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Molecular Refinement of Transformational Solvents for CO_2 Separations (FWP-72396)

Charles Freeman (for David Heldebrant)

2019 Carbon Capture, Utilization, Storage, and Oil & Gas Technologies Integrated Review Meeting
Pittsburgh, PA August 27, 2019

DOE/NETL Federal Project Manager: Andy Aurelio

Acknowledgment

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Agenda

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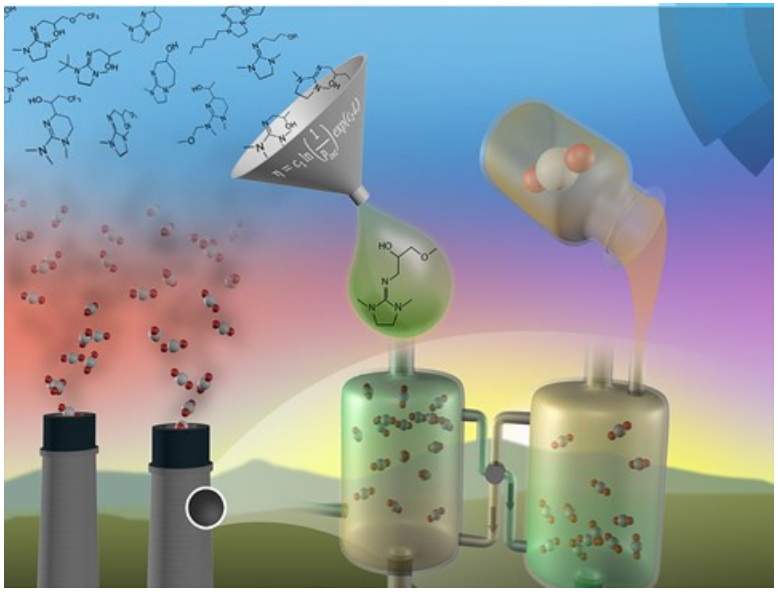
- CO_2BOLs Definition
- Project Objectives
- Project Details
- Technical Results to Date
- Summary
- Future Work
- Questions



What Are CO_2BOLs (Binding Organic Liquids)?

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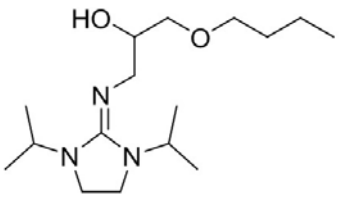
- A class of organic liquids that become zwitterionic liquids when bound with CO_2, enabling a single-constituent solvent (no blends/additives) – *simpler, lower sensible heat, higher overall loadings, less recirculation*
- Can operate with some water "water lean" (5-10 wt%) – *practical water uptake from flue gas, water wash capable*
- Change in polarity with loading – *possible use of polarity swing assisted regeneration – i.e. lower temps*
- Can exhibit viscosity increases with loading (early versions > 3000cp)

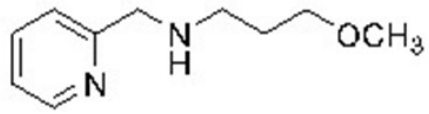
CO_2BOL Families

Alkanolguanidines



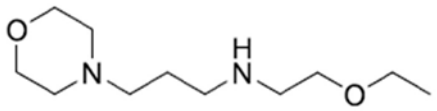
e.g. 1-BEIPADIP-2-BOL

Aminopyridines (AP)



e.g. 2-MeOEAMP

Diamines (DA)



e.g. EEMPA: N-(2-ethoxyethyl)-3-morpholinopropan-1-Amine

Project Objective

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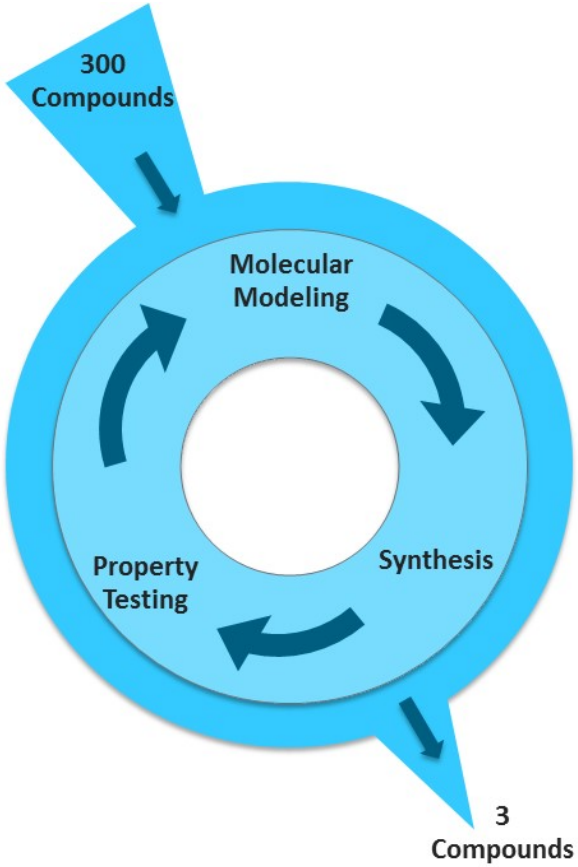
Feed the pipeline of transformational post-combustion CO_2 capture solvents towards DOE's \$30/tonne CO_2 target



- Focus on Aminopyridine and new Diamine CO_2BOLs
- Use PNNL's molecular modeling/experimental solvent development approach
  - Use established understanding to optimize viscosity, loading & heat of reaction.
  - Tackle vapor pressure, surface tension, thermal conductivity and chemical degradation.
- Inform/support all solvent development across the DOE portfolio
- Disseminate all findings via peer-reviewed publications & engage industry

Project Details

- 36-month project over three budget periods:
  - Budget period 1: 5/18 – 7/19
  - Budget period 2: 7/19 – 1/20
  - Budget period 3: 2/20 – 4/21
- $2,998,000 in federal funding
- PNNL leads the project – tied to DOCCSS solvent project and CCSI^2

Milestones/ Success Criteria

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Milestone Number	Milestone Description	Completion Date	Status
1.1	Updated Project Management Plan	Jul, 2018	Complete
1.2	Go-No Go Presentation at NETL	Jul, 2019	Complete
1.3	Delivery of final report to NETL	May, 2021	
BUDGET PERIOD 1			
2.1	Develop MD-based models for volatility and hydrolysis.	Jun, 2019	Complete
2.2	Assess MD-based surface energies for 20+ AP/DA solvents on both plastic and metal surfaces.	Jun, 2019	Complete
4.1	Synthesize & characterize (e.g. VLE, viscosity, kinetics) 20+ AP/DA solvents with predicted rich viscosity < 100 cP and vapor pressure <1 torr at 40 °C	Mar, 2019	Complete
BUDGET PERIOD 2			
6.1	Identify hydrolysis reaction mechanism (intermediates, constants, orders) for AP/DA solvents.	Nov, 2019	
7.1	Synthesize/characterize 20+ AP/DA solvents with predicted 2-3 kcal higher hydrolysis energy barriers and half the rates.	Dec, 2019	
BUDGET PERIOD 3			
8.1	Develop MD-based models for oxidation energy and rate.	Jan, 2021	
9.1	Synthesize/characterize 20+ AP/DA solvents with predicted 2-5 kcal higher oxidative energy barriers and order-of-magnitude lower rates	Mar, 2021	
11.1	Identify nitrosation reaction mechanisms (intermediates, constants, orders) for 4+ AP/DA solvents, along with mitigation pathways.	Apr, 2021	

Project Team

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Project Manager
David Heldebrant

CCSI²
Carbon Capture Simulation for Industry Impact

Solvent Synthesis Chemical Degradation

Dr. Phillip Koech
Dr. Deepika Malhotra
Dr. Katarzyna Grubel

Computational Modeling

Dr. Vanda Glezakou
Dr. Roger Rousseau
Dr. Manh-Thuong Nguyen

Property Testing & Analysis

Dr. Feng Zheng
Andy Zwoster
Dr. David Heldebrant

Molecular Modeling Tools

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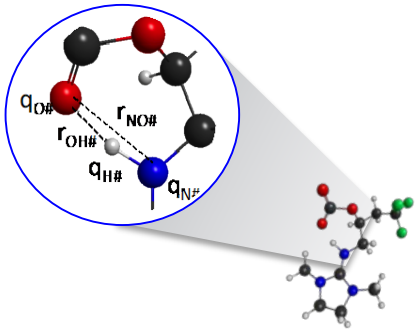
- *Ab Initio* Electronic Structure (~10^{2}-10^{3} atoms)
  - Accurate description of molecular properties
  - Atomic charges and intermolecular contacts
  - Reaction energetics: H-bonding, CO_2 absorption energy
- Classical Molecular Dynamics (~10^{4}-10^{5} atoms)
  - Accurate description of molecular liquid structure
  - Universal OPLS with *ab initio* charges
  - Transport properties: diffusion and viscosity
- Reduced ordered models
- Codes, Software:
  - CP2K (www.cp2k.org),
  - NWChem (www.nwchem.org)

Viscosity Reductions Guided by Molecular Modeling

- Prior work:
  - Focused on alkanolguanidines and diamines
  - Viscosity driver: population of internal hydrogen bonds (P_{int})
  - ~300 candidates evaluated/synthesized/tested
  - 3 solvents identified with <30 cP at rich loading (99% reduction) – included DOCCS solvent (EEMPA)



$$P_{int} = c_1 X + c_2$$

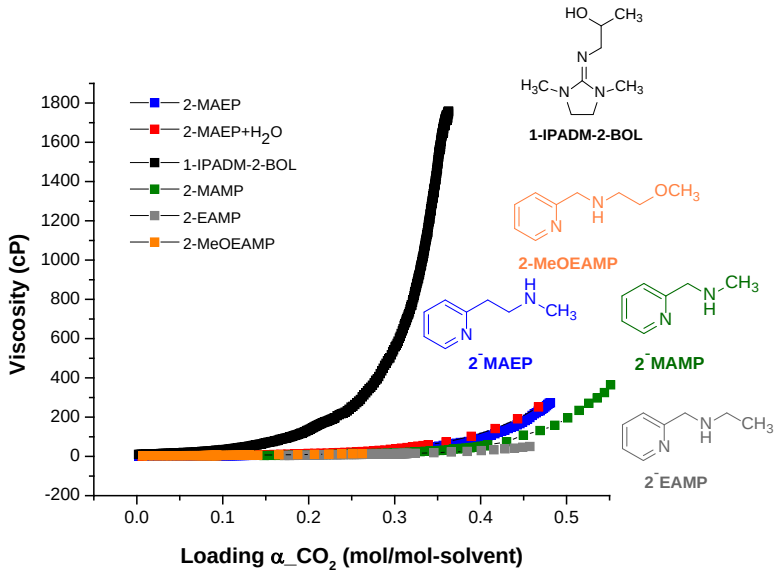
$$X = \frac{q_N q_O}{r_{NO}} - \frac{q_O q_H}{r_{OH}}$$

- Current project:
  - Focused on aminopyridines and new diamines
  - ~100 candidates evaluated/synthesized/tested to date
  - 4 viable candidates identified for with low volatility & low viscosity – as low as 3 cP at rich loading

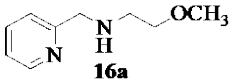
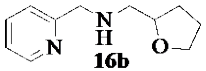
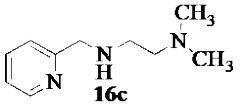
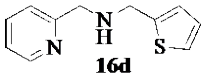
Volatility Reduction for Aminopyridine (AP) Solvents

- Low viscosity (via high P_{int}) originally drove higher volatilities.
- New structural motifs added to reduce vapor pressure (2-order-of-magnitude reduction achieved).

Initial AP solvents:



AP solvents optimized in BP1:

Compounds	MW	BP (°C)	Vapor Pressure @ 25°C (Torr)	CO2 Loading (wt%)	CO2 Loading (mol%)
 16a	166	239	0.0414	15%	57%
 16b	192	304	0.0009	9%	41%
 16c	179	262	0.0112	14%	58%
 16d	204	316	0.0004	7%	33%

CAPEX Reduction Opportunity via Plastic Packings

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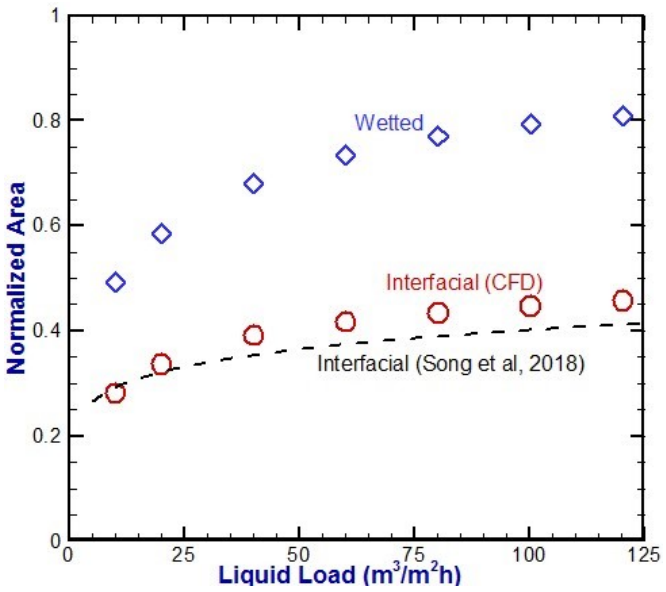
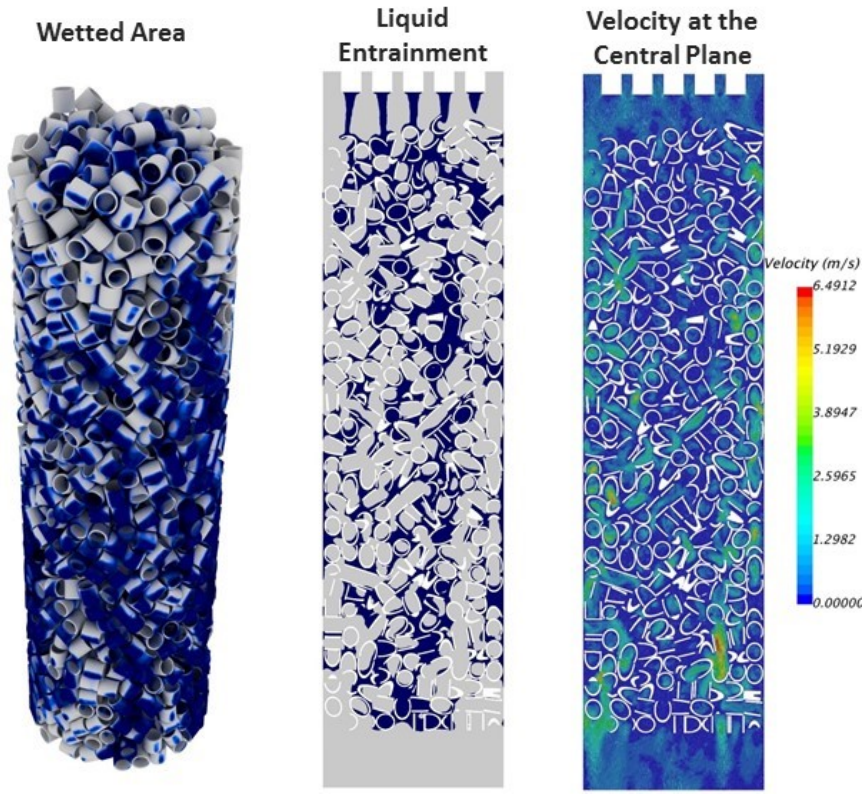
- Plastic process components could offer a number of advantages:
  - Cheaper than steel – $5/tonne CO2 savings via packing only
  - More durable than steel (reduced corrosion and metals leaching)
  - More easily manufactured into unique structures (e.g. gyroids)
- The challenge is wettability – an attribute of water-lean solvents

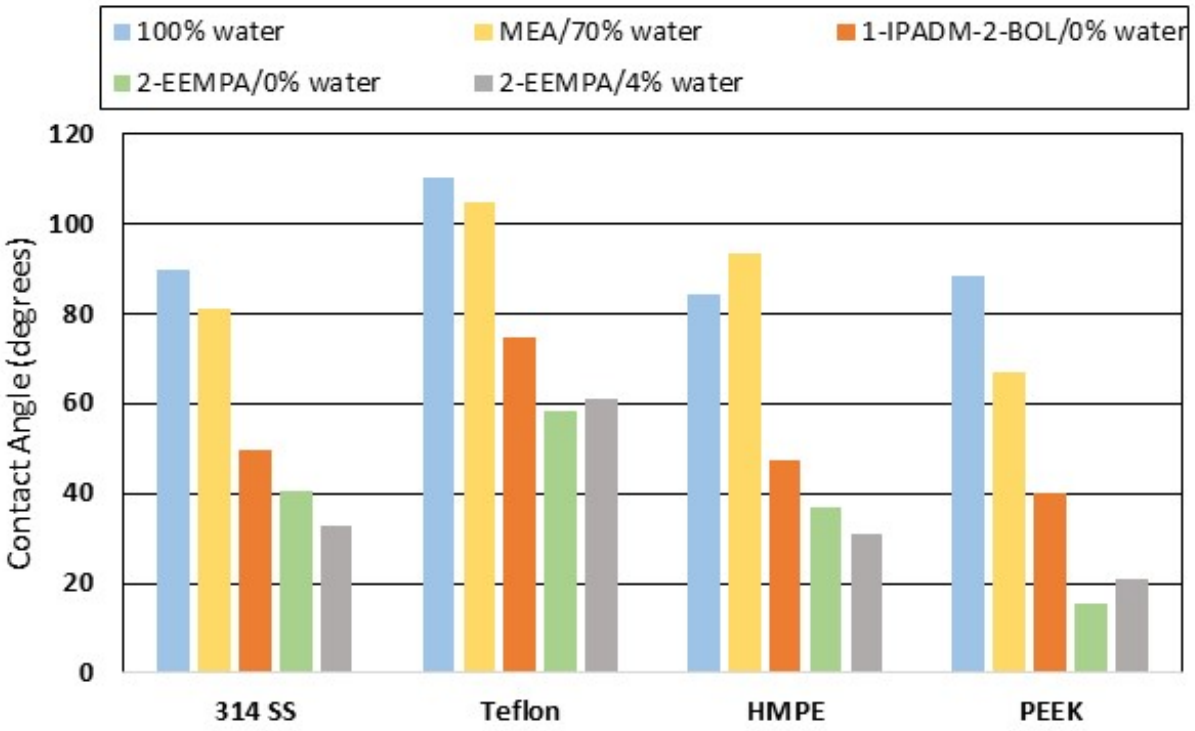
Connections to DOCCSS and CCSI2 Programs

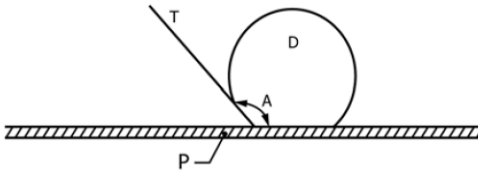
- Contact angle measurements, surface tensions and interfacial properties are feeding absorber modeling and packing designs





Experimental Contact Angle Results





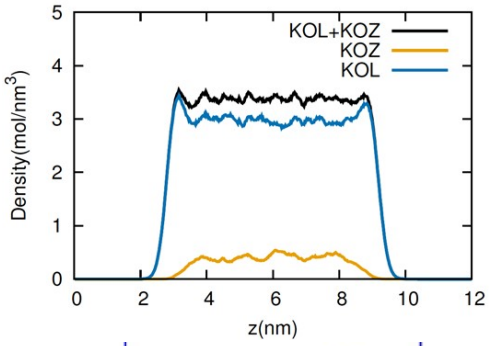
A = contact angle
D = drop of liquid
P = specimen
T = tangent at specimen surface

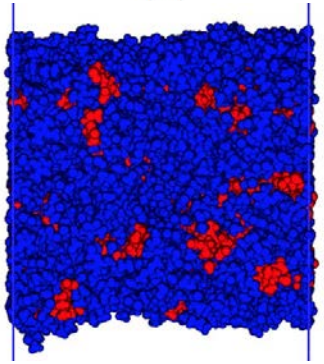
FIG. 1 Measuring Angle of Contact

- Key Observations:
  - CO_2BOLs wet both steels and plastics better than water and MEA
  - EEMPA wet some plastics (HMPE and PEEK) better than steel

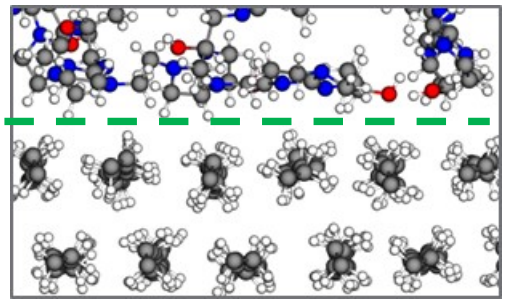
Molecular Modeling Insights: *Wetting*

- Unloaded CO2BOL solvent (non polar) migrates to non polar air & plastic surface
  - Drives wetting of plastics
  - Could explain high mass transfer observations
- Loaded solvent (polar) migrates to polar steel surfaces
  - Possibly creates a stagnant layer, which is why steel and plastic contact angles are similar.



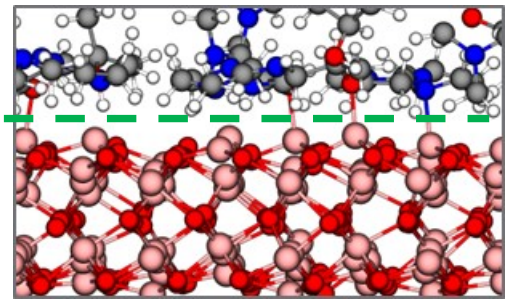


Solvent/plastics



Interface plane

Solvent/steel



Oxidative Degradation Measurements for EEMPA (*DOCCSS project*)

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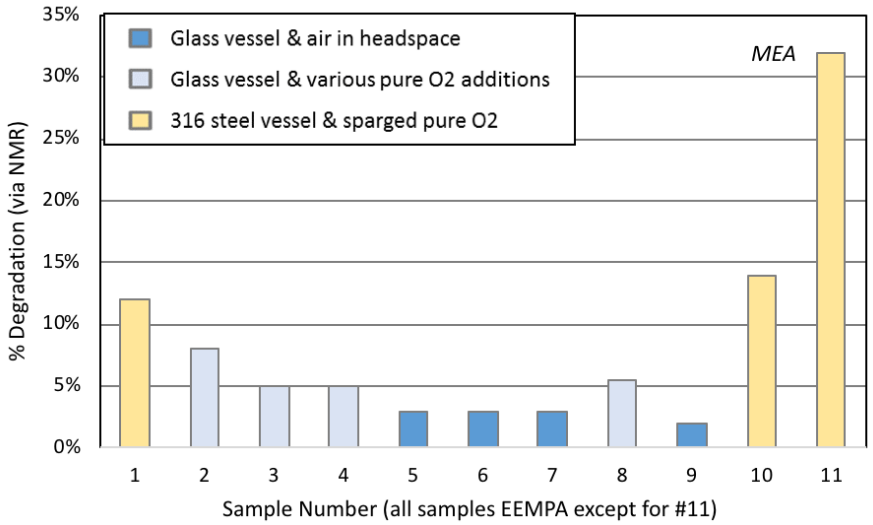
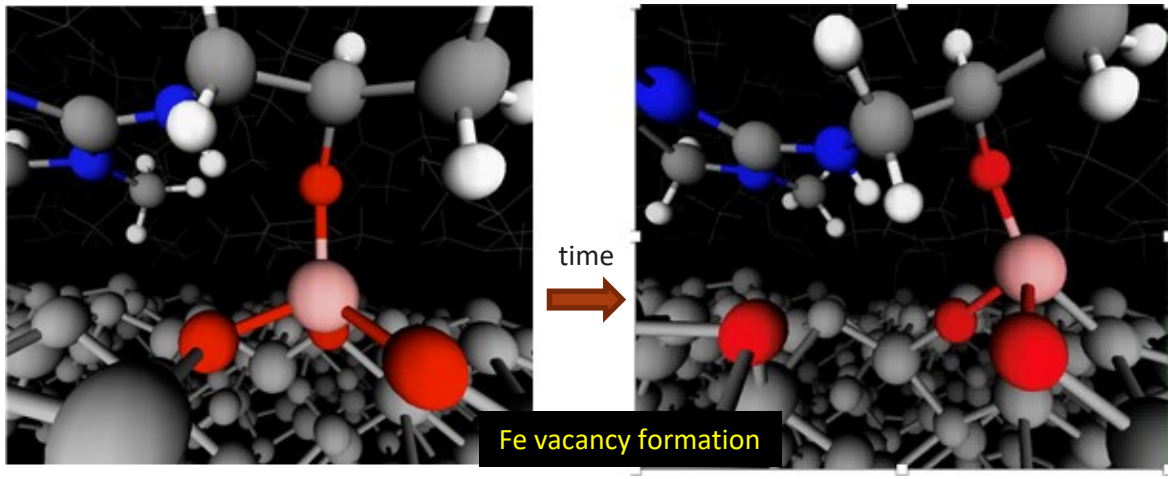
- These were extreme measurements (e.g. pure O_2)
- Higher degradation observed in steel vessels vs plastic or glass
- Lower degradation compared to MEA



Reaction Conditions: 16.5 h @ 100 ˚C

Molecular Modeling Insights: *Solvent Degradation*

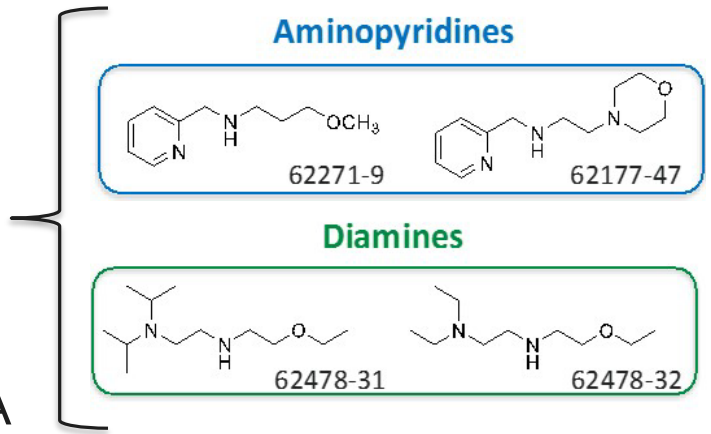
- Over time solvent ligand predicted to slowly pull iron off surface (expected to be similar for aqueous amines).
- Experimental data suggests that leached metals are catalyzing degradations.
- Therefore, plastics may reduced solvent degradation along with reducing CAPEX.



Fe: pink, O: red

Summary of Results to Date

- Comprehensive MD analysis and screening of ~100 solvent identified 4 new AP/DAs for future study
  - Low volatility (<0.0004 torr)
  - Low viscosity (<5 cP fully loading)
  - Energetics potentially better than EEMPA (currently at 2.1 GJ/tonne).



- DA solvents shown to wet some plastics better than steel.
  - Potential CAPEX saving of \$5/tonne CO_2 (packing only).
- For all solvents (incl. aqueous amines) steel interfaces not chemically inert
  - Could lead to both corrosion and solvent decomposition

Future Work

- BP2 (current): Focus on oxidative degradation and hydrolysis
- BP3: Focus on nitrosation
- Continue to engage commercial partners on the newest CO_2BOL solvents (i.e. feed the pipeline)

Publication Outputs

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- **Accepted Manuscripts:**
  1. "Directed Hydrogen Bond Placement: Low Viscosity Amine Solvents for CO_2 Capture." *ACS Sustainable Chem. Eng.*, **2019**, 7 (8), pp 7535–7542.
  2. "Attempting to Break the 2 GJ/tonne CO_2 Barrier; Development of an Advanced Water-Lean Capture Solvent From Molecules to Detailed Process Design." GHGT-14 Energy Procedia (April 29, **2019**). Available at SSRN: https://ssrn.com/abstract=3379731
  3. "Are Water-Lean Solvents a Game-Changer in Post-Combustion CO_2 Capture?" GHGT-14 Energy Procedia (April 29, **2019**). Available at SSRN: https://ssrn.com/abstract=3379760

- **Manuscripts in Process:**
  1. "Molecular-Level Overhauling of GAP-1/TEG Post Combustion Carbon Capture Solvents" This manuscript covers the molecular design, synthesis and characterization of the new DA compounds that were finalized in Tasks 3 and 4.
  2. "Interfacial phenomena of water-lean solvents on carbon capture infrastructure." This manuscript covers the interfacial phenomena and observed speciation and potential catalytic degradations of water-lean solvents on varied interfaces in Task 2.

- **Awarded United States Patents:**
  1. PNNL filed US patent application with Dr. Robert Perry, entitled "NOVEL DIAMINE SOLVENT SYSTEM FOR CO_2 CAPTURE - IPID 31486-E" filed on March 25, 2019. This patent application covers the molecular design of the new DA compounds that were finalized in Tasks 2 and 3.

Acknowledgements

- **Office of Fossil Energy and NETL:** Andy Aurelio (NETL PM), Lynn Brickett, and John Litynski
- **PNNL Team:** Dave Heldebrant (PM) Phillip Koech, Deepika Malhotra, Kat Grubel, Vanda Glezakou, Roger Rousseau, Mahn-Thuong Nguyen, Richard Zheng, and Andy Zwoster
- **CCSI2 Team:** Mike Matuszewski, et al.

Questions?