Membrane and Solvent Development for Pre-Combustion Carbon Capture

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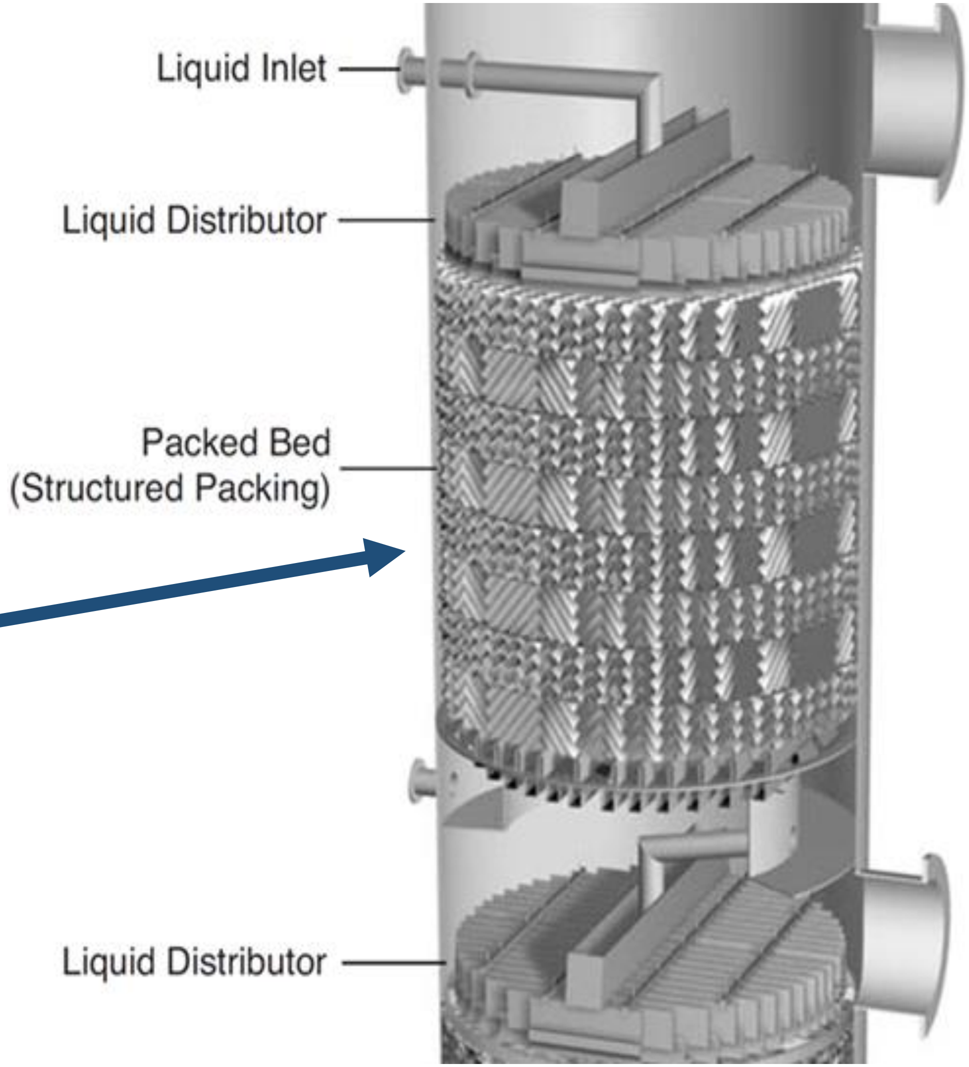
Applications for Physical Solvents for Gas Separation

Tailored markets: **Blue Hydrogen**

- Pre-combustion CO_2 Capture at IGCC-CCS
- Generation of H_2 from SMR-CCS

Polygeneration of fuels, fertilizers, & chemicals



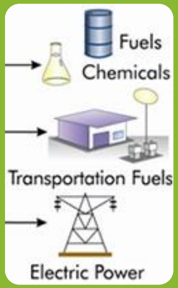
Background and Prior Gap Analysis

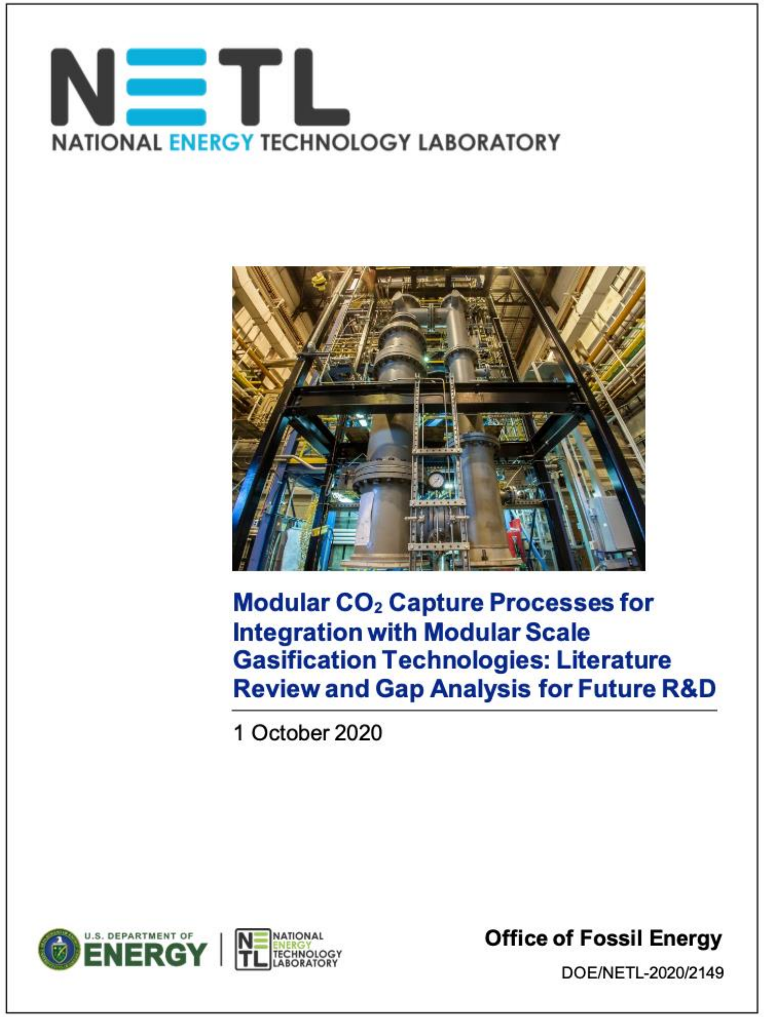
Modular design

Diverse feedstocks

Location

Polygeneration





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Modular CO_2 Capture Processes for Integration with Modular Scale Gasification Technologies: Literature Review and Gap Analysis for Future R&D

1 October 2020

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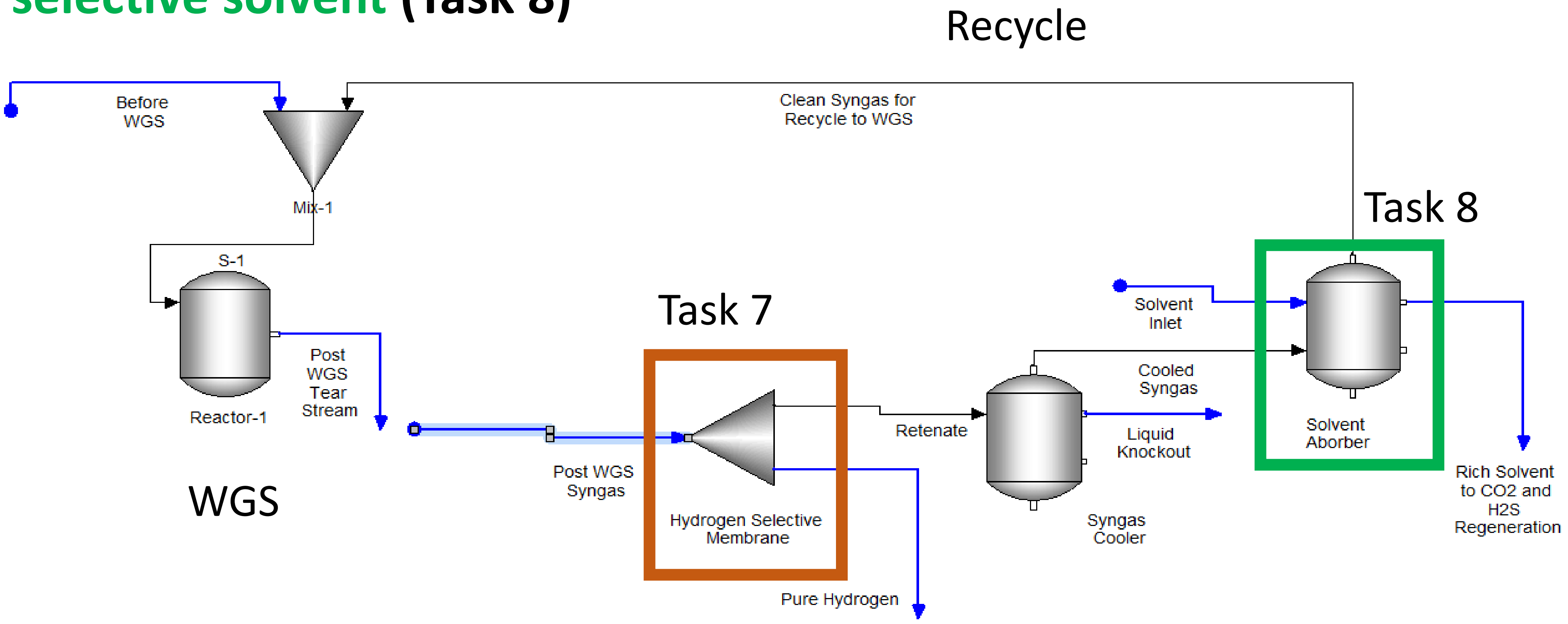
Office of Fossil Energy

DOE/NETL-2020/2149

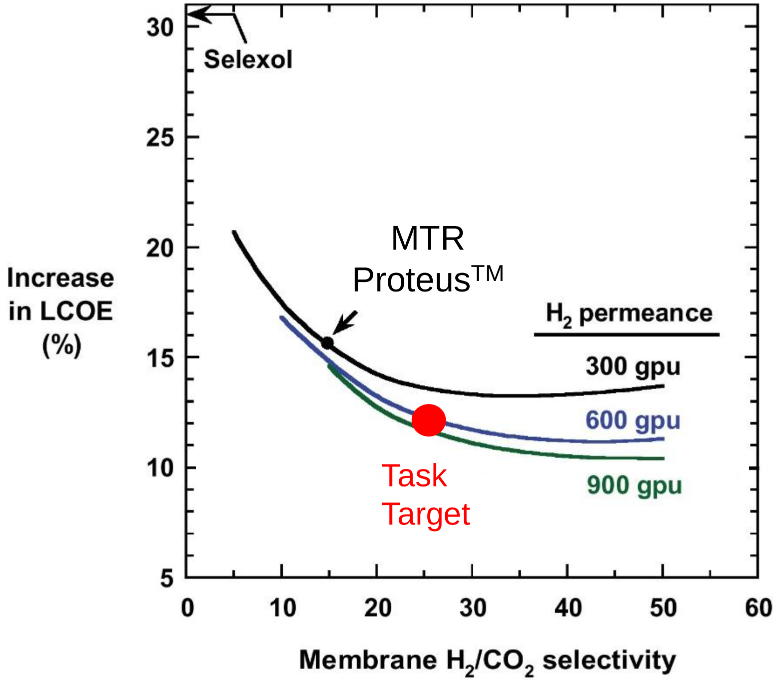
Report available from NETL website: Link

Hybrid Precombustion Capture for Flexible Operations

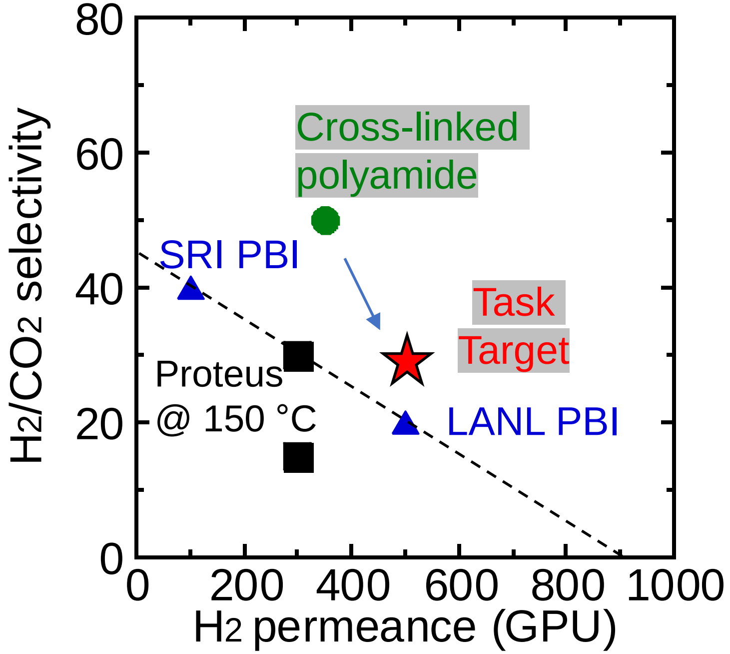
- **Upstream H_2 selective membrane (Task 7)**
- **CO_2 selective solvent (Task 8)**



Comparison with Existing membrane technologies



J. Membr. Sci., 2012, 389, 441
TEA for IGCC-CCS process



1. *J. Mater. Chem. A*, 2018, 6, 30
2. SRI PBI: https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Jayaweera_0.pdf
3. LANL PBI: US patent 2016/0375410 A1
4. Proteus: https://www.netl.doe.gov/sites/default/files/2018-12/DOE-FE0031632-Project-Kickoff.pdf

Cross-linked polyamide shows promising results for H_2/CO_2 separation, but its permeance (~350 GPU) needs to be higher.

Task 7 H_2-selective Membrane Development

Milestones:

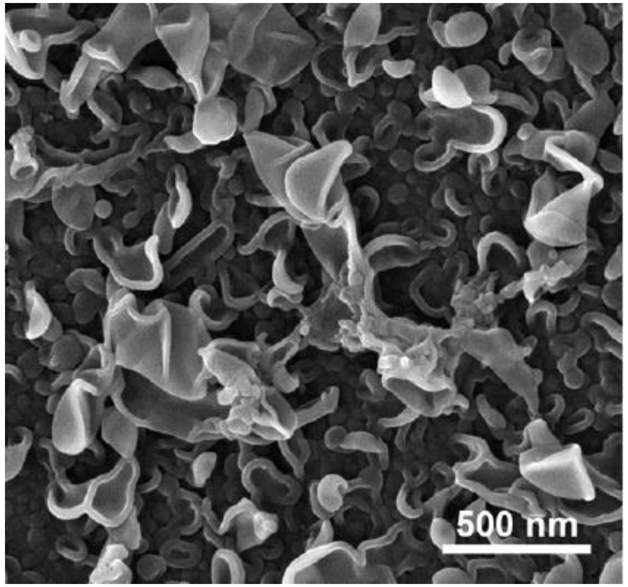
EY22: Demonstrate a laboratory-scale coupon polyamide composite membrane with mixed-gas H_2 permeance of ≥ 500 GPU and H_2/CO_2 selectivity of ≥ 25 at 100–250°C, showing no obvious aging for 50 hours.

EY23: Complete the fabrication and assembly of a small flat-sheet membrane module, and demonstrate the membrane module with H_2 permeance of 500 GPU and H_2/CO_2 selectivity of 25 in a laboratory screening test using a simulated-shifted syngas at 100–250°C.

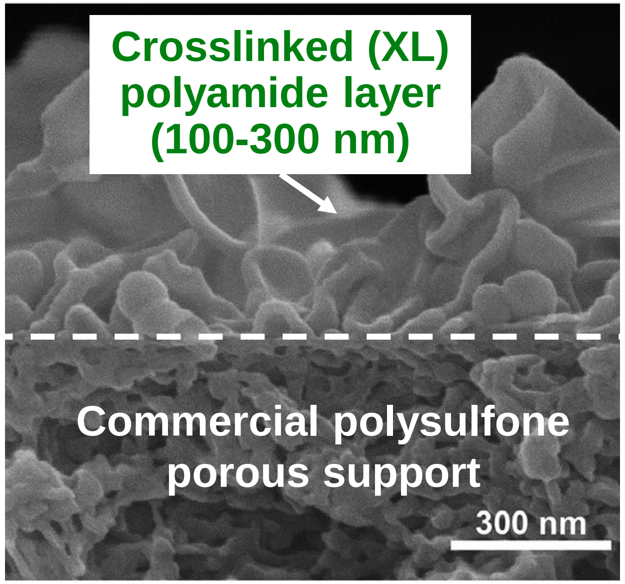
EY24: Completion of AspenPlus models with economic screening using experimentally determined data collected at UNDEERC and/or UK-CAER. AspenPlus models with economic screening will be done for each membrane/solvent system tested.

Approaches to higher-permeance polyamide membranes

Surface



Cross-section



J. Mater. Chem. A, 2018, 6, 30

Common commercial porous support materials	Glass transition temp.(°C)*
Polyacrylonitrile (PAN)	82 to 145
Polyethersulfone (PES)	225
Polysulfone (PSF)	179 to 194
Polyvinylidene fluoride (PVDF)	-67 to 5

* www. polymerdatabase.com, accessed on 08/2022

NETL Selected Support Material	Glass transition temp.(°C)*
Polymer X	**> 400**

- **Higher operating temperature** using **more thermally stable porous support** (commercial porous supports can hardly operate at or above 200 °C)
- **Thinner separation layer** via smoothening out the wrinkled polyamide layer

Thermally stable porous support development

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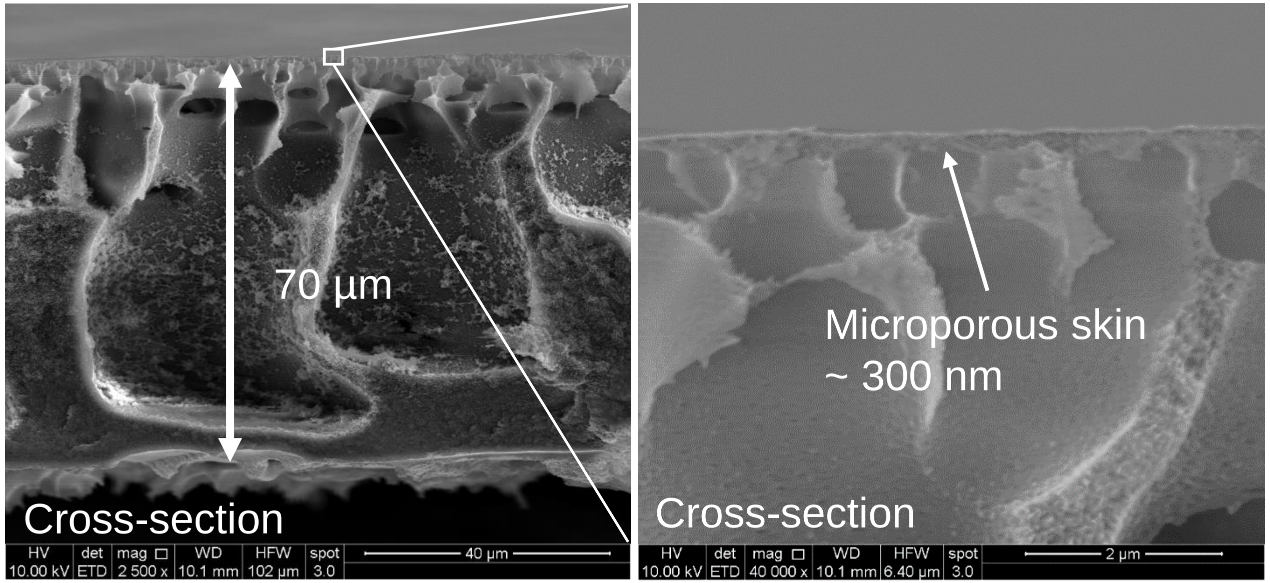

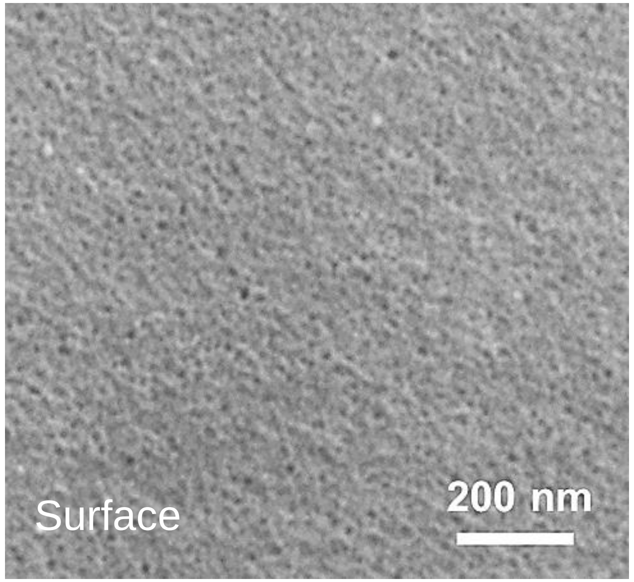

H_2 permeance: 160,000 GPU* (*vs.* ~500 GPU for polyamide membranes)
CO_2 permeance: 44,000 GPU
H_2/CO_2: 3.7
Pressure difference rating: ≥ 13.6 bar

After thermal exposure at 200 °C for 24 h
H_2 permeance increased by 5 – 10%*
No changes on H_2/CO_2 selectivity (3.7) and surface morphology

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* Permeation testing at 23 °C

Thinner and smoother polyamide layer development

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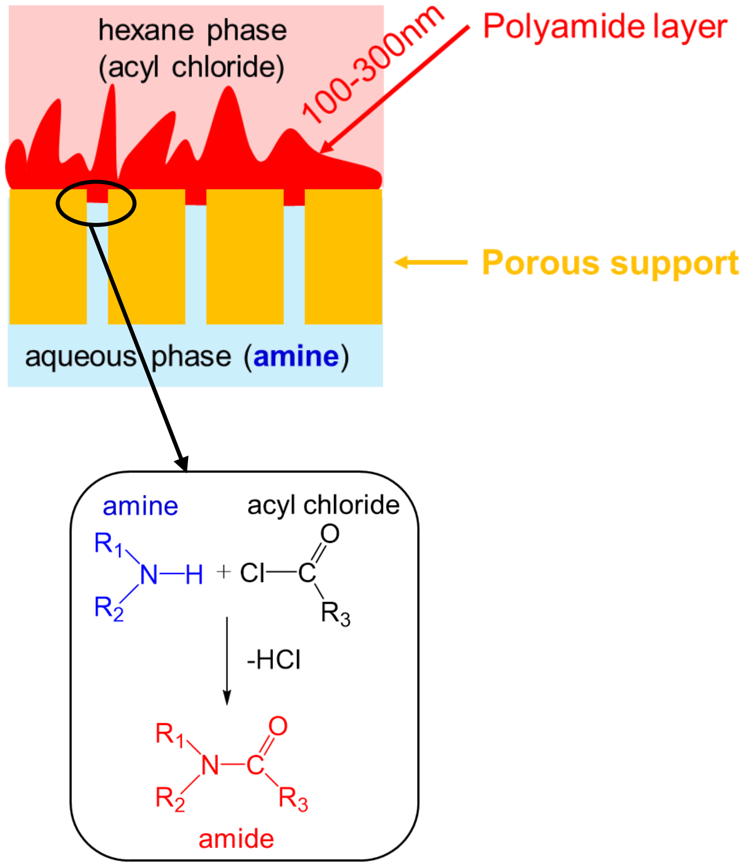
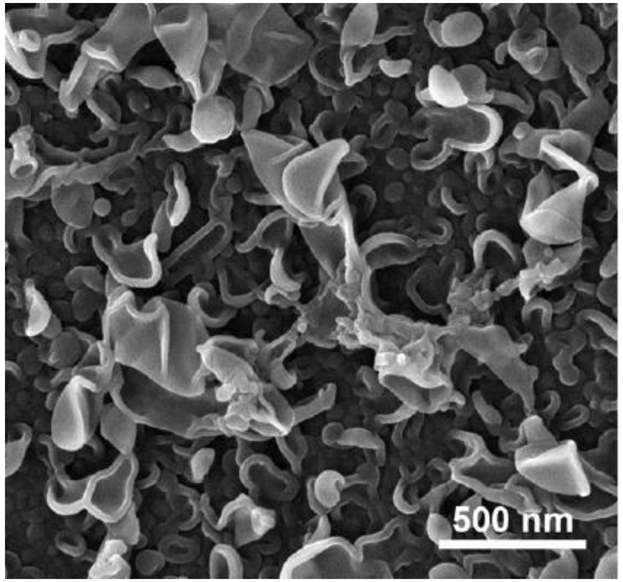
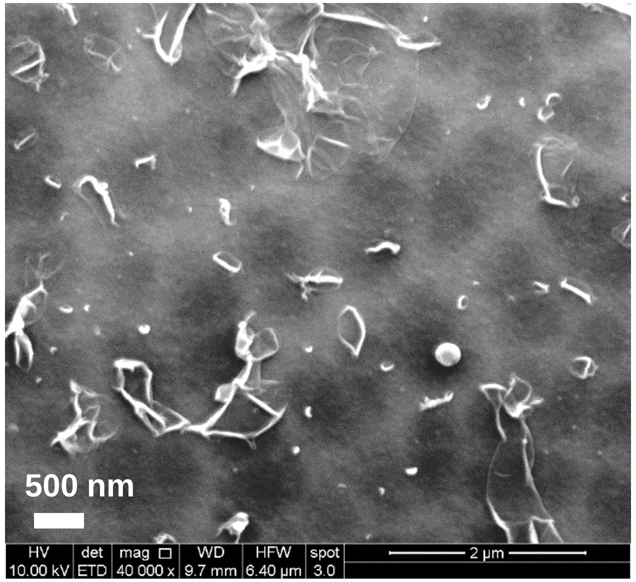
Traditional interfacial polymerization (IP) method

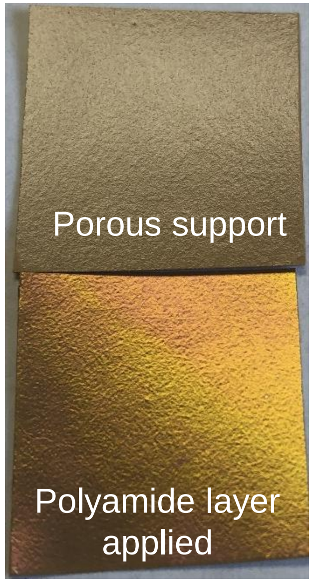




Ref. *J. Mater. Chem. A*, 2018, 6, 30

Rough and wrinkled surface with a polyamide layer thickness of <u>100 – 300 nm</u>

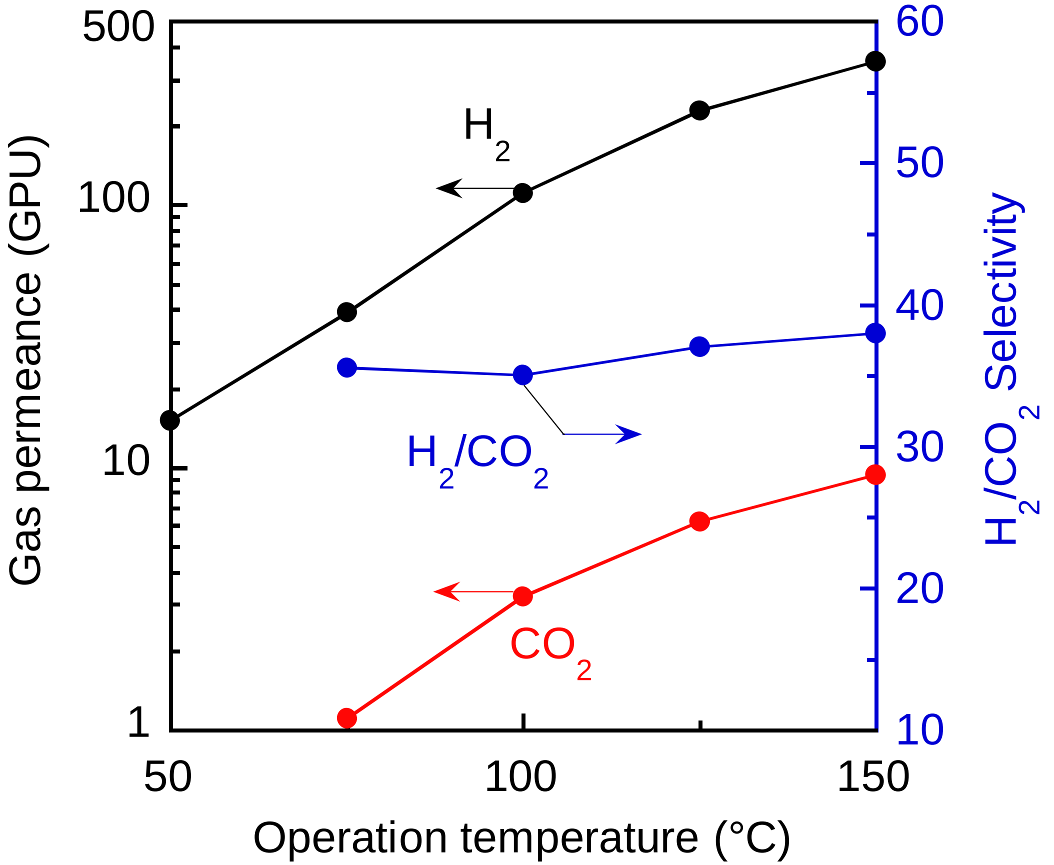




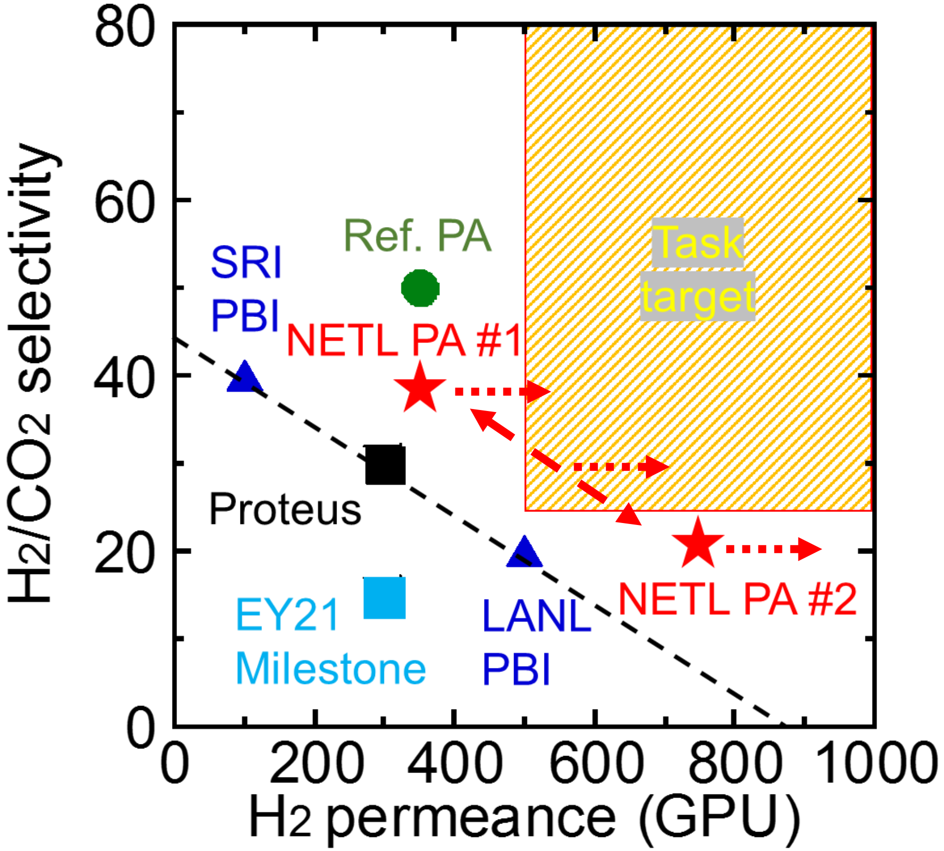
This study

A <u>*modified method*</u> produces smoother surface with a polyamide layer thickness of <u><30 nm</u>

Membrane H_2/CO_2 separation performance



Selective layer: a 26-nm cross-linked polyamide
Test condition: pure & dry gas



PA#1 avg = 26 nm

PA#2 avg= 15 nm

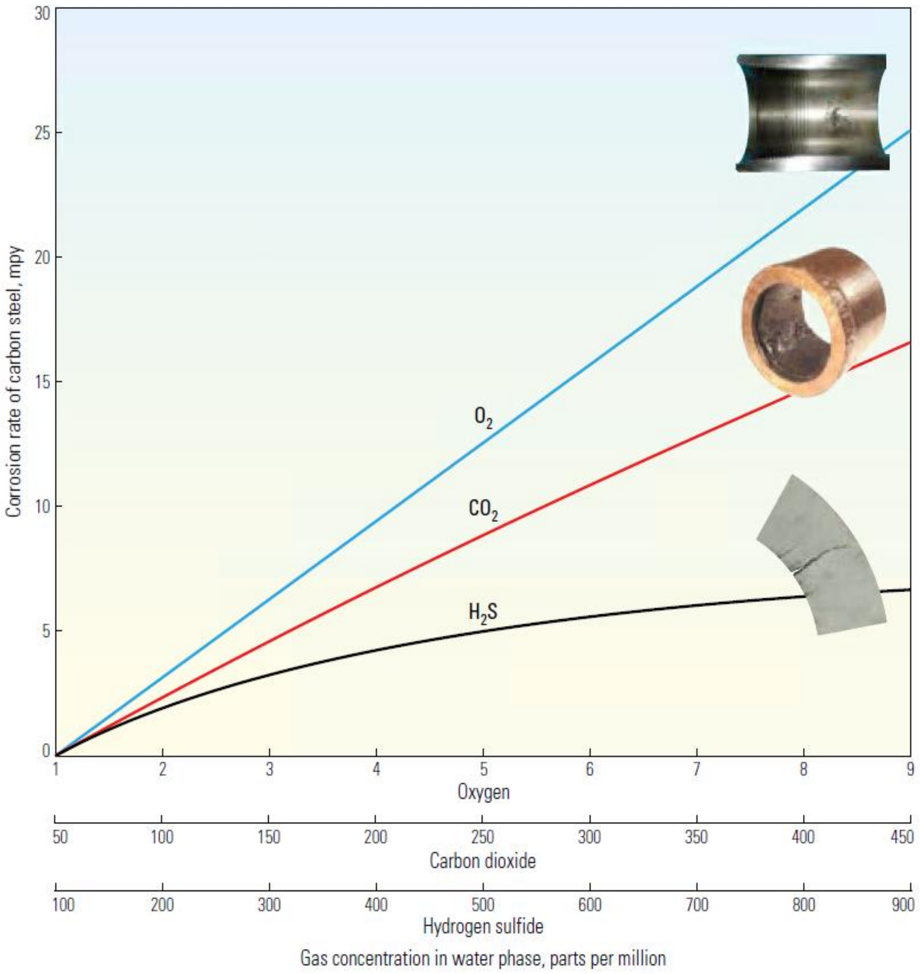
NETL PA: cross-linked polyamide composite membranes tested at 150 °C

Project Status and Future Work

Schedule	Milestones	Status
EY21 (Task 14 of Transformational Carbon Capture FWP)	Demonstrate a laboratory-scale coupon polyamide composite membrane with H_2 permeance of 300 GPU and H_2/CO_2 selectivity 15 at 100-250°C.	Completed
EY22 (04/22 – 03/23)	Demonstrate a laboratory-scale coupon polyamide composite membrane with mixed-gas H_2 permeance of ≥ 500 GPU and H_2/CO_2 selectivity of ≥ 25 at 100–250°C, showing no obvious aging for 50 hours.	**On-track:** membrane fabrication optimization & mixed-gas permeation system modification
EY23 (04/23 – 03/24)	Complete the fabrication and assembly of a small flat-sheet membrane module, and demonstrate the membrane module with H_2 permeance of 500 GPU and H_2/CO_2 selectivity of 25 in a laboratory screening test using a simulated-shifted syngas at 100–250°C.	
EY24 (04/24 – 03/25)	Completion of AspenPlus models with economic screening using experimentally determined data collected at UNDEERC and/or UK-CAER. AspenPlus models with economic screening will be done for each membrane/solvent system tested.	

Task 8: Corrosion Research Objective

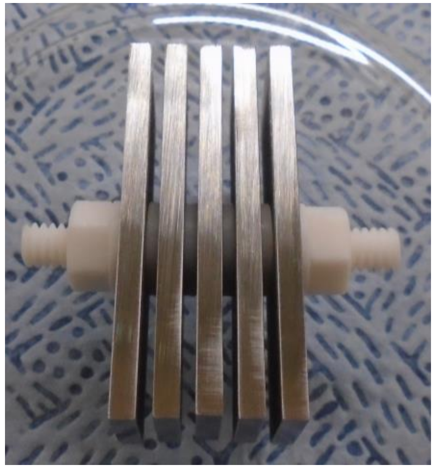
- The objective of the presented task is to investigate the potential materials degradation and corrosion risks in the construction of solvent-based pre-combustion carbon capture processes and related material selection issues
- The CO_2, after being dissolved into water and converted to carbonic acid, can corrode steel equipment, and consequently damage the integrity of steels
- Presently, the corrosion rate in the presence of carbon dioxide, water, hydrogen, and capture solvents in pre-combustion cannot be estimated accurately due to lack of corrosion data at high CO_2 partial pressure
- The investigation will cover both commercial solvents and NETL-developed hydrophobic solvents used for pre-combustion applications.



M. A. Billingham, et al., Corrosion and Materials Selection Issues in Carbon Capture Plants, Energy Procedia, 4 (2011) 2020-2027 Oilfield Review, 28 (2016) 34-49

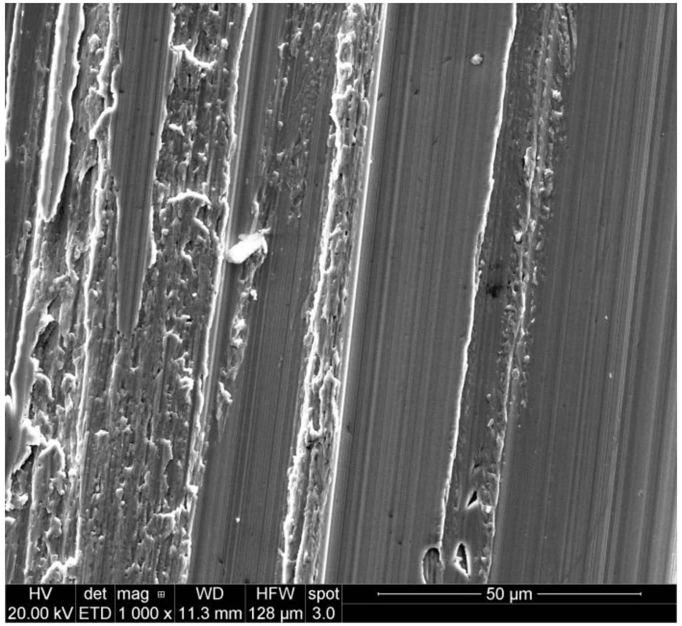
Corrosion Testing Parameters

- Materials Tested: C1020 carbon steel or SS304 stainless steel
- Coupon set is submerged in 150 mL of solvent
- Solvent corrosion rates were determined by weight lost (ASTM Method G1-03)
- Gas Composition: 100% CO_2 (8 bar or 20 bar) & 50%/50% CO_2/H_2 (16 bar)
- Temperature: 21°C (uncontrolled) or at 40°C (controlled)
- Time Duration: 1, 2, 4, 8, 16 weeks

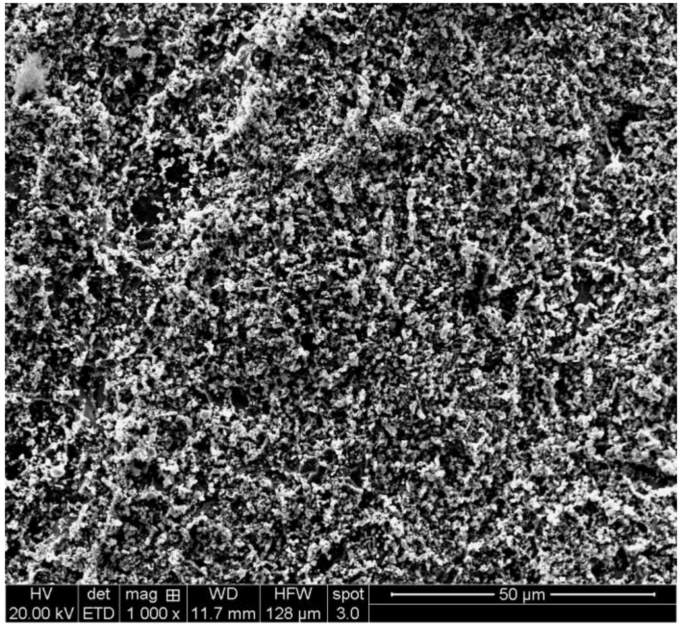


C1020 – SEM Images of Coupons

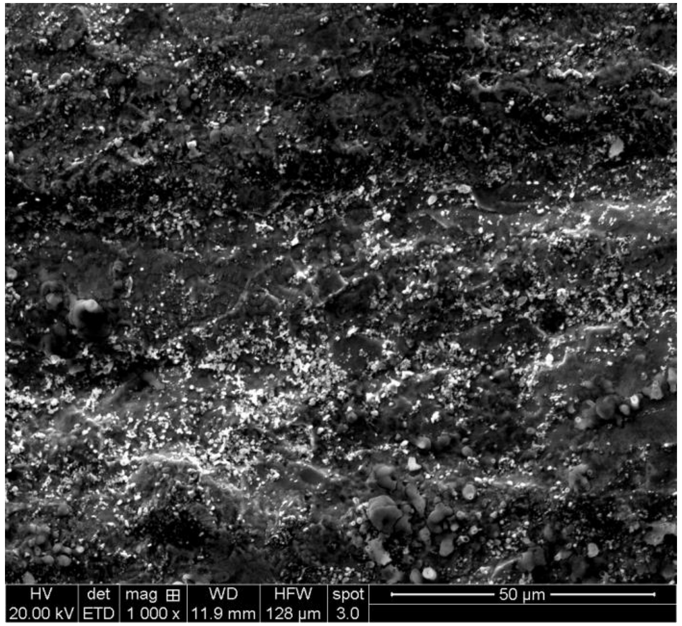
Carbon steel in 1M HCl test



before testing



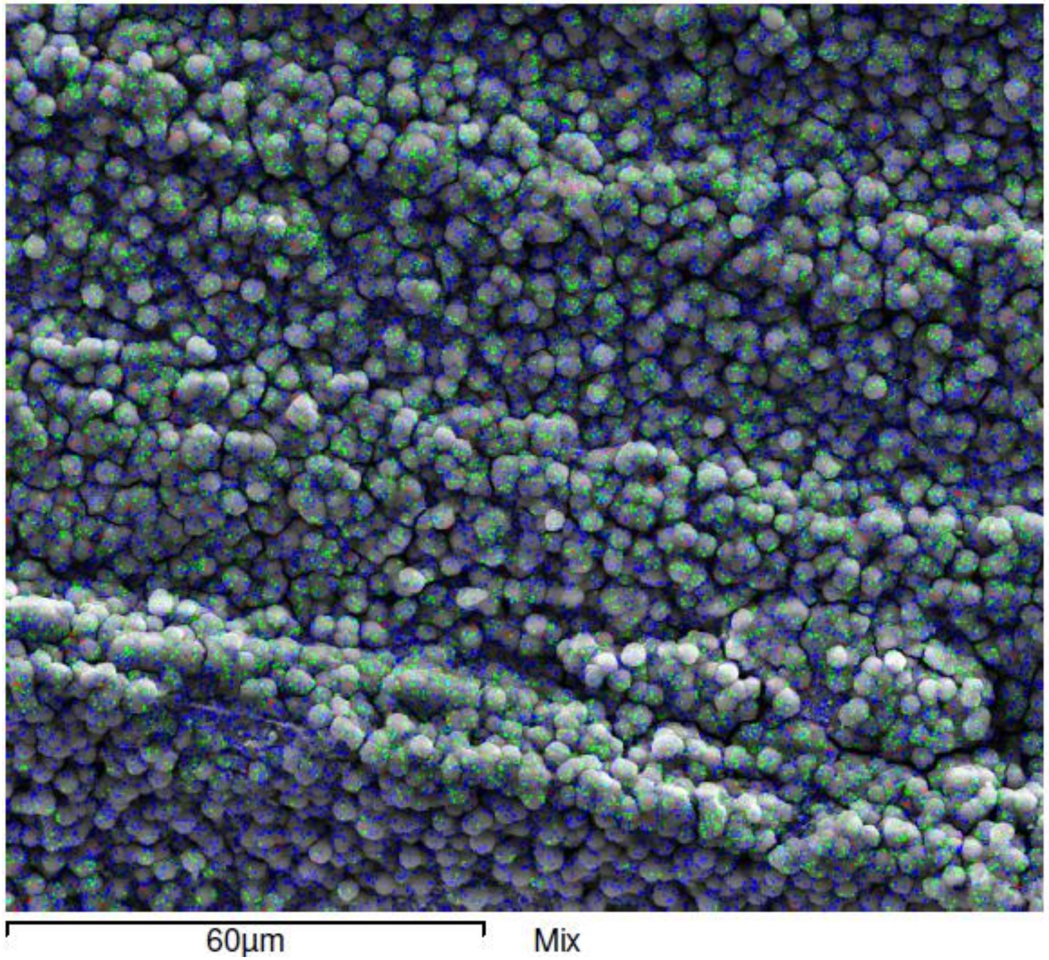
before cleaning



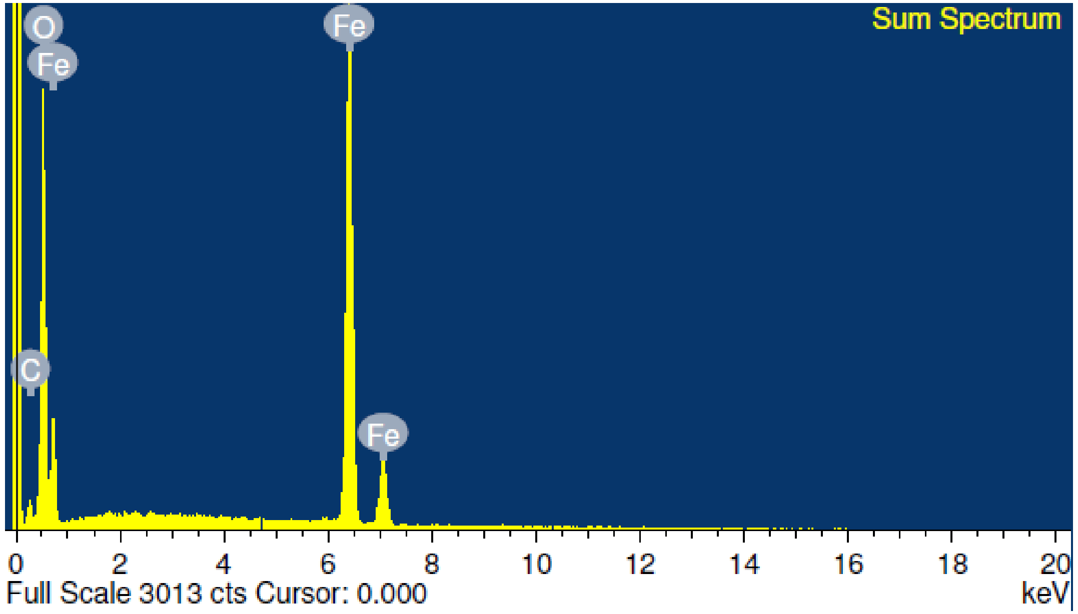
after cleaning

Corroded C1020 - Before Cleaning

Carbon steel in 1M HCl test : SEM/EDS results



Fe in green, C in red, O in blue

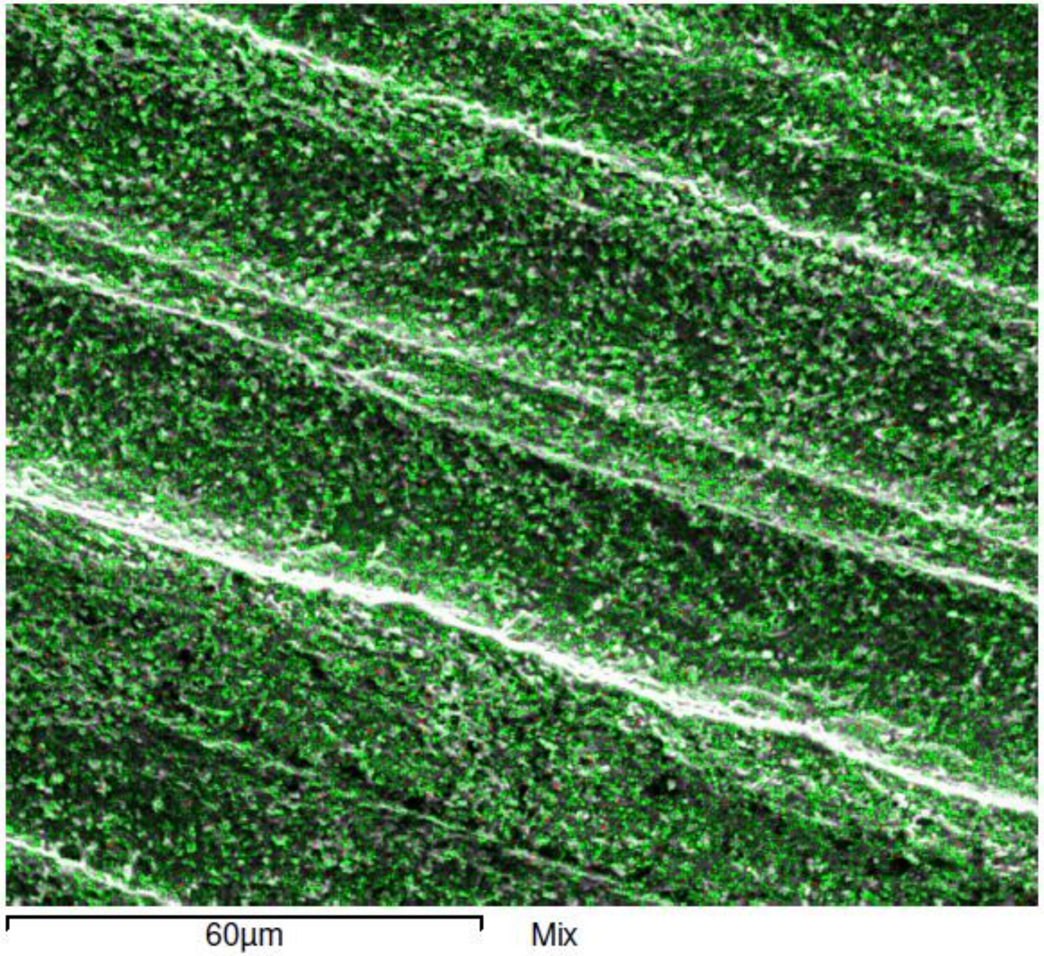


Element	Weight%
Fe	63.00
C	6.34
O	30.65
Totals	100.00

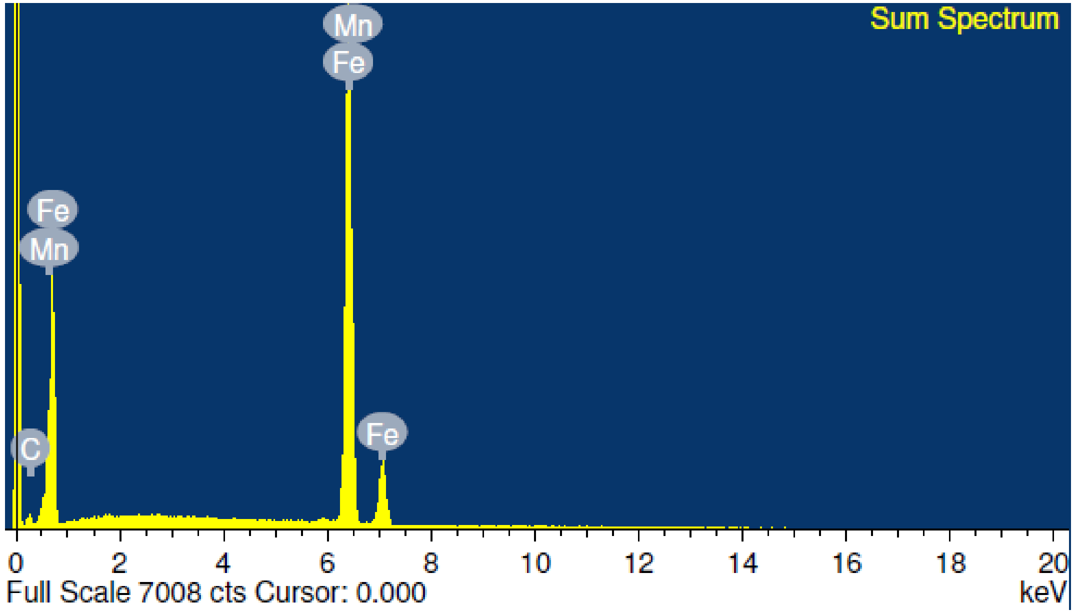
Surface particles of $FeCO_3$ completely cover the surface of the coupon.

Corroded C1020 - After Cleaning

Carbon steel in 1M HCl test : SEM/EDS results



O in blue has disappeared from the surface.



Element	Weight%
Fe	95.18
C	4.25
Mn	0.57
Totals	100.00

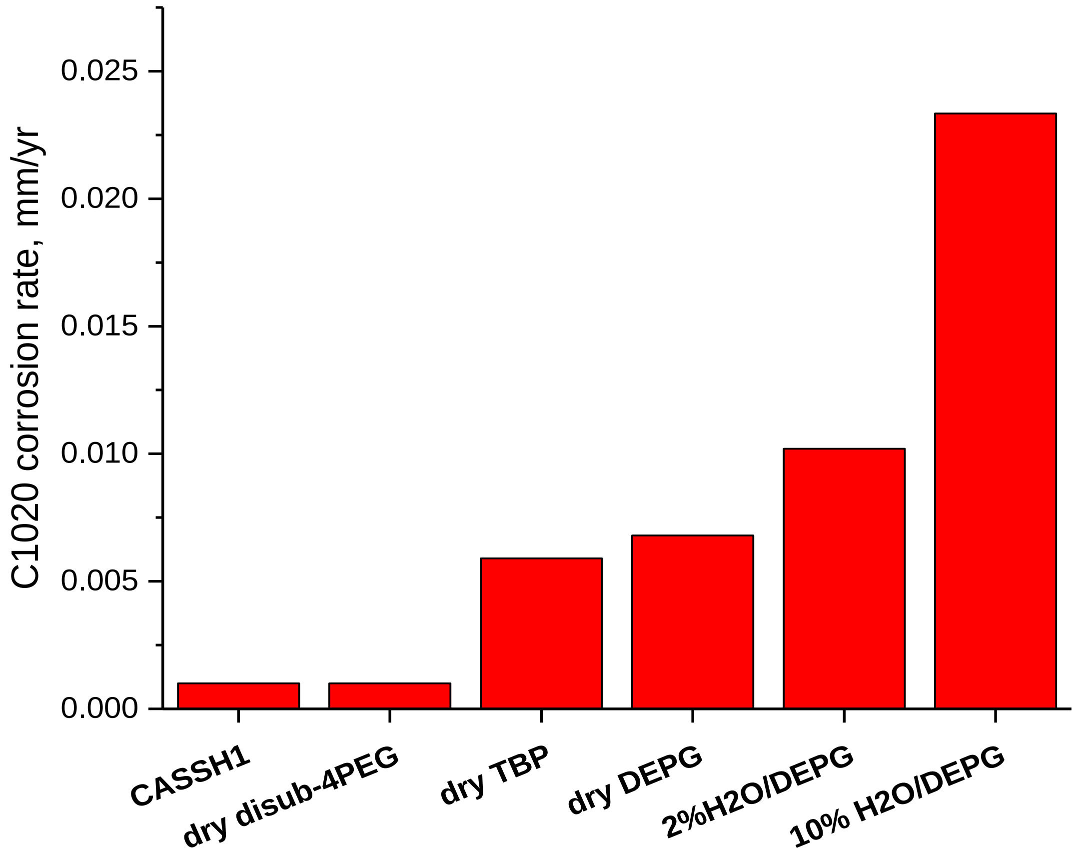
Surface particles of $FeCO_3$ have been removed after chemical cleaning, as shown by elimination of O atoms from the coupon.

Corrosion Solvents Studied to Date

Parr reactors

Aqueous:
- DI H_2O
- 1M HCl
- 1M NaOH
- 1M $NaHCO_3$
- 1M Na_2CO_3
- 1M NH_4OH
- 1M NaCl
- 1M KCl
- 1M K_2CO_3

Organic:
- MDEA
- **10 wt% H_2O/Selexol**
- **2 wt% H_2O/Selexol**
- **dry Selexol**
- **TBP**
- **disub-4PEG**
- **CASSH-1**



CSTR

Aqueous:
- DI H_2O

Organic:
- CASSH-1

NETL/RIC patented hydrophobic solvents have the lowest corrosion rates

20N-25; S-166,194; U.S. Pat. App Ser. No. 17/867,094 Hydrophobic Alkyl-Ester Physical Solvents for CO2 Removal from H2 Produced from Synthesis Gas; U.S. Provisional Patent Application Serial No. 63/223,422; DOE Ref. No. S-166,194

Corrosion Rates With and Without Hydrogen

CSTR testing for H_2 conditions

Corrosion Rate, µm/yr	DI Water		90% Selexol / 10% H_2O		CASSH1	
Temp, °C	25	40	25	40	25	40
CO_2 100%	**607**	**624**	**23**	**43**	**8**	**13**
CO_2/H_2 50%/50%	**602**	**445**	**Future Testing**		**10**	**14**

- On-going research to extract effect of temperature and added hydrogen to corrosion rates

Corrosion Task - Conclusions

- Corrosion rates in aqueous solvents are highest at low pH
- Corrosion of SS304 is negligible in all solutions under all conditions tested
- Corrosion of C1020 is significantly lower in organic solvents compared to aqueous solutions under all conditions tested

- NETL/RIC patented hydrophobic solvents have the lowest corrosion rates, near zero corrosion rate even for carbon steel
- NETL/RIC will be coordinating with OLI Systems to incorporate the experimental data their Corrosion Analyzer software

Acknowledgements

- NETL pre-combustion solvent research group: David Hopkinson, Kevin Resnik, Robert Thompson, Lei Hong, Fangming Xiang, Jeff Culp, Wei Shi, Jan Steckel, Kathryn Smith, Victor Kusuma, Lingxiang Zhu, Nicholas Siefert (PI)
- Dushyant Shekhawat, Reaction Engineering Team Supervisor (U.S. Department of Energy, National Energy Technology Laboratory)
- Andrew Jones, Technology Manager (U.S. Department of Energy, National Energy Technology Laboratory)
- HQ PM (Mani Gavvalapalli) and HQ DD Lynn Brickett (U.S. Department of Energy, Office of Fossil Energy)

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References and Patents

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- Di-substituted siloxane solvents for gas capture, DP Hopkinson, N Siefert, RL Thompson, M Macala, L Hong, US Patent 10,589,228
- Effect of Molecular Structure on the CO_2 Separation Properties of Hydrophobic Solvents Consisting of Grafted Poly Ethylene Glycol and Poly Dimethylsiloxane Units, RL Thompson, J Culp, SP Tiwari, O Basha, W Shi, K Damodaran, ... Energy & Fuels 33 (5), 4432-4441
- 20N-25; S-166,194; U.S. Pat. App Ser. No. 17/867,094 Hydrophobic Alkyl-Ester Physical Solvents for CO2 Removal from H2 Produced from Synthesis Gas; U.S. Provisional Patent Application Serial No. 63/223,422; DOE Ref. No. S-166,194

Backup Slides

Aqueous CO_2 Corrosion Mechanism

CO_2 dissolution:

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

cathodic reactions:

$$2\ H_2CO_3 + 2\ e^- \longrightarrow H_2 + 2\ HCO_3^-$$

$$HCO_3^- \longrightarrow H^+ + CO_3^{2-}$$

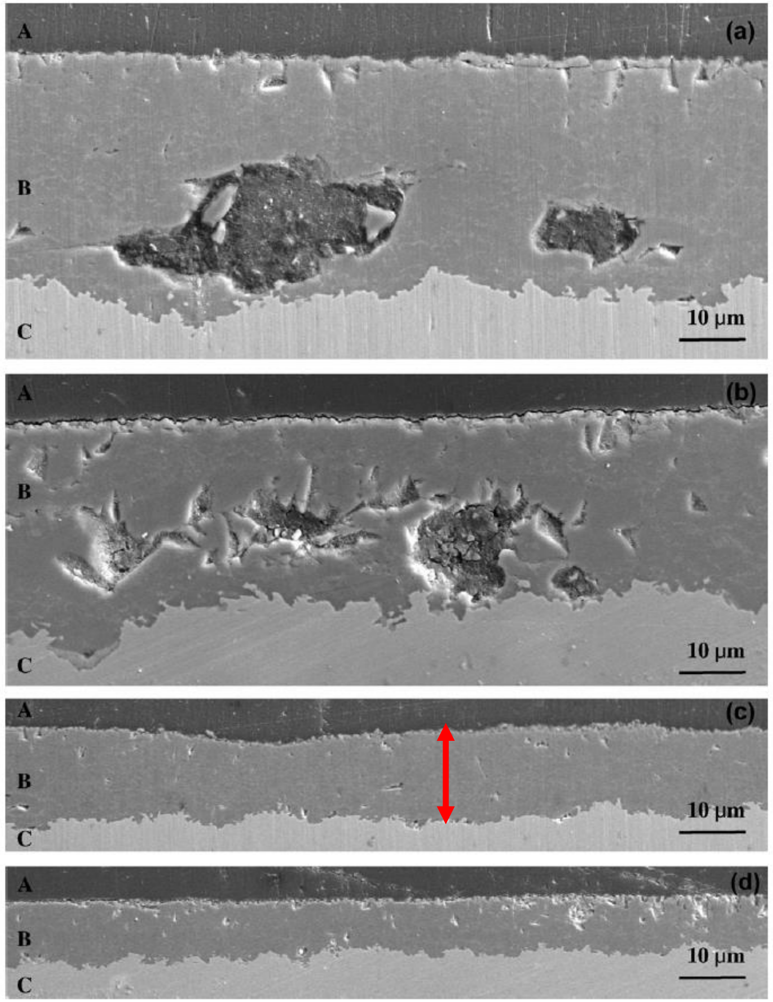
$$2\ H^+ + 2\ e^- \longrightarrow H_2$$

anodic reaction:

$$Fe \longrightarrow Fe^{2+} + 2\ e^-$$

overall corrosion reaction:

$$CO_2 + H_2O + Fe \longrightarrow FeCO_3 + H_2$$



dense scale layer forms protective barrier for subsurface Fe

Cross-section morphologies of CO_2 corrosion product scales formed under low CO_2 partial pressure for 168 h immersion at 50 C (a), 80 C (b), 110 C (c) and 130 C (d) (A: epoxy, B: scale, C: steel substrate).

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from Y. Zhang, et al., Corrosion Sci., *59*, 186 (**2012**)

Corrosion Rate Equations

gravimetric corrosion rate:

$$corrosion\ rate = \frac{K\ x\ W}{A\ x\ T\ x\ D}$$

where K = 87,500 mm/yr (conversion factor),
W = coupon weight lost (in g),
A = coupon surface area exposed per coupon (in cm^2),
T = experiment time (in hr),
and D = coupon density (in g/cm^2)

this equation provides corrosion rate in units of mm/yr