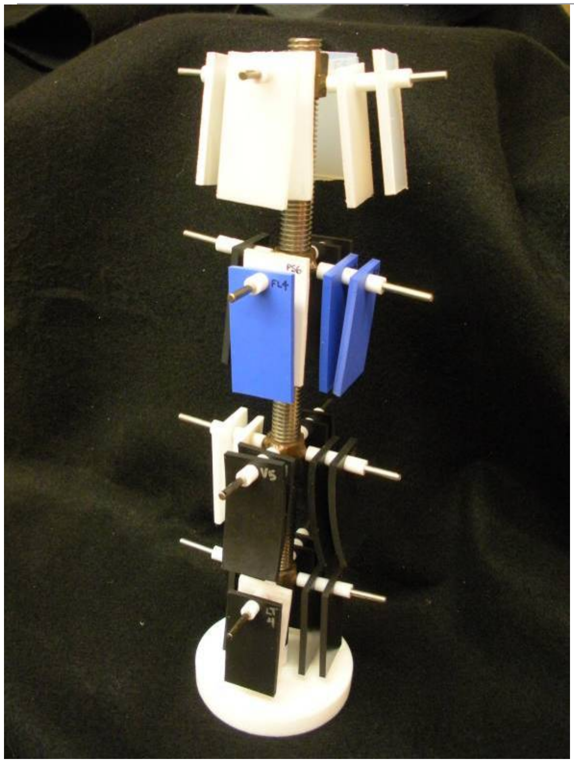
- Limited data and understanding of pCO_2 higher than 20 bar.
- Corrosion rate of CS decreases with increasing partial pressure of CO_2, at moderate pressures it may be due to formation of $FeCO_3$ films.

Limited understanding and data at high partial pressures of CO_2.

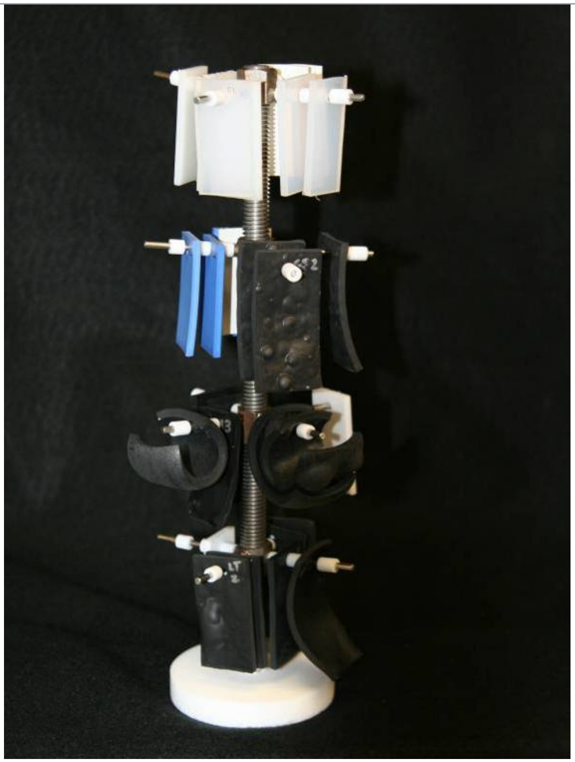
Summary of Electrochemical Data



Effect of supercritical CO_2 on polymers

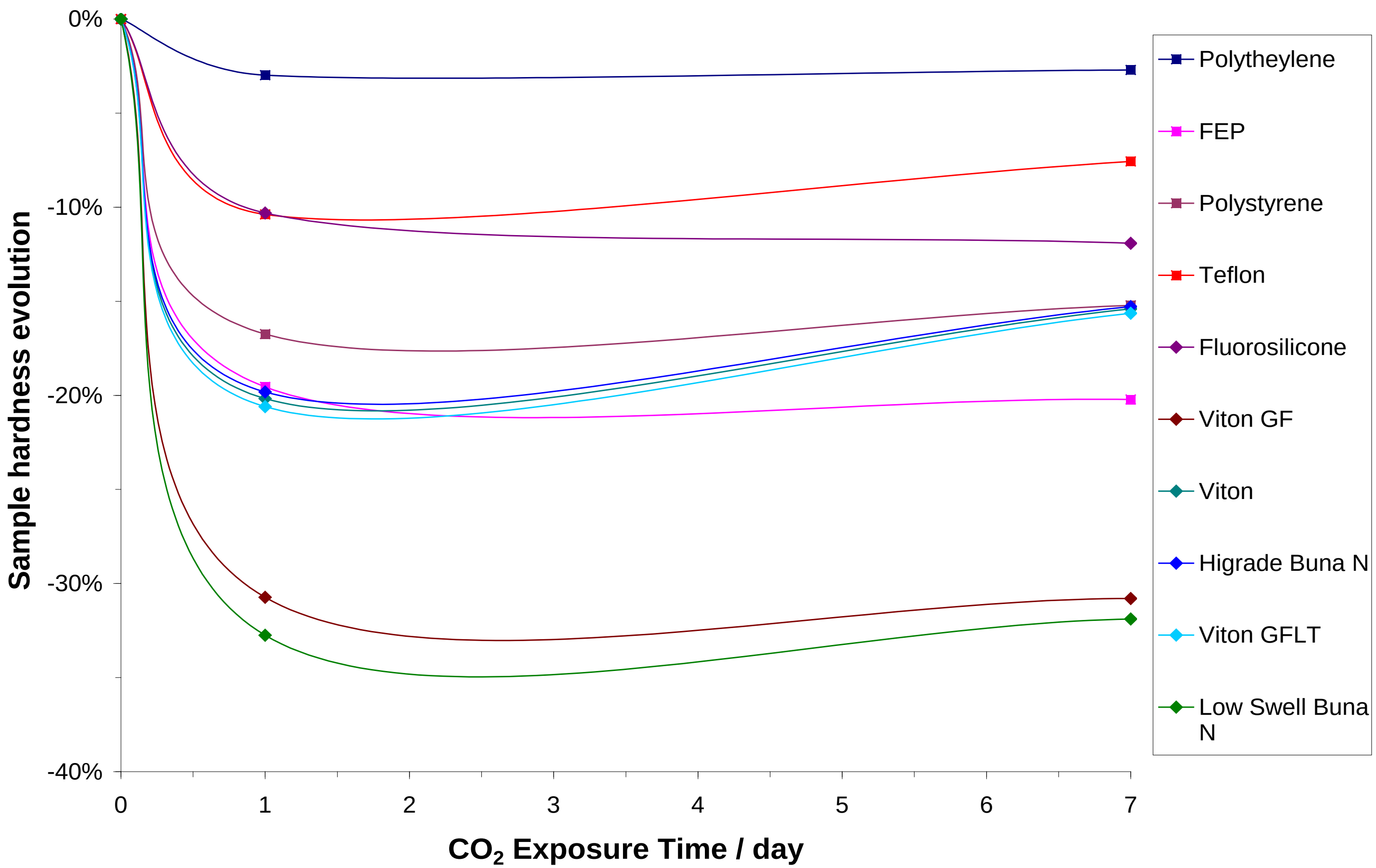


Before



After exposure
1d, 1200 psi, 25 C

Effect of supercritical CO2 on polymers



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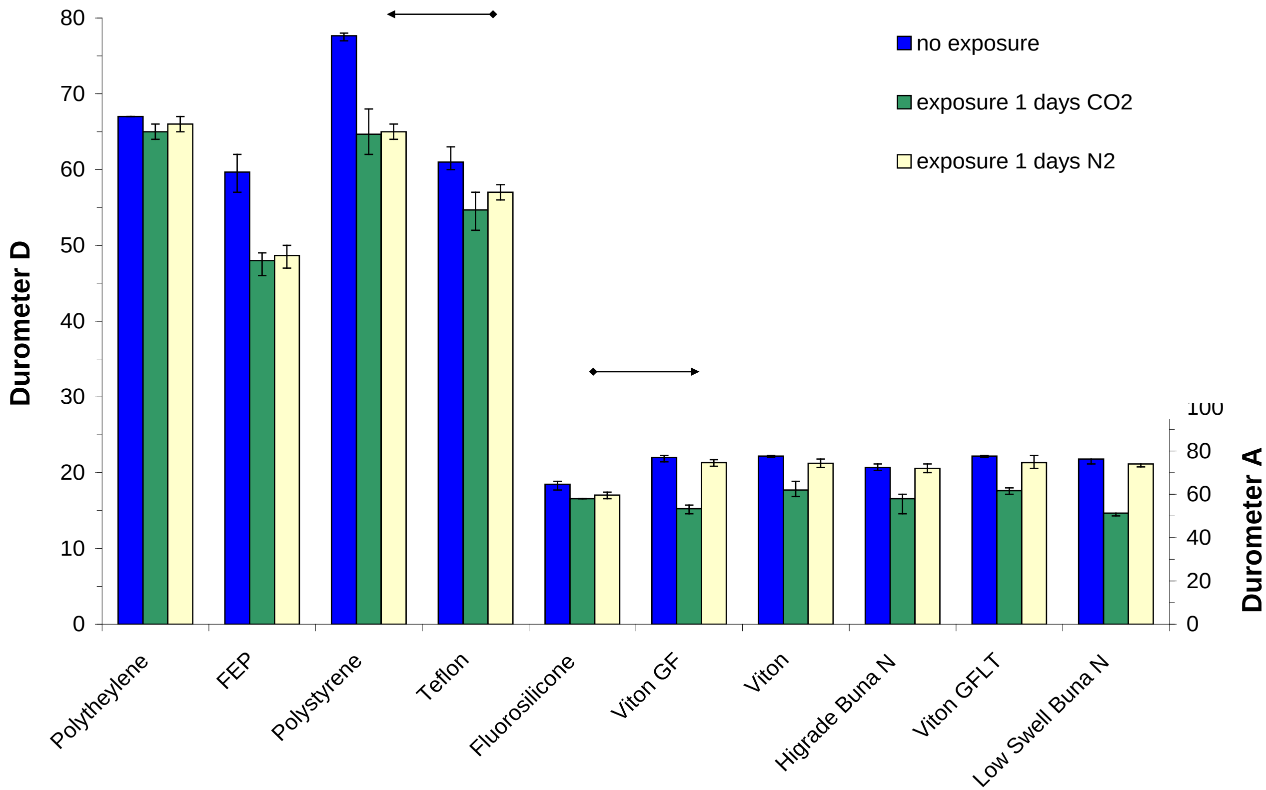

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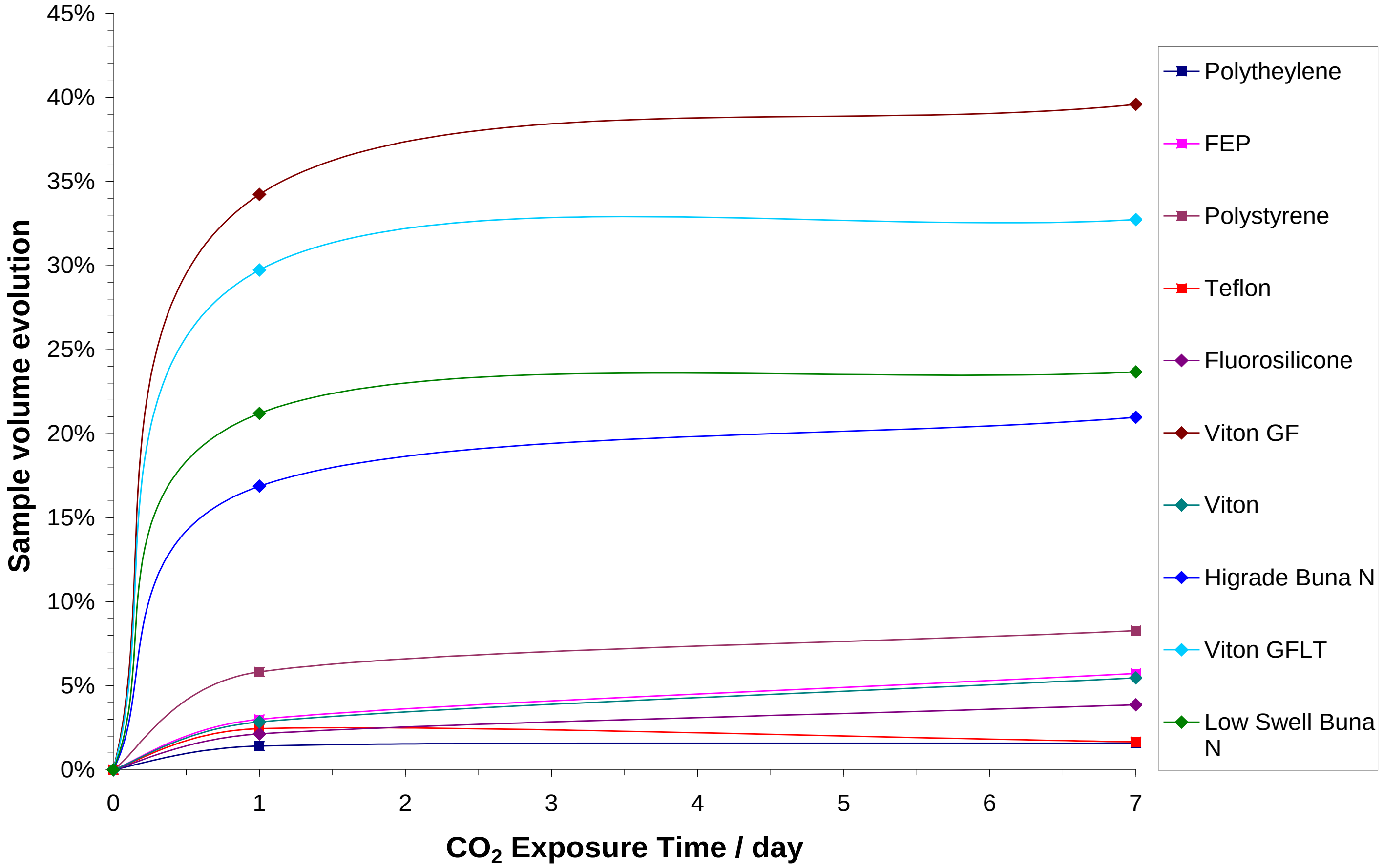

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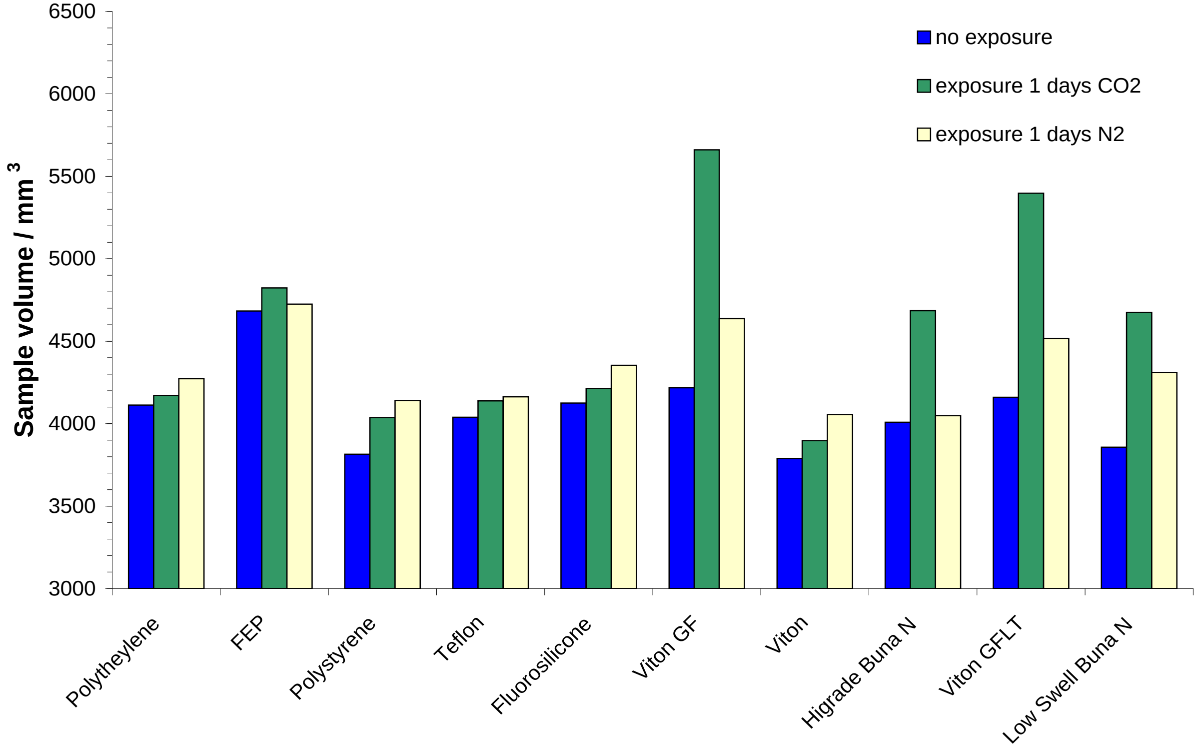
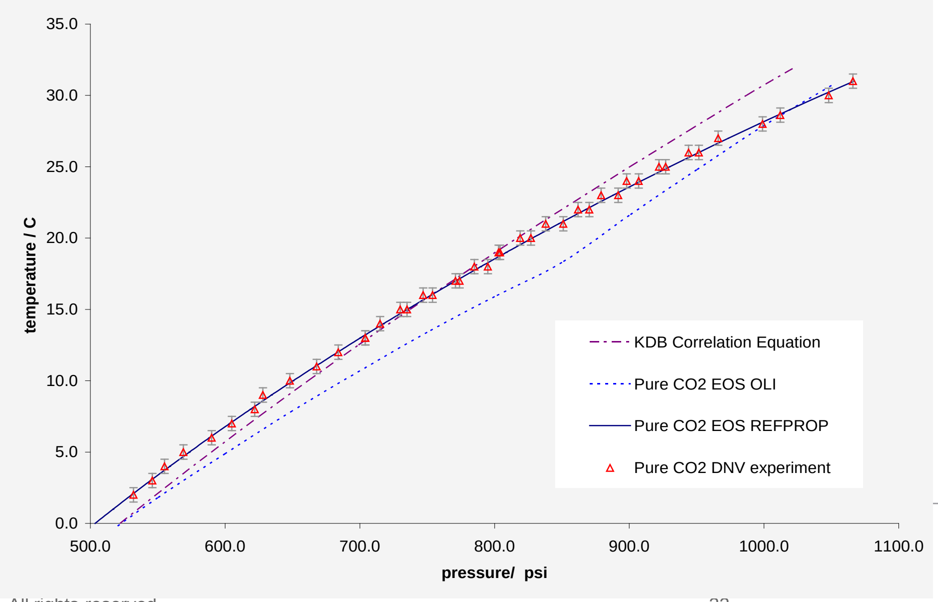
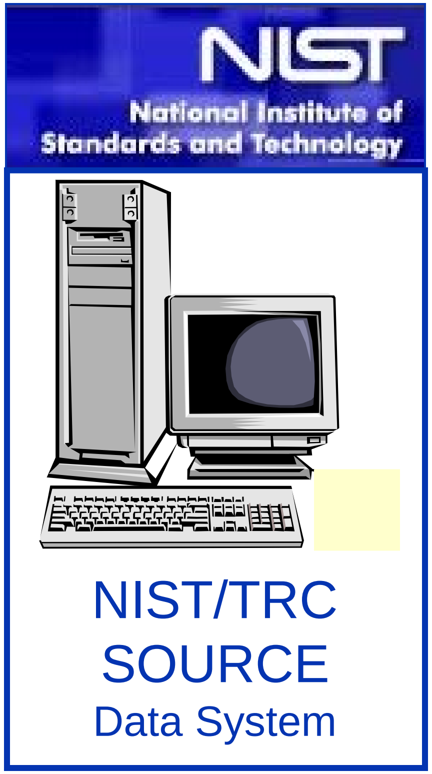


CO_2 Equations of State

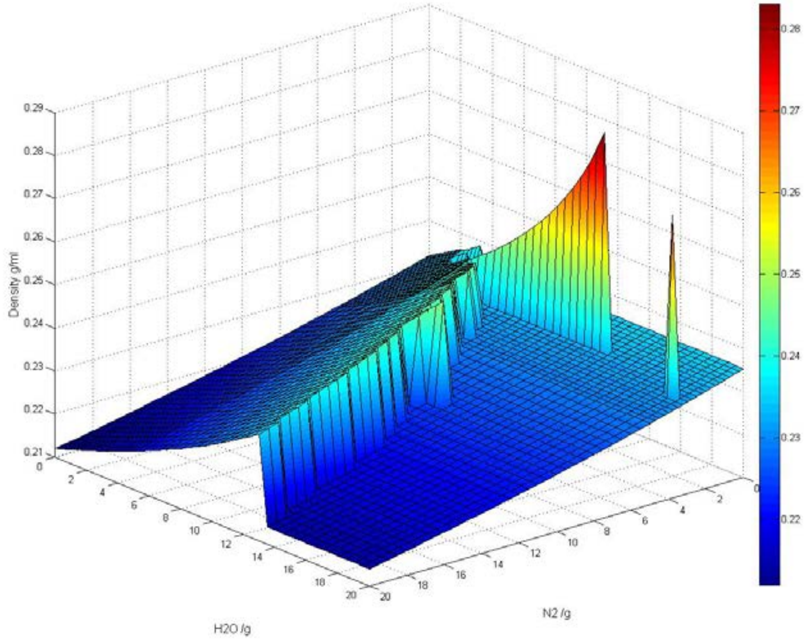
- Many models available, but none of them perfect
- NIST data and modeling source
- Gaps remain:
  - Impurity effects still sometimes pose concerns
  - Water, NOx
  - Models seem to fail more often in complex systems (e.g., 3 component CO_2 + water + N_2)
  - Models have discontinuities and some errors

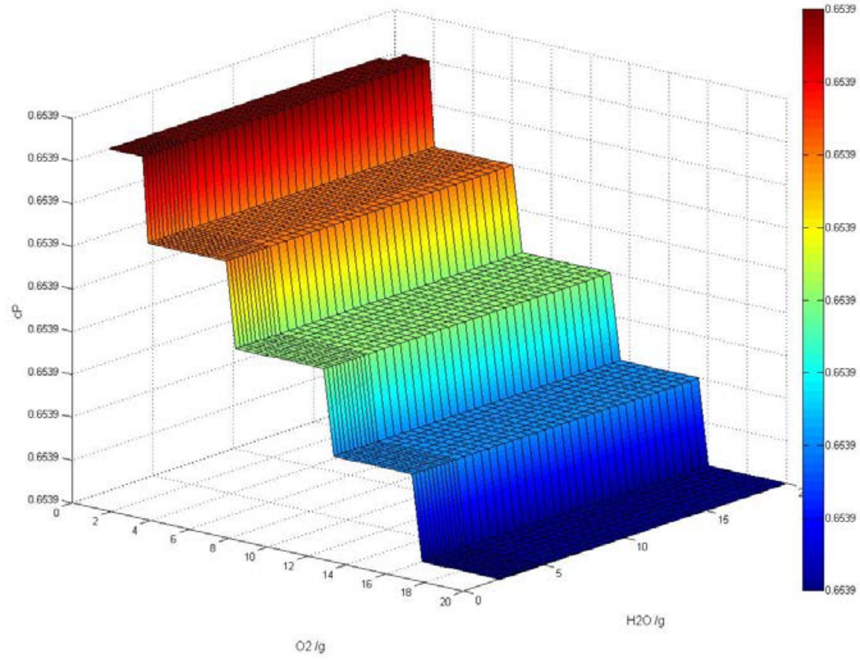




Where don’t they work so well?

Other problems: discontinuity in calculations





Gaps and challenges for CO_2 pipelines

- Equations of state and phase behavior calculations need significant improvement
  - Effect of impurities
- Internal corrosion direct assessment (ICDA) for CO_2 pipelines
  - Understand phase and flow behavior (e.g., water dropout locations)
  - Gas quality specification
  - Model corrosion
  - Manage corrosion (inhibition, dehydration, etc.)
- Gaskets and seals
  - Long-term elastomer performance in CO_2 with impurities
  - Rapid decompression effects
- Fracture behavior
  - Reasonably well understood
  - Improved understanding of phase behavior will enable better design
- Facilities and equipment
  - Non-ferrous materials
  - Dynamic seal performance

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