Reducing Degradation of Carbon Capture Solvents

PROJECT NUMBER: FWP 77217
[NETL/DOE PROJECT MANAGER: Carl Laird]

Phillip Koech

U.S. Department of Energy
National Energy Technology Laboratory
Carbon Management and Natural Gas & Oil Research Project Review Meeting
Virtual Meetings August 2 through August 31, 2021

PNNL-SA-165447

Acknowledgment

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by **Battelle** *Since 1965*

"This material is based upon work supported by the U.S. Department of Energy under Field Work Proposal FWP-77217."

Project Overview

Total Project Funding: $1,459,000/18 months

Overall Project Performance Dates: 01/01/2021-06/30/2022

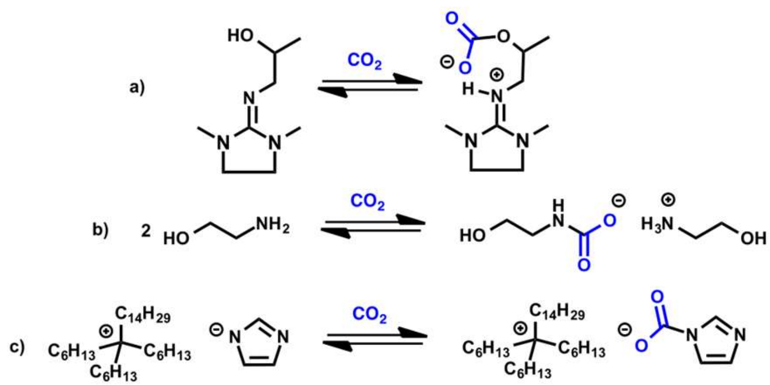
Overall Project Objectives

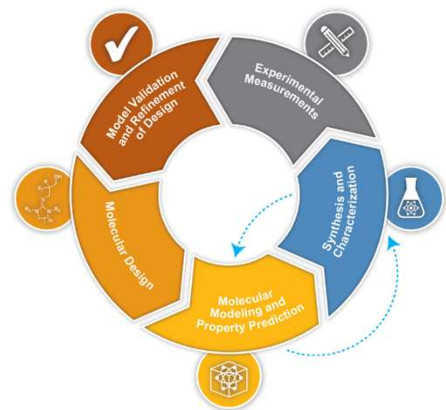
- Shut-down catalytic oxidative decomposition by steel interfaces by simply passivating the interface with coatings.
- Enable utilization of cheaper carbon steel (304) by surface modification
- Nitrosamine mitigation may enable abandoned economically viable CO_2 capture solvents.
- Evaluate water-lean CO_2BOLs as active ingredients in next generation aqueous solvent systems
- Demonstrate at least for 72 hrs. of continuous flow testing achieving >95% capture from simulated coal-derived flue gas

Technology Background

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

PNNL has spent the past few years refining water-lean solvent classes, optimizing 2° and 3° physical and thermodynamic properties that may limit performance.





Potentially limiting properties of water-lean solvents

- ✓ Viscosity
- ✓ Vapor pressure
- ? Thermal conductivity
- ✓ Binding enthalpy
- ✓ Contact angle
- ○ Chemical durability

Thermal and Oxidative Solvent Degradation

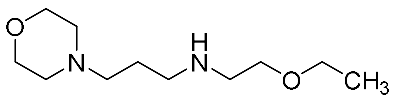
- Water-lean solvents appear more stable than aqueous solvents for thermal and oxidative degradations.
  - Due to fundamental differences in pH, charge solvation, dielectric, and H-bonding.

- Alkanolguanidines are less robust than diamines in all degradations.

Go from this:

To this:

EEMPA water-lean solvent age under flue gas conditions.



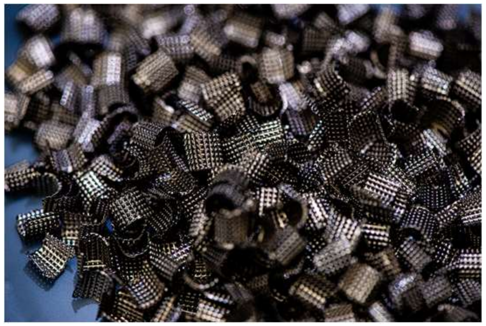
N-(2-ethoxyethyl)-3-morpholinopropan-1-amine (**2-EEMPA**)

Influence of Steel Interfaces on Solvent Degradation

Steel interfaces are not chemically inert to solvents, acting as catalysts for degradations.

- Stainless steel packings increase oxidation rate for CO_2 capture solvents.
- PNNL hypothesizes that the Chromium Oxide (CrO) or other surface oxides on the surface of 316 SS act as catalysts.
  - CrO are known oxidation catalysts for amine and alcohol moieties.
  - The CrO makes stainless steel corrosion-resistant.
  - Passivating steel interfaces increases solvent lifetime, reducing make-up rates.

****Suggests other decomposition products (e.g. oxidation via NOx) could be controlled, potentially avoiding nitrosamines.***



Propak™ ½" packings top; uncoated, Bottom; Siltek® coated.
Note the opalescence of the silane-coating.

Project Scope

- **Task 1. Evaluation of Solvent Degradation/Byproduct Formation**
  - Subtask 1.1 – Identification of steel coating candidates
  - Subtask 1.2 – Molecular modeling
  - Subtask 1.3 – Batch testing (multi solvents, additives, coated/uncoated steels, etc.)
  - Subtask 1.4 – Small-scale continuous testing

- **Task 2. Evaluation of CO_2BOLs/Alternate Aqueous Solvent Additives**
  - Subtask 2.1 – Basic solvent property testing of CO_2BOLs at higher water contents
  - Subtask 2.2 – Preliminary Techno-Economic Analysis (TEA)
  - Subtask 2.3 – Molecular modeling
  - Subtask 2.5 – Commercial solvent cost projections

BP1 Milestones

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by **Battelle** *Since 1965*

Milestone Number	Milestone Description	Estimated Completion Time
1.1	1L of 304 and 316 stainless-steel Propak ½” packings coated by both urethane and imidazole coatings.	June 30, 2021
1.2	5-week (batch) oxidative degradation studies of 4 or more solvents completed, 50% reduction in degradation for urethane, 75% for imidazole coatings.	November 30, 2021
1.3	Molecular modeling of interfacial phenomena complete. Identification of structural motifs that are most susceptible to catalytic activation by steel interfaces.	November 30, 2021
2.1	VLE, kinetic data collected for 4 aqueous solvent blends of 2-EEMPA/commercial amines	November 30, 2021
2.2	Preliminary TEA of 4 aqueous solvent blends with total equivalent work and total costs of capture quantified for a simple-stripper configuration.	November 30, 2021

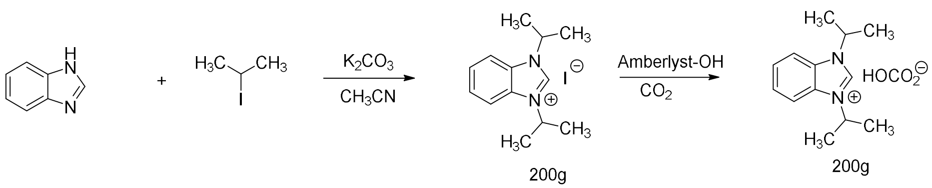
Success Criteria

Fiscal Year	Date	Success Criteria
2021	9/30/2021	1) Identification of structural motifs that are most susceptible to oxidative catalytic activation by steel interfaces and demonstrate at least 50% reduction in nitrosation of 4 solvents comprised of diamine, aminopyridine, alkanolamine classes. 2) Obtain VLE, and kinetic data for 4 aqueous solvent blends of 2-EEMPA/commercial amines and perform preliminary TEA with total equivalent work and total costs of capture quantified for a simple-stripper configuration. Key metrics include viability towards \$30/tone CO_2 and reboiler duties ~2.0 GJ/tone CO_2.
2022	9/30/2022	1) Perform continuous flow parametric testing on LCFS with coated steels and show reduction in nitrosation by >50% using coated steels 2) Demonstrate steady-state continuous flow testing of CO_2BOLs based aqueous solvents for at least 72 hrs.. achieving >95% capture from simulated coal-derived flue gas and complete final TEA. Key metrics include at or near \$30/tonne CO_2 and reboiler duties <2.0 GJ/tonne CO_2.

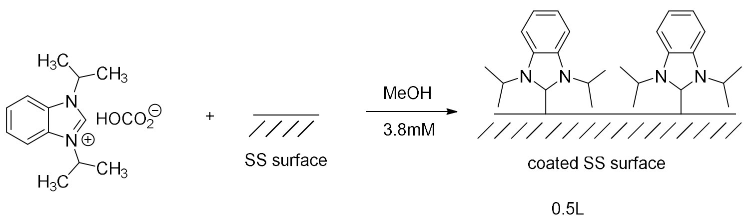
Coated Steel Packing Material

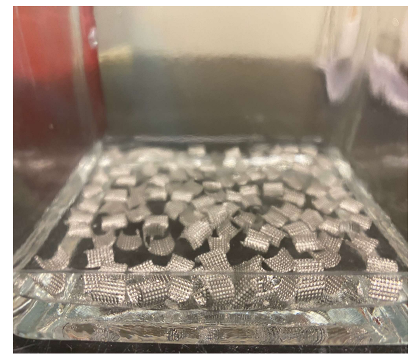
Identified coatings for steel with potential to be thermally and chemically stable under both absorber and stripper conditions

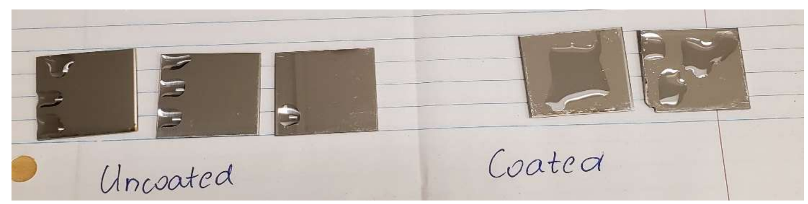
Synthesis of Imidazolium Salt



Surface Modification of Steel



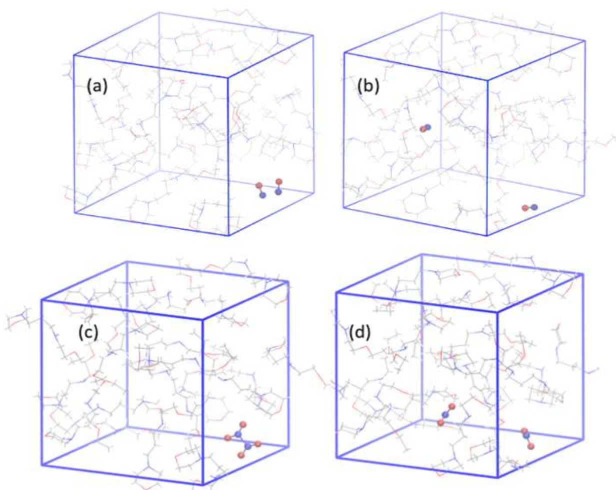


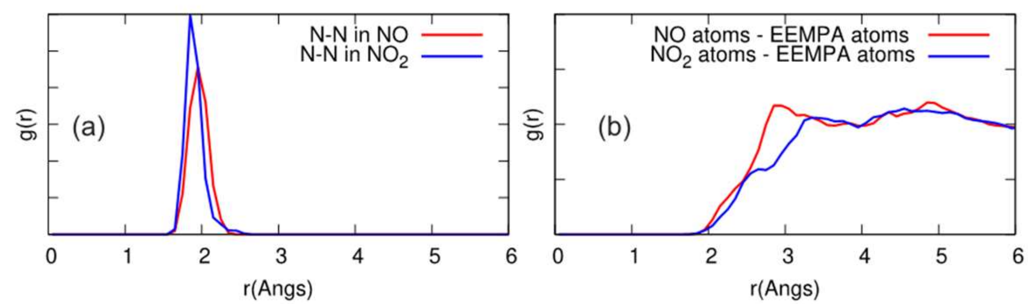


	Uncoated	Coated
Contact Angle (deg)	36, 35, 34, 34, 35, 31, 36	20, 14, 13, 14, 14, 16, 12
Average of six (discarded)	35 (31)	14 (20)

Ab initio Molecular Dynamics Simulations: Effects of NO_x on 2-EEMPA

AIMD simulations for 2-EEMPA with and without NO_x show that NO is less likely to react with EEMPA under anhydrous conditions.



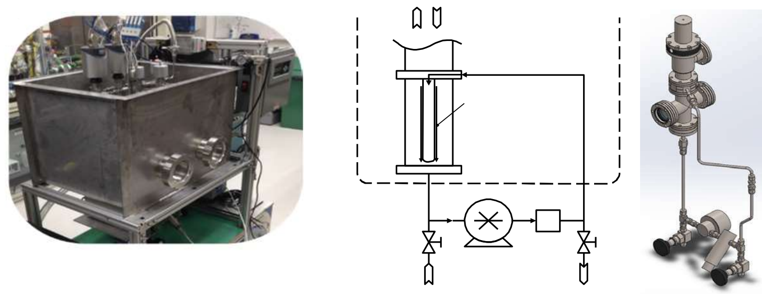


- NO is stable as a dimer it is likely to form clusters in a box of anhydrous 2-EEMPA.
- NO_2 is less stable as a dimer in dry 2-EEMPA.
- NO/NO_2 show weak interactions with 2- EEMPA with N-N distribution centered at about 2Å.

Evaluation of CO_2BOLs as Alternate Aqueous Solvent Additives

Basic solvent property testing of CO_2BOLs at higher water content using PNNL's custom PVT cell

Pressure Volume Temperature (PVT Cell)



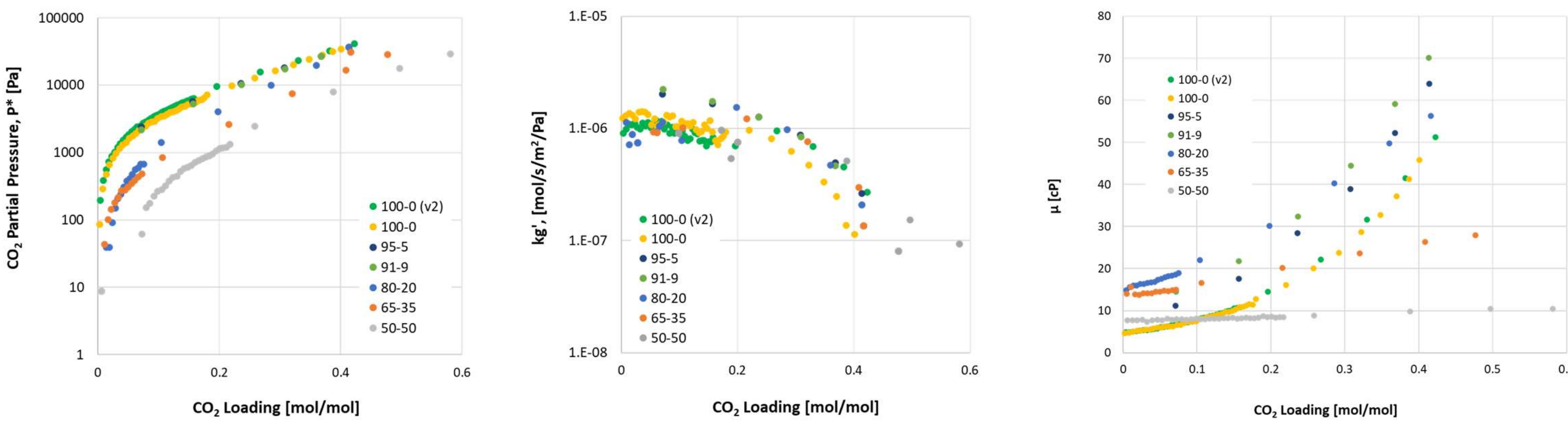
Wetted-Wall Contactor

- A PTx instrument consisting of Pressure, Volume & Temperature cell, internal wetted conductor and an in-line viscometer.
- Measure VLE, absorption rate, viscosity and vapor pressure at different CO_2 loadings and temperature.
- This instrument requires only 50 mL of solvent.

Isotherms for 2-EEMPA at Higher Water Content

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

2-EEMPA has potential to be an additive in aqueous solvents

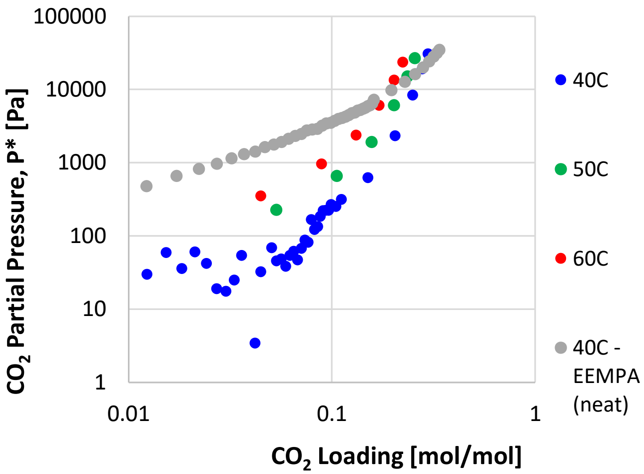


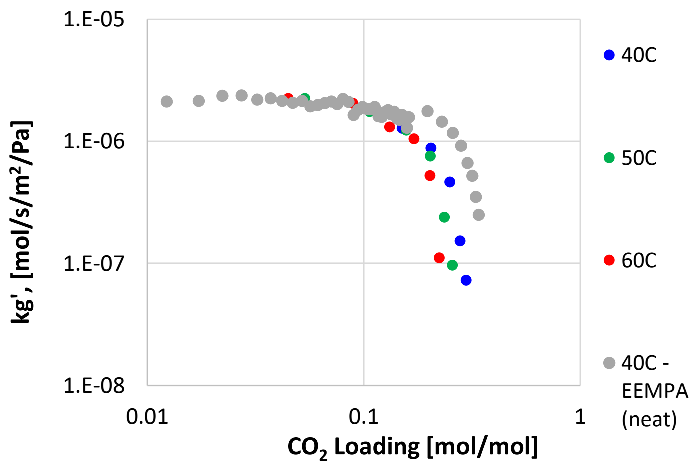
- ► CO_2 uptake capacity increase with water loading.
- ► Rate of reaction Kg' is consistent with that water-lean solvent, that is decreasing with CO_2 loading.
- ► Viscosity increase with water content up to 20 wt.% in 2-EEMPA.

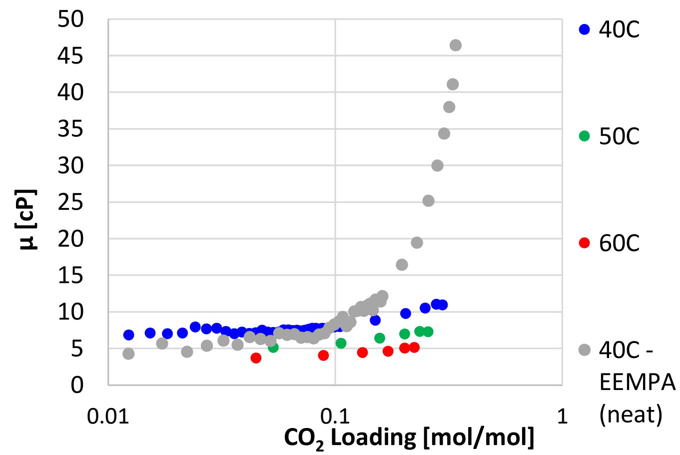
2-EEMPA as an Alternate Aqueous Solvent Component

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

2-EEMPA is a potential substitute ingredient for an unstable component of a leading proprietary aqueous amine (a-amine) solvent formulation .







- Equilibrium partial pressure VLE shows a-amine/2-EEMPA formulation is stronger CO_2 capture solvent than pure EEMPA.
- Rate (mass transfer coefficient) is comparable to that of 2-EEMPA.
- A-amine/2-EEMPA has lower viscosity at higher loading than pure 2-EEMPA.

Summary and Future Work

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

Key Findings

- Identified and synthesized imidazole coatings for steel with potential to be thermally and chemically stable.
- Developed AIMD simulations models for evaluating amine interactions with NO_x.
- VLE data shows that 2-EEMPA is a stronger solvent in water and optimal water content for minimum viscosity is 50 wt.%.
- Preliminary results showing that 2-EEMPA has potential to be an additive in aqueous solvent.

Future work

- Completed solvent degradation studies for 2-EEMPA and others with NOx.
- Utilized molecular simulations to identify and degradation pathways and propose mitigation strategies.
- Complete comprehensive property testing for 2-EEMPA as an additive in aqueous solvents.
- Perform preliminary TEA for the best 2-EEMPA/ aqueous solvent formulation.

Organization Chart

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by **Battelle** *Since 1965*

Vanda Glezakou

Roger Rousseau

Manh Nguyen

Difan Zhang

Computational Modeling

Phillip Koech

Deepika Malhotra

Kat Grubel

Solvent Synthesis
Coatings, Chemical Durability

Dushyant Barpaga

David Heldebrant

Richard Zheng

Andy Zwoster

Property Testing
and Analysis

Gantt Chart

	FY21												FY22											
	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S
0. Project Management				X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			
1. Solvent Degradation/Byproduct Formation				X	X	X	X	X	X	X	X	X	X	X	X	X	X	X						
1.1 Identification of steel coating candidates				X	X	X																		
1.2 Molecular modeling				X	X	X	X	X	X	X	X	X												
1.3 Batch testing (multi solvents, additives, coated/uncoated steels, etc.)				X	X	X	X	X	X	X	X	X												
1.4 Small-scale continuous testing													X	X	X	X	X							
1.5 Task 1 reporting																	X	X						
2. Evaluation of CO2BOLs as Aqueous Solvent Additives				X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			
2.1 Basic solvent property testing of CO2BOLs at higher water contents				X	X	X	X	X	X	X														
2.2 Preliminary Techno-Economic Analyses (TEA)										X	X	X												
2.3 Molecular modeling													X	X	X	X	X	X						
2.4 Batch testing for degradation/byproduct formation													X	X	X	X	X	X						
2.5 Commercial solvent cost projections													X	X	X	X	X	X						
2.6 Small-Scale Continous Testing																			X	X	X			
2.7 Final TEA & Task 2 Reporting																				X	X			