Low Corrosion Pre-Combustion Solvents for Novel Solvent/Membrane Hybrid Capture Processes

PI: Nicholas Siefert (Presenter)

TPL: David Hopkinson

RSS Solvent Research Team: Robert Thompson, Fan Shi, Fangming Xiang, Jeff Culp, Wei Shi, Kevin Resnik

U.S. DEPARTMENT OF ENERGY

NATIONAL ENERGY TECHNOLOGY LABORATORY

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

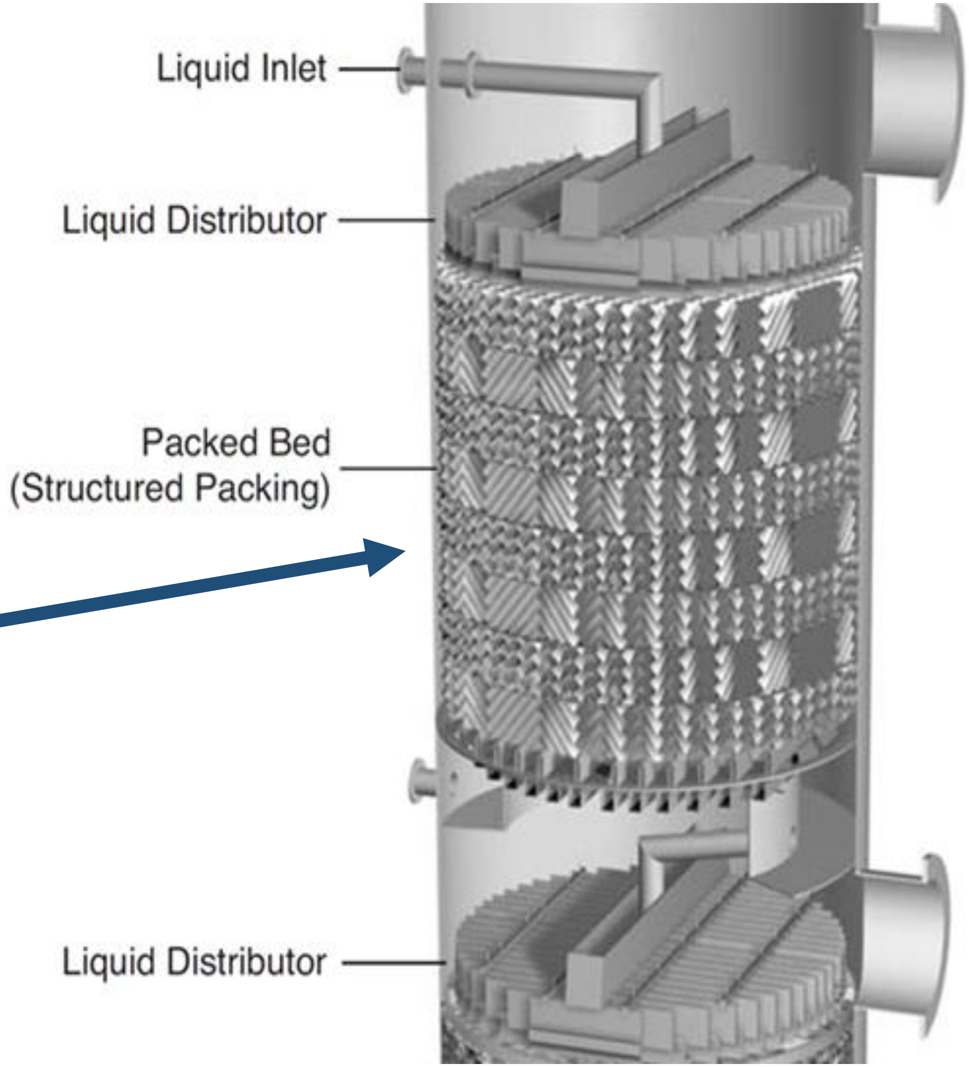


Image from: https://dakotagas.com/sites/CMS/files/images/home-hero/DGC-aerial-homepage.jpg

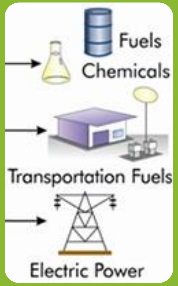
Background and Prior Gap Analysis

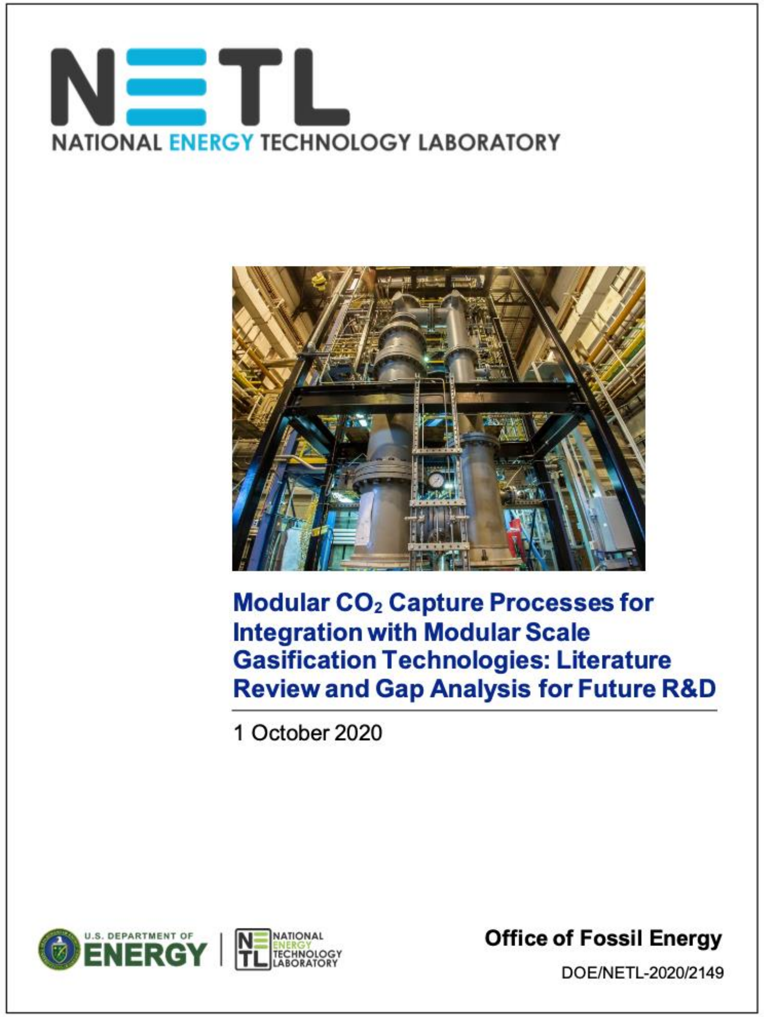
Modular design

Diverse feedstocks

Location

Polygeneration





NATIONAL ENERGY TECHNOLOGY LABORATORY

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

1 October 2020

U.S. DEPARTMENT OF ENERGY | NATIONAL ENERGY TECHNOLOGY LABORATORY

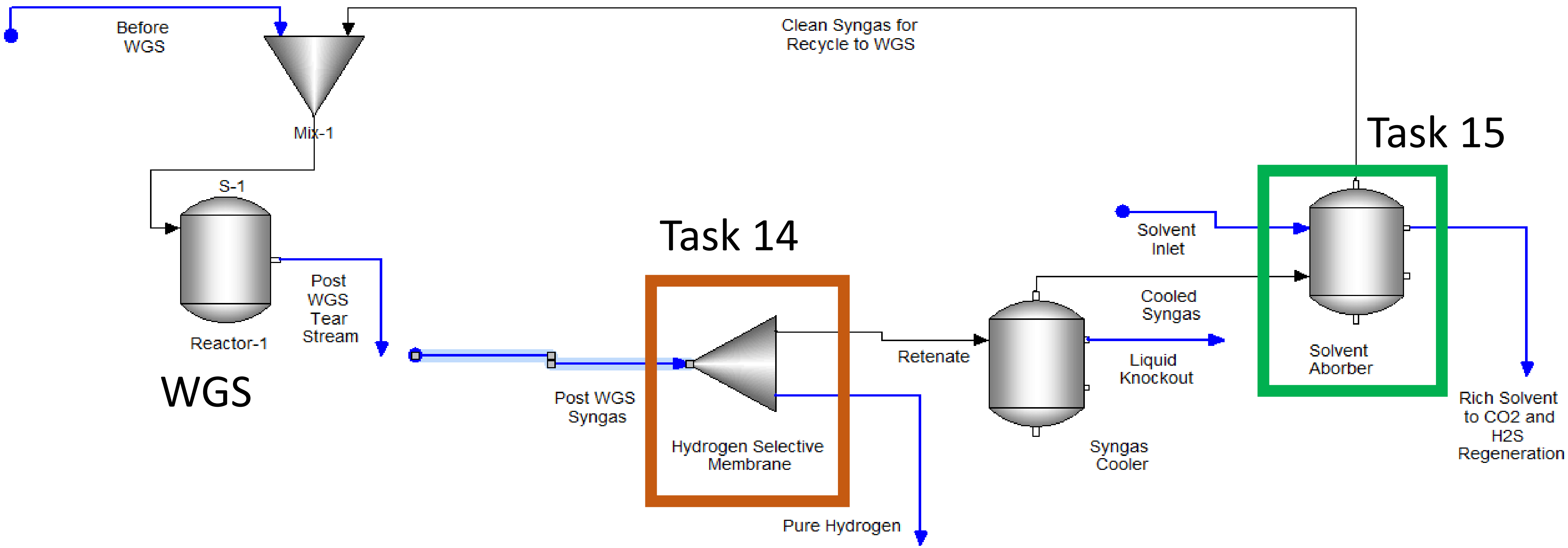
Office of Fossil Energy

DOE/NETL-2020/2149

Report available from NETL website: Link

Hybrid Precombustion Capture for Flexible Operations

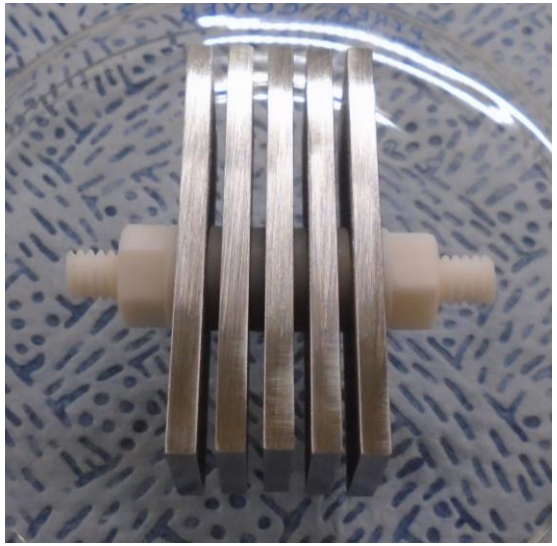
- **Upstream H_2 selective membrane (Task 14 of Capture FWP)**
- **CO_2 selective solvent (Task 15 of Capture FWP…<u>focus of this talk</u>)**



Research Objective and Hypothesis

- Objective: To measure the corrosion rates in carbon and stainless steels from solvent-based pre-combustion carbon capture processes

- The selection of optimal materials for piping, vessels and all types of equipment will be vital in ensuring the long-term performance and safety assertion of the capture plants through their lifetime



- Presently, the corrosion rate in the presence of carbon dioxide, water, hydrogen, and organic solvents in pre-combustion conditions is difficult to estimate accurately due to lack of public corrosion data at high CO_2 partial pressure

- Hypothesis: Hydrophobic solvents will have lower corrosion rates than hydrophilic solvents

- Investigation of corrosion rates will provide insight in the corrosion mechanisms, which can be applied for material selection and process design of the full-scale plant

1. Yucheng Zhang, et al., Inhibition of Steel Corrosion Under Aqueous Supercritical CO2 Conditions, NACE, Corrosion 2011, Paper No. 11379
2. Chandrabhan Verma, et al., Ionic Liquids as Green Corrosion Inhibitors for Industrial Metals and Alloys, Chapter 6, Hosam El-Din Saleh, edited, Green Chemistry, 2018

Research Approach Overview

- In EY20, baseline testing was conducted in a variety of aqueous solutions, which have different pH, in order to validate the experimental facilities, testing procedures, and characterization approaches
- In EY20, the results obtained from aqueous baseline testing were compared with predictions by OLI Studio’s Corrosion Analyzer software
- In EY20, CO_2 corrosion in commercial pre-combustion CO_2 capture solvents, such as Selexol and MDEA, were measured
- In EY20, CO_2 corrosion in latest in-house developed hydrophobic solvents, including disub-4PEG and CASSH-1 solvents, were measured
- In EY21, this year corrosion is being measured in gas mixture of CO_2 and H_2 to mimic syngas composition

Project Approach

Overall Approach

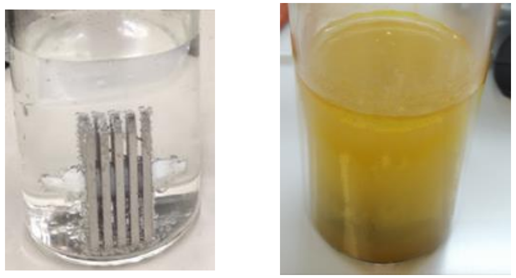
- Stainless 304 and Carbon Steel coupons are submerged for weeks/months within Parr reactor vessels fitted with Teflon liners.
- After testing is concluded, the coupons are chemically cleaned and dried according to ASTM Method G1-03 and weight loss is recorded
- The used solvent is also tested to quantify transition metals lost into solution using ICP-MS analysis.
- ICP-MS analysis useful for fundamental understanding
- Before and after cleaning, coupon surfaces are imaged using SEM and surface elemental analysis is achieved using EDS to provide pictures of the coupons
- Testing Parameters: Temperature = 25°C & 40°C
  Pressure = 8 bar CO_2 & 20 bar CO_2
  Composition = 100% CO_2 and 50%CO_2 / 50% H_2

CR calculated by Weight Loss

$$\text{Corrosion rate (mm/y)} = \frac{8.76\times10^{4}\ (\text{mm}\cdot\text{h/cm}\cdot\text{y})\times\text{weight loss (g)}}{\text{area (cm}^2)\times\text{density (g/cm}^3)\times\text{time (h)}}$$

CR calculated by Fe/Co/Ni/Mn/Cu ions

$$CR_{iron\ count} = \frac{m_{loop}\cdot C_{ppmv}}{100000\cdot A\cdot \rho_{Fe}\cdot t}$$

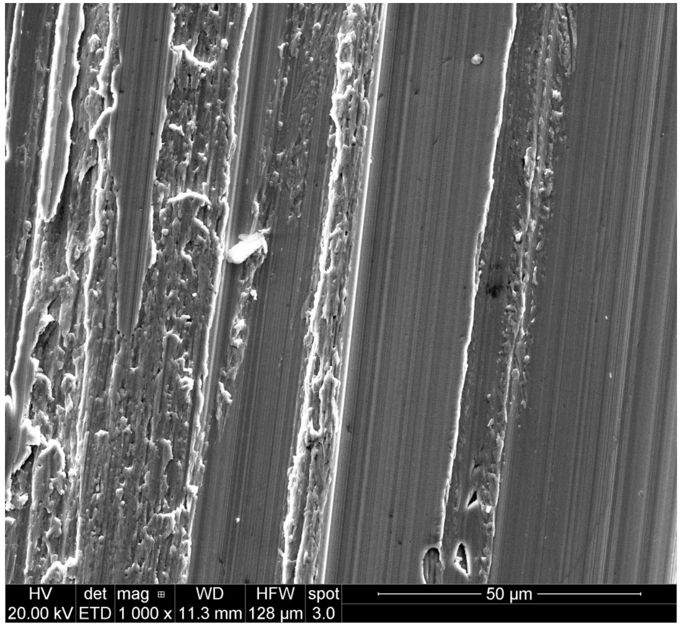


After 1 week:
25°C, CO_2 at 100 psig:
(Left) Stainless304
(Right) C1020

1. Bjørn H. Morland, Arne Dugstad, Gaute Svenningsen, Corrosion of carbon steel in dense phase CO2 with water above and below the solubility limit, Energy Procedia 114 (2017) 6752 – 6765
2. Bjørn Helge Morland, Arne Dugstad, Corrosion of carbon steel in water equilibrated with liquid and supercritical CO2, NACE 2016, Paper 7740

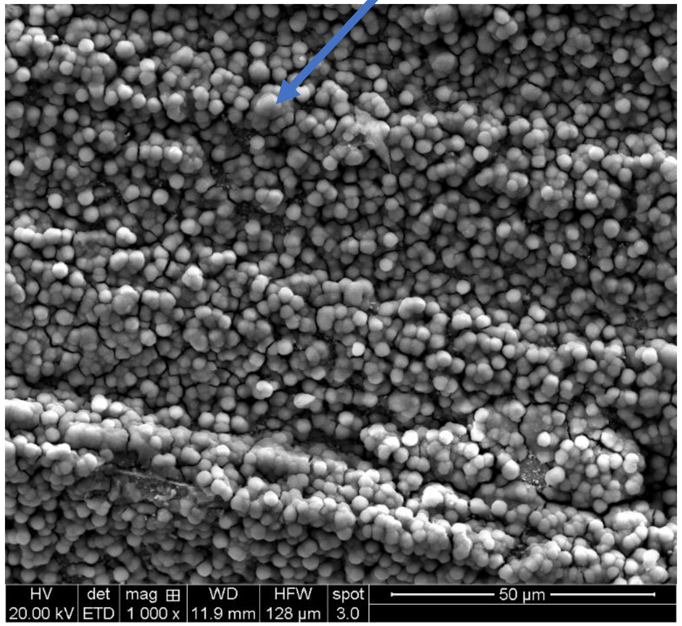
C1020 – Baseline, 8 bar CO_2

Carbon steel Baseline test: SEM results

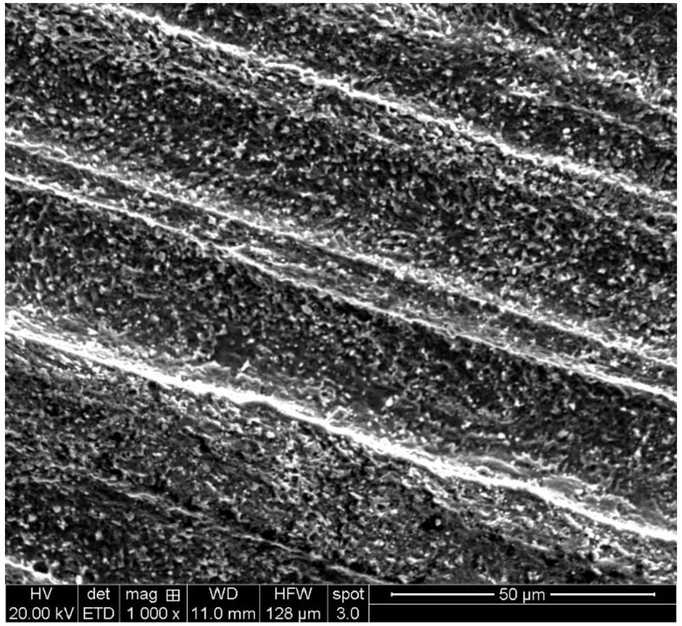


before testing

FeCO$_3$ nodules



before cleaning



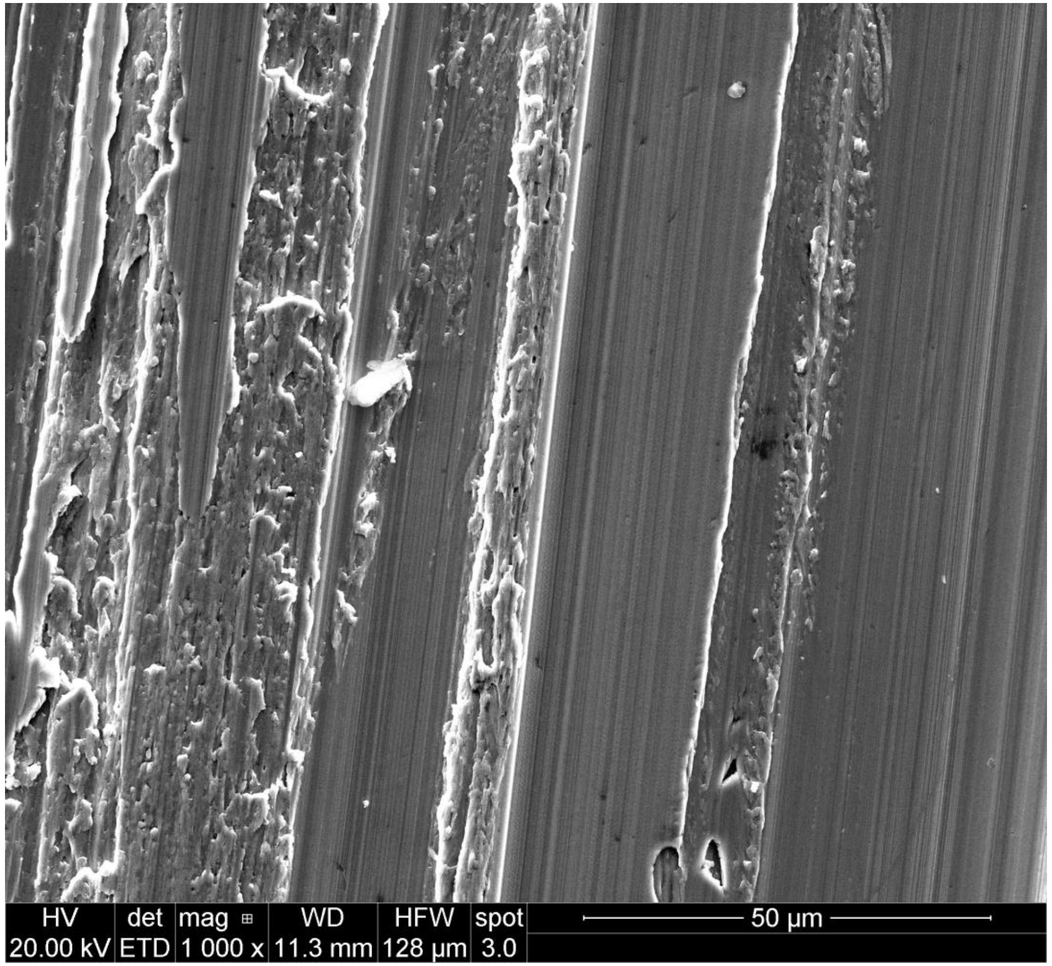
after cleaning

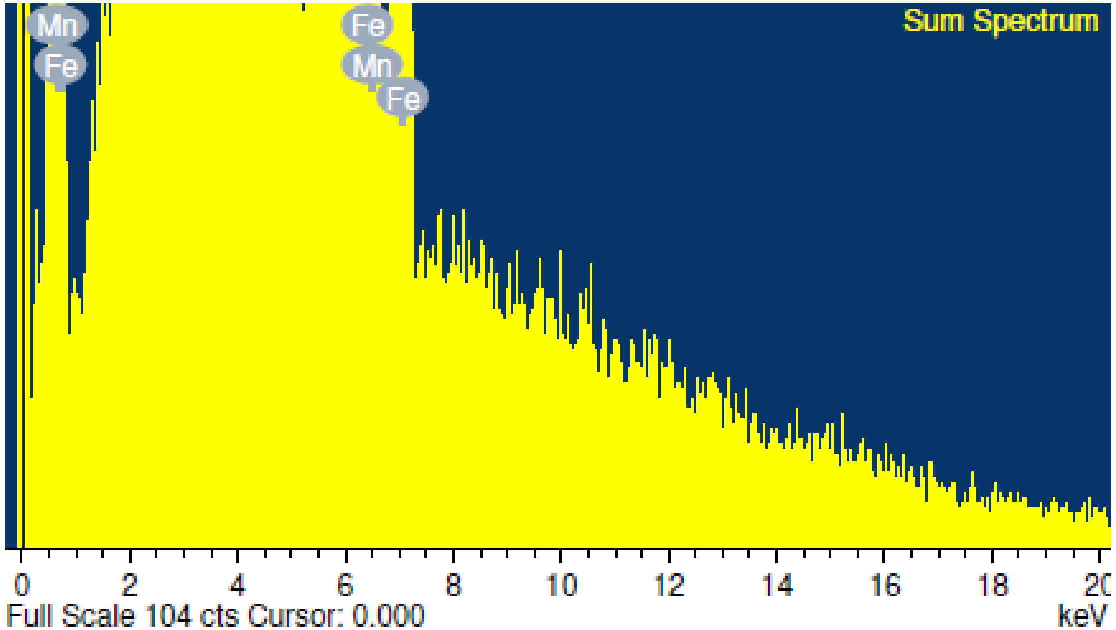
Clean steel surface before test

Surface particles completely cover the surface of the coupon.

Virgin Carbon Steel C1020

SEM/EDS results



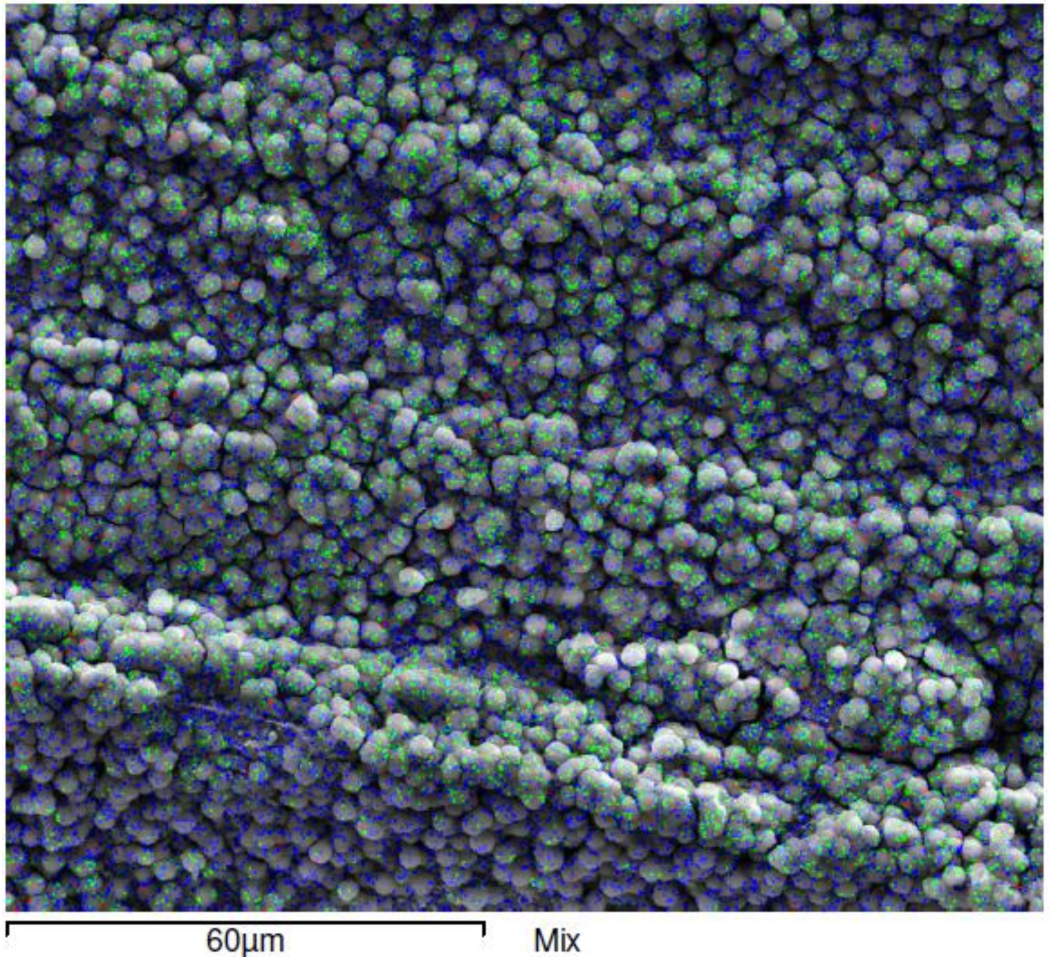


Element	Weight%
Mn	0.48
Fe	99.52
Totals	100.00

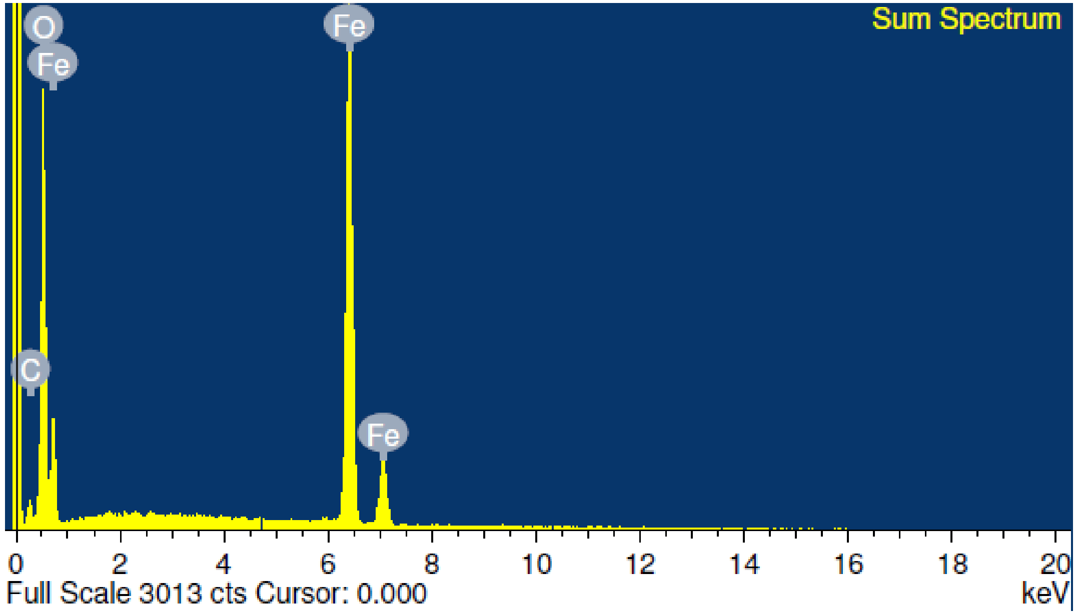
Clean steel surface before test

Corroded Carbon Steel C1020 before cleaning

Carbon steel in Baseline test before cleaning: SEM/EDS results



Fe in green, C in red, O in blue

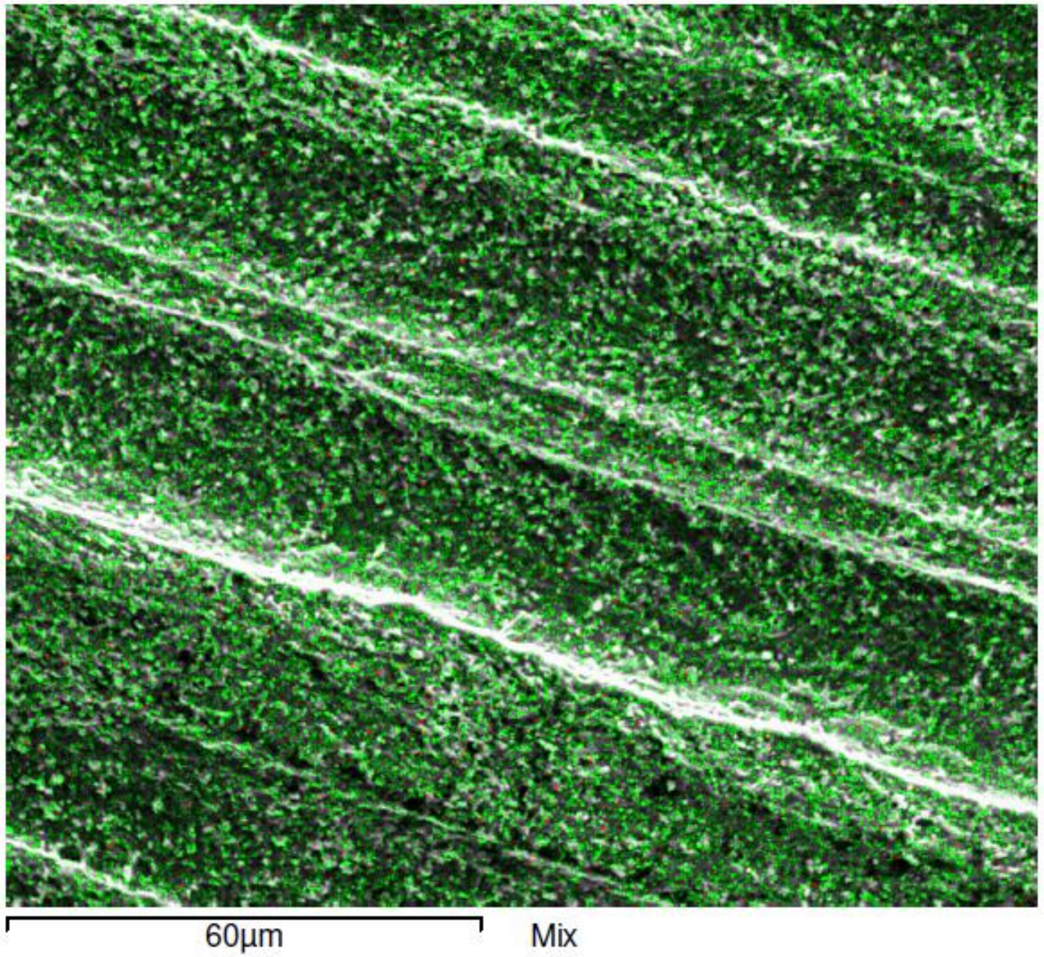


Element	Weight%
Fe	63.00
C	6.34
O	30.65
Totals	100.00

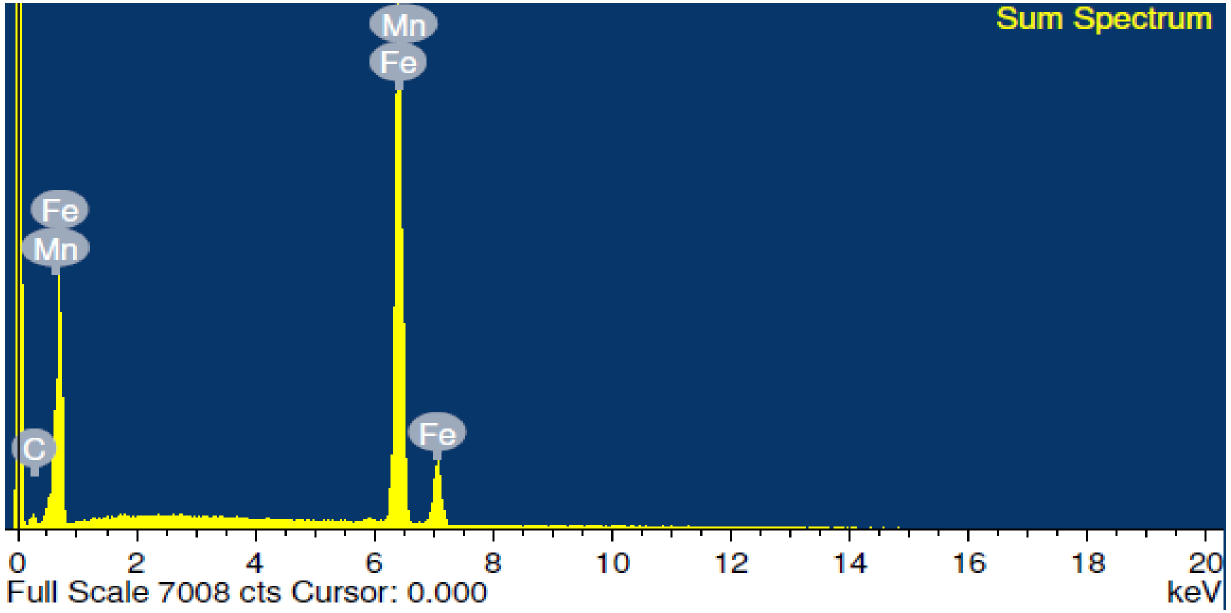
Surface particles completely cover the surface of the coupon.

Corroded Carbon Steel C1020 after cleaning

Carbon steel in test: SEM/EDS results



Fe in green, C in red, O in blue



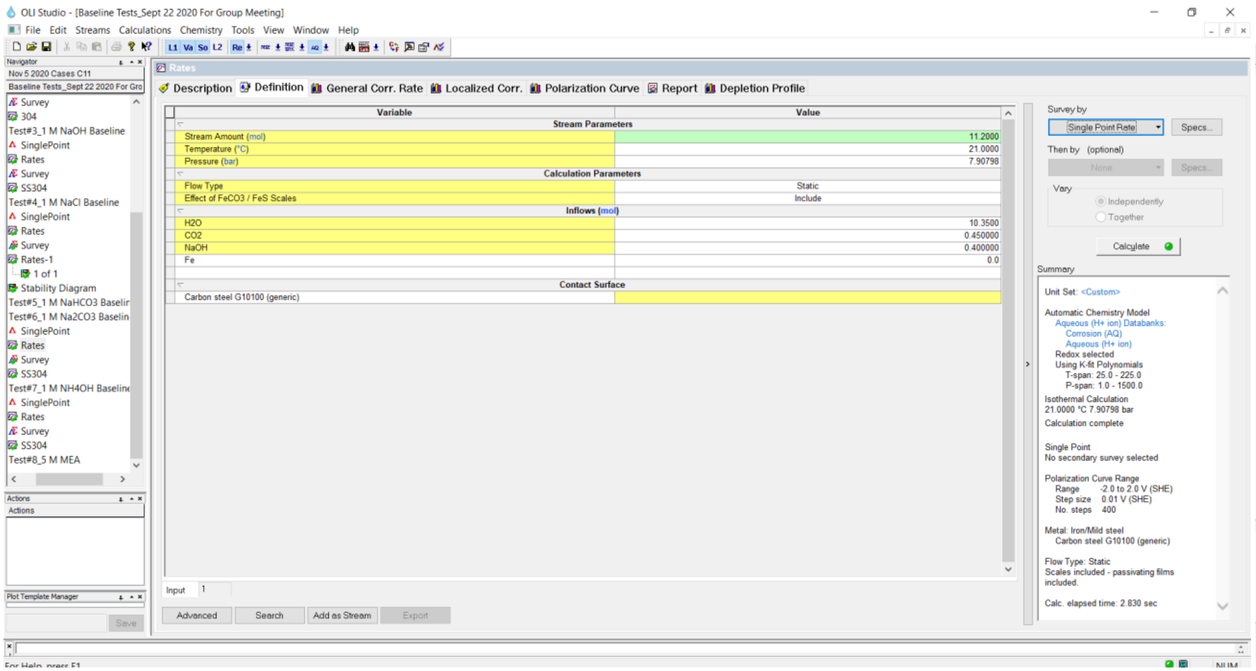
Element	Weight%
Fe	95.18
C	4.25
Mn	0.57
Totals	100.00

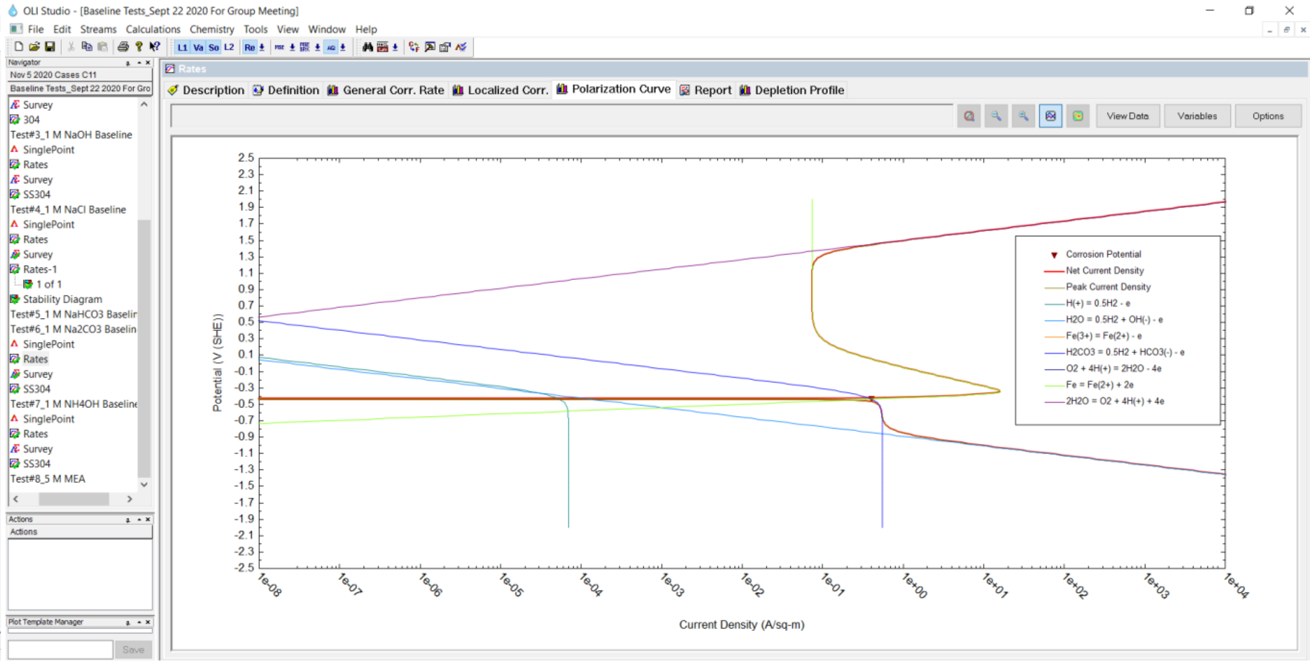
Surface particles, most likely made of $FeCO_3$, Fe_2O_3 or Fe_3O_4, have been removed after cleaning, as shown by elimination of O from the coupon.

O in blue has disappeared from the surface

Corrosion Rates Simulated using OLI Corrosion Analyzer

NATIONAL ENERGY TECHNOLOGY LABORATORY





- NETL/RIC has a license for OLI Corrosion Analyzer, which can predict the corrosion rate for a range of aqueous systems
- Model predicts corrosion rate, corrosion potential, and rates for individual reactions

OLI systems, inc.

Results: Corrosion Measurements Gravimetric Method

- <u>**Achieved high sensitivity at low corrosion rates by >500 hr testing**</u>
- **Corrosion rates highest at low pH (as expected from OLI Simulations)**
- **Baseline testing for commercially-available solvents as well as NETL patented solvents**

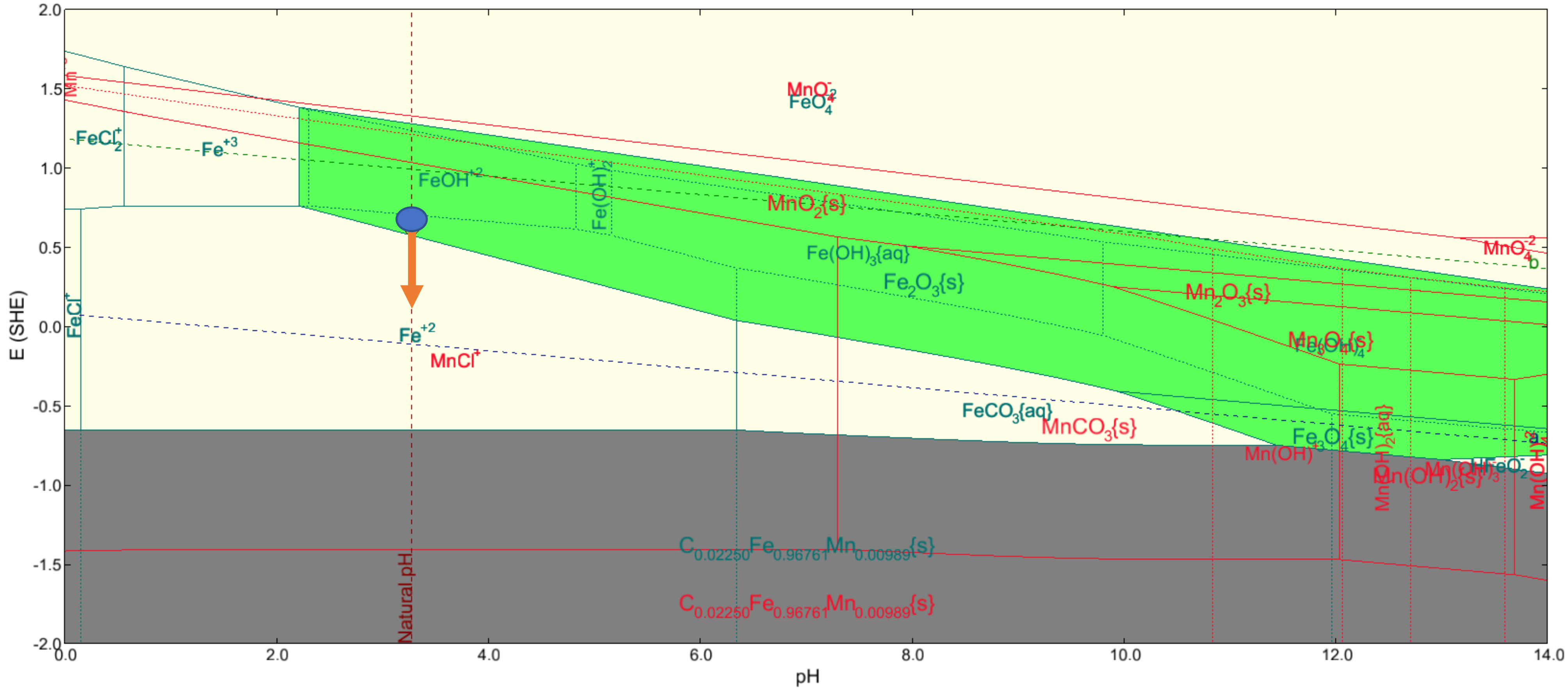
Solvent	DI H2O	1M NaCl	1M $NaHCO_3$	3M MEA	wet MDEA	90%PEGDME / 10%H_2O	98%PEGDME / 2%H_2O	dry disub-4PEG	dry CASSH1
Temperature (°C)	21	21	21	21	21	21	21	21	21
CO_2 pressure (atm)	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8
Total test time (hr)	164	167	167	167	219	335	335	335	529
CR on SS304 (µm/yr)	1.1 ± 0.6	2.0 ± 0.5	1 ± 1	2 ± 1	1.2 ± 0.5	1.5 ± 0.5	1.0 ± 0.5	0.0 ± 0.4	0.0 ± 0.3
CR on C1020 (µm/yr)	300 ± 150	500 ± 100	25 ± 20	60 ± 20	2 ± 1	20 ± 10	7 ± 3	0.0 ± 0.4	0.0 ± 0.3
OLI Simulations									
pH	3.5	3.3	6.6	7.3	NA	NA	NA	NA	NA
CR on SS304 (µm/yr)	3	7	3	3	NA	NA	NA	NA	NA
CR on CS_G10100 (µm/yr)	5600	5100	500	200	NA	NA	NA	NA	NA

- **NETL patented hydrophobic solvents <u>near-zero</u> <u>corrosion rates even for carbon steel</u>**

Shi *et. al.*, Hydrophobic Alkyl-Ester Physical Solvents for CO_2 Removal from H_2 Produced from Synthesis Gas., US S-166,194

Effect of Hydrogen: OLI Studio Corrosion Analyzer

Pourbaix Diagram: ORP vs pH



Corrosion rate is a strong function of both pH and ORP

Testing started under high pressure

50%CO_2 / 50% H_2 mixtures

Conclusions

- Corrosion rates in Carbon Steel and SS304 are measured for 8 different solvents and aqueous solutions
  - Two Pressures, Two Temperatures, and Two Different Gas Compositions
- Corrosion rates were calculated through two different methods (weight loss and dissolved metals)
- Corrosion rate and solution speciation were simulated by OLI Studio Software, and compared well with experimental data for stainless steels
- **NETL/RIC patented hydrophobic solvents have the lowest corrosion rates, near zero corrosion rate even for carbon steel**

Acknowledgements

- NETL pre-combustion solvent research group (David Hopkinson, Kevin Resnik, Robert Thompson, Lei Hong, Fangming Xiang, Jeff Culp, Wei Shi, Fan Shi, Jan Steckel, Kathryn Smith, Shouliang Yi, Lingxiang Zhu)
- Dan Hancu, Dushyant Shekhawat (U.S. Department of Energy, National Energy Technology Laboratory)
- Lynn Brickett (U.S. Department of Energy, Office of Fossil Energy)

Disclaimers & Copyright Status

- **Disclaimer of Liability:** This system is made available by an agency of the United States Government. Neither the United States Government, the Department of Energy, the National Energy Technology Laboratory, nor any of their employees, makes any warranty, express or implied, including warranties of merchantability and fitness for a particular purpose, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.
- **Disclaimer of Endorsement:** Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favor by the United States Government, the Department of Energy, or the National Energy Technology Laboratory. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government, the Department of Energy, or the National Energy Technology Laboratory, and shall not be used for advertising or product endorsement purposes.
- **Copyright Status:** Most of the information available on this server is in the public domain and therefore not copyrighted. However, some of the information is copyrighted by third parties and is made available under a license granted for use by or for the government. For non-government uses, the user is responsible for securing the proper permission from the copyright holder.