Carbon Capture, Utilization, Storage and Oil and Gas Technologies Integrated Review Meeting, Pittsburgh, PA, August 26-30, 2019

Advancing Post-Combustion CO_2 Capture through Increased Mass Transfer and Lower Degradation

FE-00031661

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University of Kentucky - Center for Applied Energy Research

caer.uky.edu/power-generation/

Project Overview

- Funded as part of the Novel and Enabling CO_2 Capture Technologies
- Project consists of three primary area: (1) using novel 3-D printed polymeric absorber packing; (2) modifying solvent physical properties to increase solvent wetting on absorber packing; (3) developing an effective process to decompose nitrosamines from waterwash systems

- **Project Period:** 10/1/2018 - 9/30/2021 (3 years)
- **Funding**: Federal - $2.9M; CS - $725K; Total - $3.6M

Center for Applied Energy Research

Lawrence Livermore National Laboratory

Project Objectives

Developing process enhancements/technologies that can be broadly applied to amine-based post-combustion CO_2 capture systems:

1. 3-D printed hydrophobic/hydrophilic packing material to increase solvent turbulence and CO_2 mass transfer

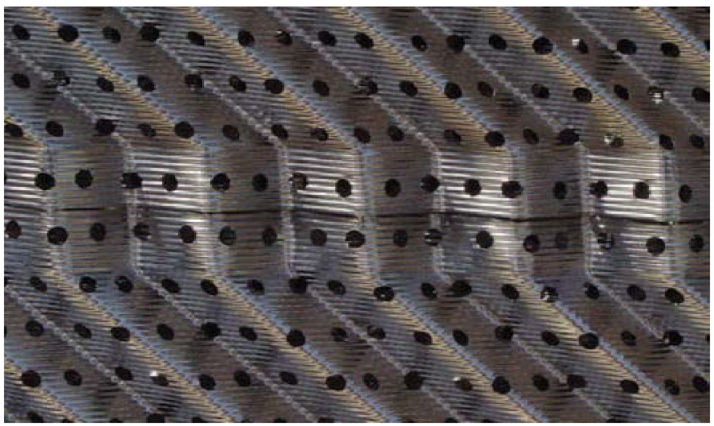
2. A better understanding of solvent physical properties, specifically those related to increasing CO_2 mass transfer

3. Nitrosamine decomposition using electrochemical decomposition within the waterwash

How does packing wettability translate to CO_2 Flux?

- $$flux = A \cdot k_G \cdot (P^{g}_{CO_2} \text{-} P^{*}_{CO_2})$$

Where $k_G \propto \frac{\sqrt{D_{CO_2} \cdot k_2 \cdot [amine]}}{H_{CO_2}}$



	MEA	PZ	MDEA
Rate Constant	5.94	69.21	0.004
Self-concentrated amine	1.0	3.5	~1
Calculated Kg' impact from [M]	1	1.87	~1
Calculated Kg' impact from k_2	1	3.41	0.03
Calculated Kg' Overall	**1**	**6.39**	**0.03**
Measured Mass Flux (WCC@0.1)	1	2.20	0.18

- Most solvents do not take full advantage of packing
- Improved mixing can help to overcome this issue

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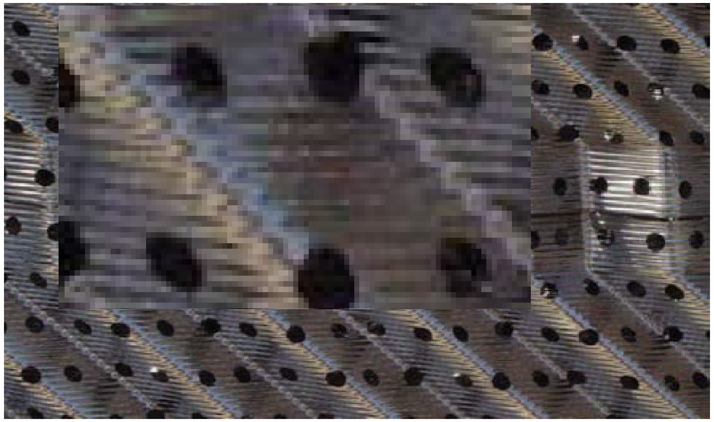

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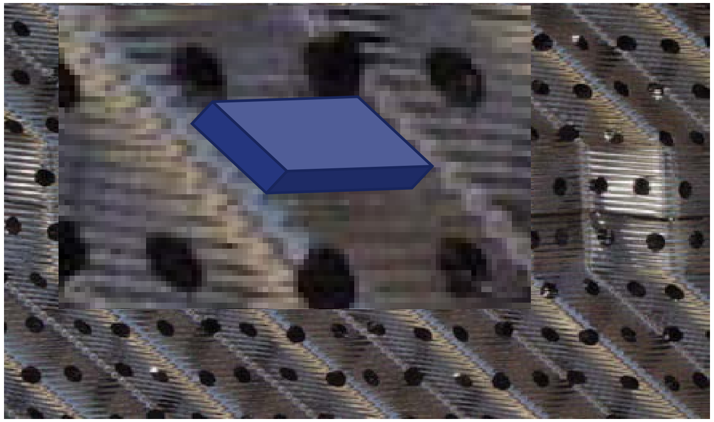

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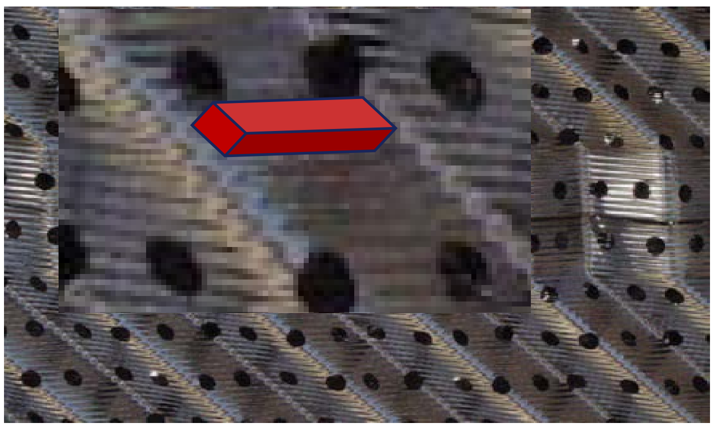

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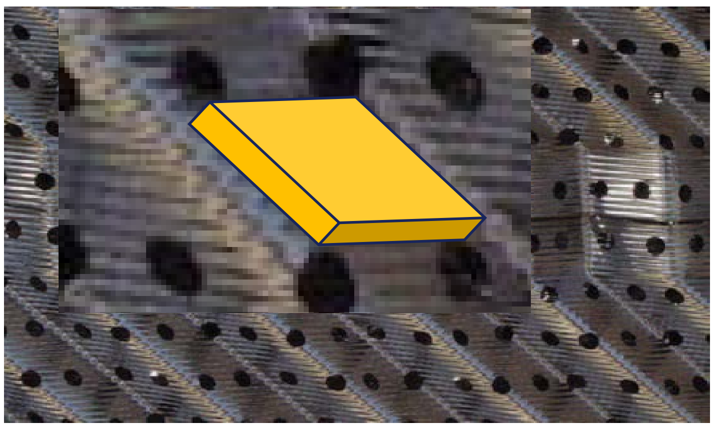

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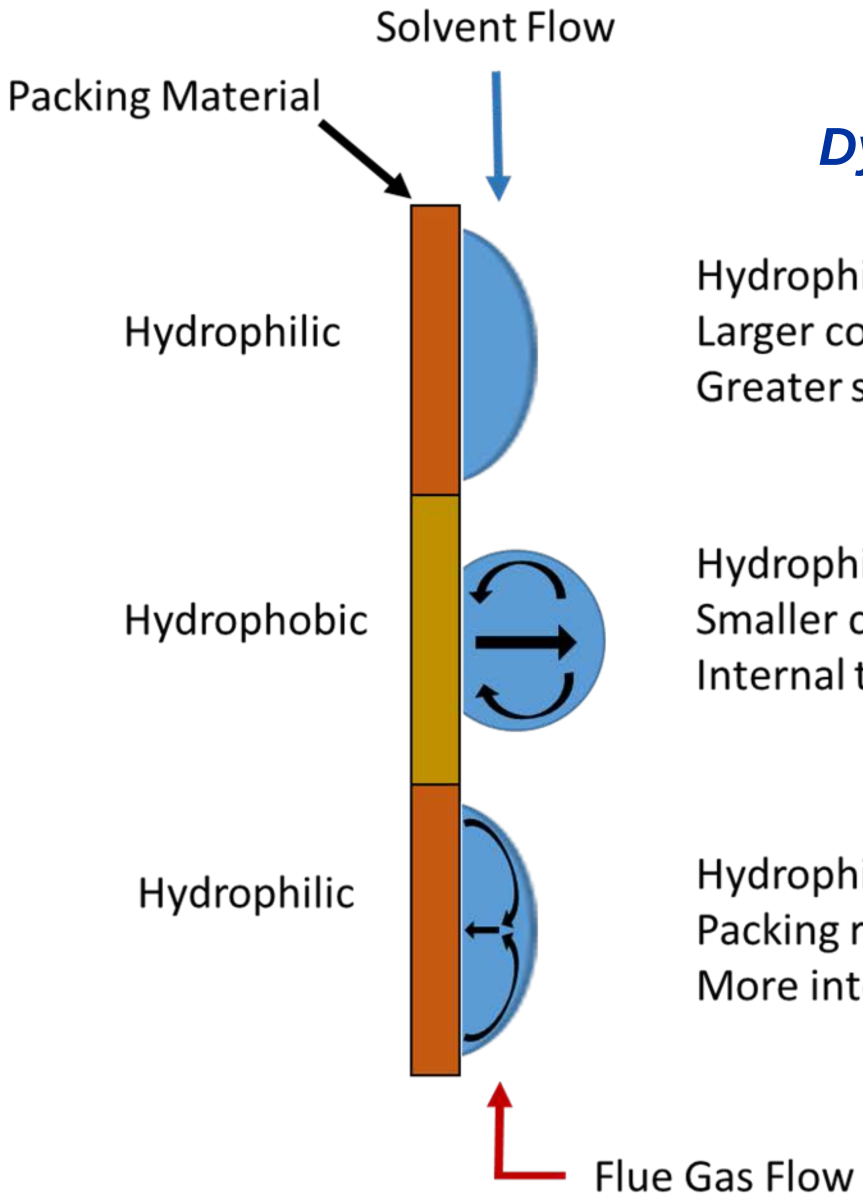
Technology Background – Dynamic Packing



Dynamic Packing + 3D Printing

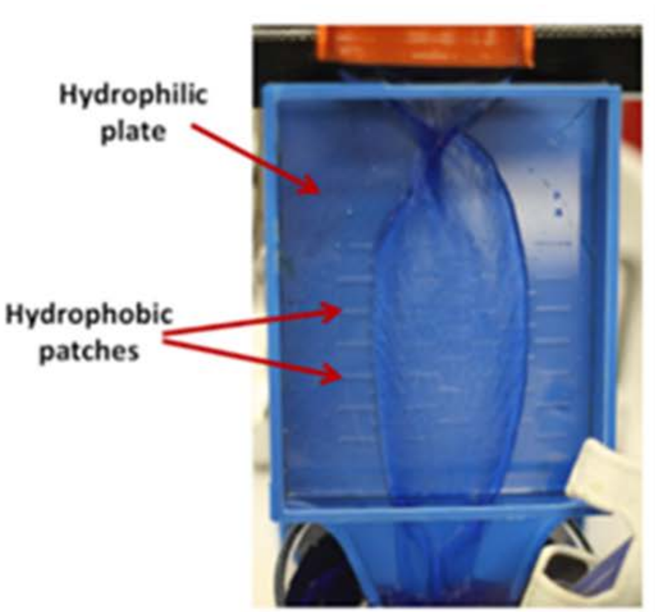
Hydrophilic-hydrophilic interaction
Larger contact angle
Greater surface contact

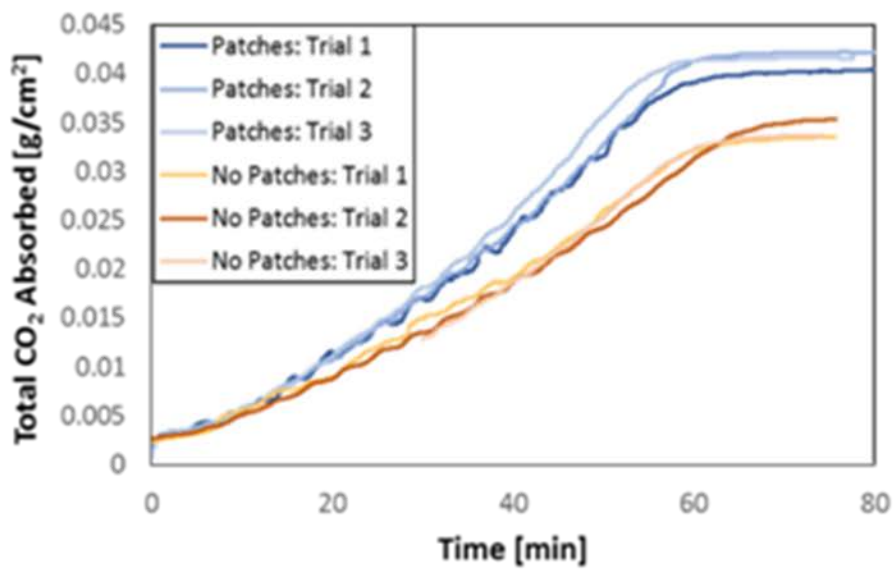
Hydrophilic-hydrophobic interaction
Smaller contact angle
Internal turbulence from solvent drawing up

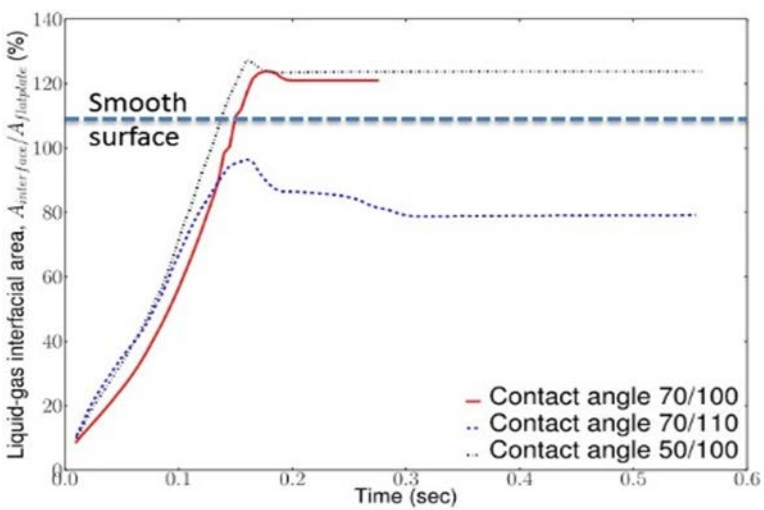
Hydrophilic-hydrophilic
Packing re-wetting
More internal turbulence and mixing

Surface wetting and contact angle

Technology Background – Dynamic Packing







Target: Polymers that are stable to amine solvents and typical absorber temperatures

Contact angle differences between the two polymeric materials of >15° up to 30°

Stolaroff, 2017 NETL CO_2 Capture Technology Meeting

Polymer stability when exposed to amine solvents

High Density Polystryene (HDPS)

Acrylonitrile butadiene styrene (ABS)

Nylon

Polylactic Acid (PLA)

1. Measure contact angle of water (reference) and CO_2-rich solvent
2. Measure mass, thickness and tensile strength of each coupon
3. Place coupons into CO_2-rich solvent for 1000 hrs
4. Re-measure and calculated changes to mass, thickness and tensile strength
5. Re-measure contact angle of water (reference) and CO_2-rich solvent
6. Repeat measurements after exposure at 60 °C for 1000 hours

Polymer stability when exposed to amine solvents

ABS

HDPS

Nylon

PLA

ABS
Mass, thickness and contact angle unchanged

HDPS
Mass, thickness and contact angle unchanged

Nylon
Mass, thickness and contact angle unchanged

PLA
Coupon unstable after 60 °C amine exposure

Polymer	Treatment (1000 hrs)	Contact Angle w/water	Contact angle w/amine
High density polystyrene (HDPS)	Before	82.57	62.19
	After amine exposure at 60 ºC	82.87	70.51
ABS	Before	84.51	69.03
	After amine exposure at 60 ºC	84.06	69.04
Nylon	Before	63.72	56.87
	After amine exposure at 60 ºC	63.35	57.65

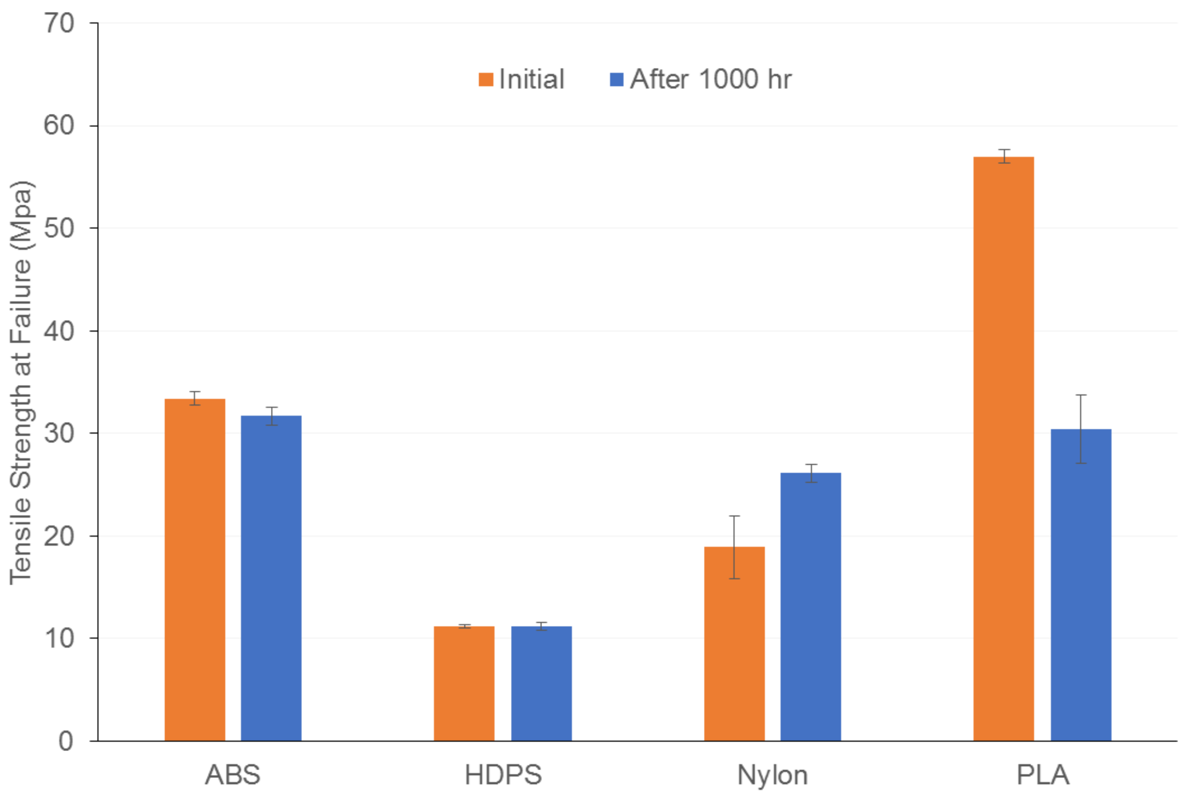
Polymer stability when exposed to amine solvents

ABS

HDPS

Nylon

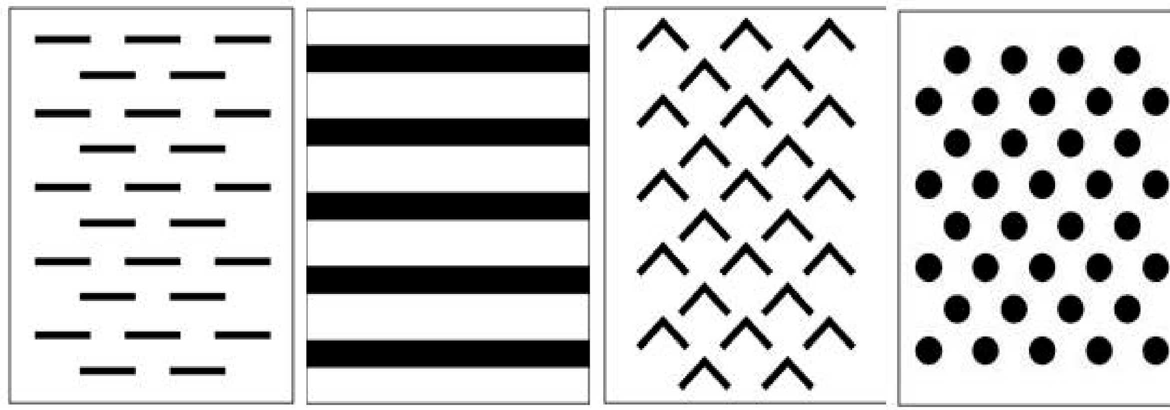
PLA



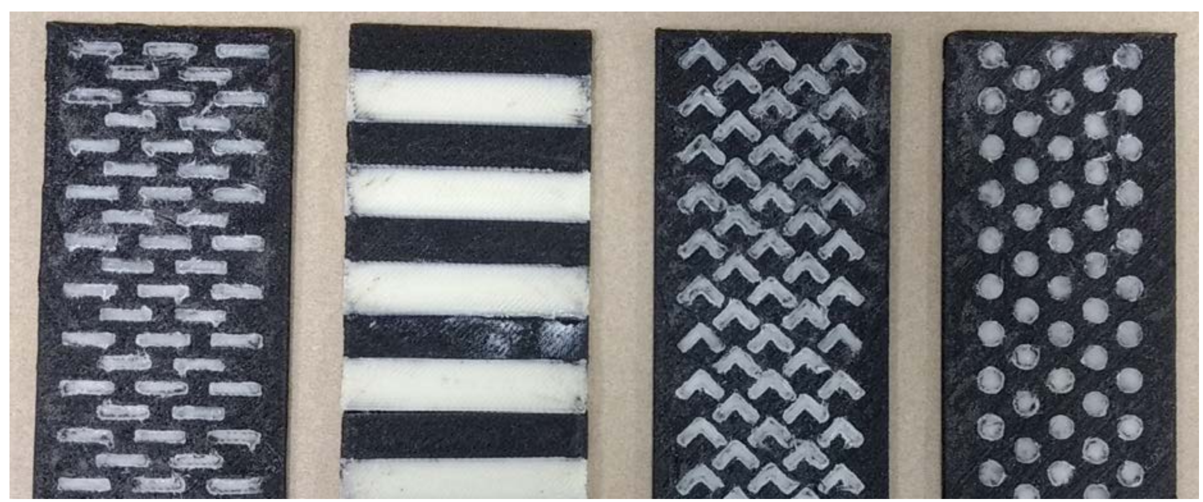
Dynamic Packing Patterns

- LLNL has an initial finite element model to help tune the pattern of the hydrophilic/hydrophobic areas. The model uses a Multiphysics approach combining level set and laminar flow equations (turbulent conditions can also be applied)

- Post treatments can also be used to modify the hydrophobicity and hydrophilicity of the base polymers

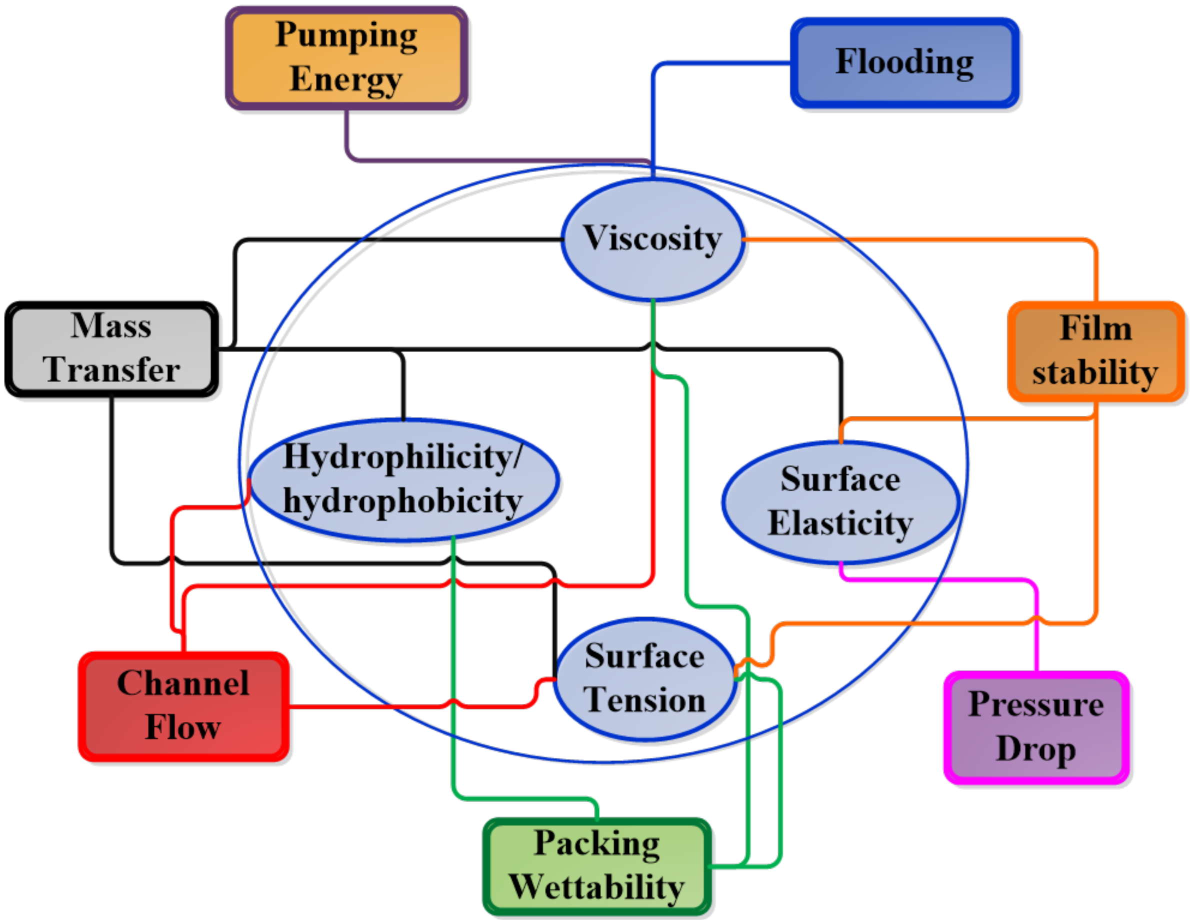


- Currently performing FDM test printing of ABS/Nylon and evaluating solvent wettability and CO_2 capture enhancement at the lab-scale

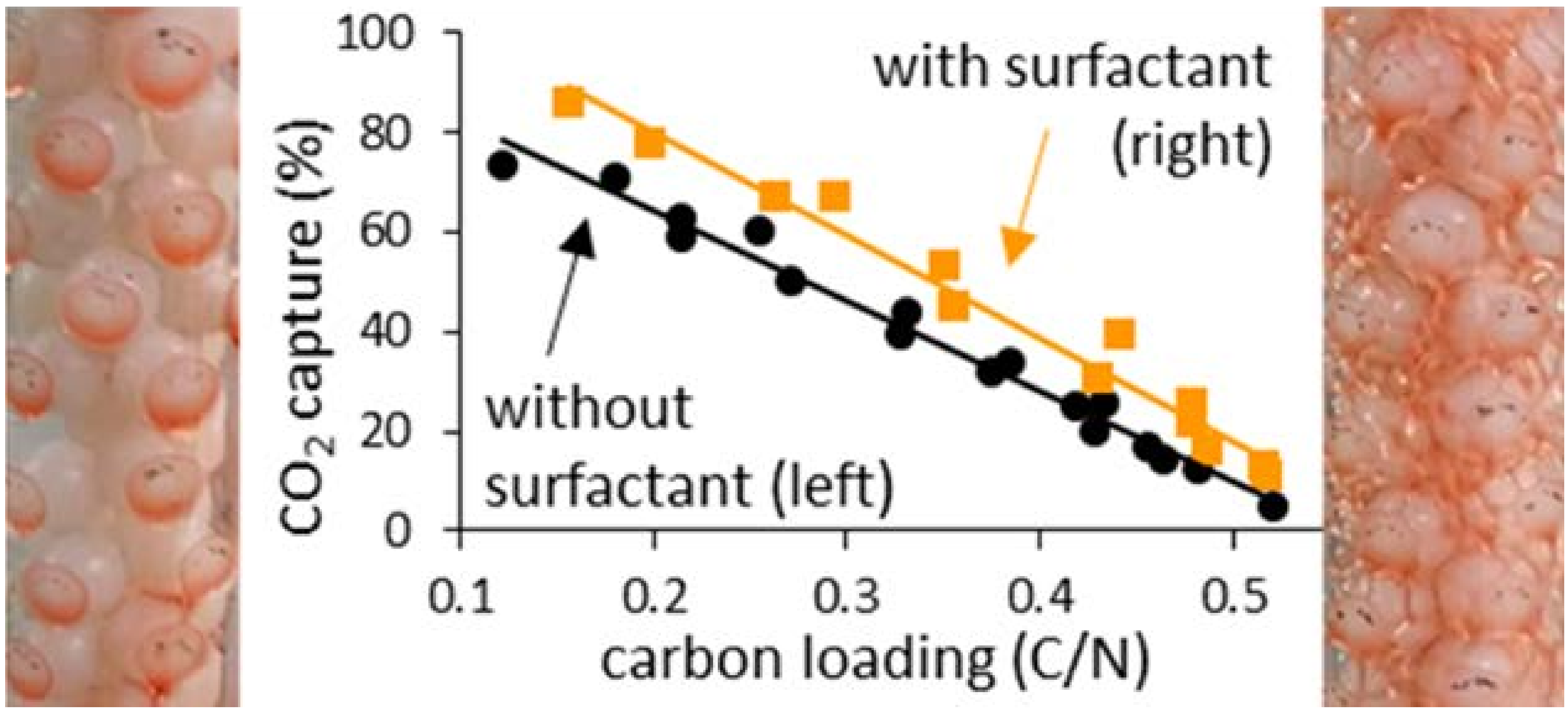


Physical Properties of Amine Solvents

- Focus on ways to modify physical properties of solvents to increase CO_2 mass transfer (decrease diffusion resistance)
- Additives can be used to modify physical properties, including surface tension and contact angle (wettability)

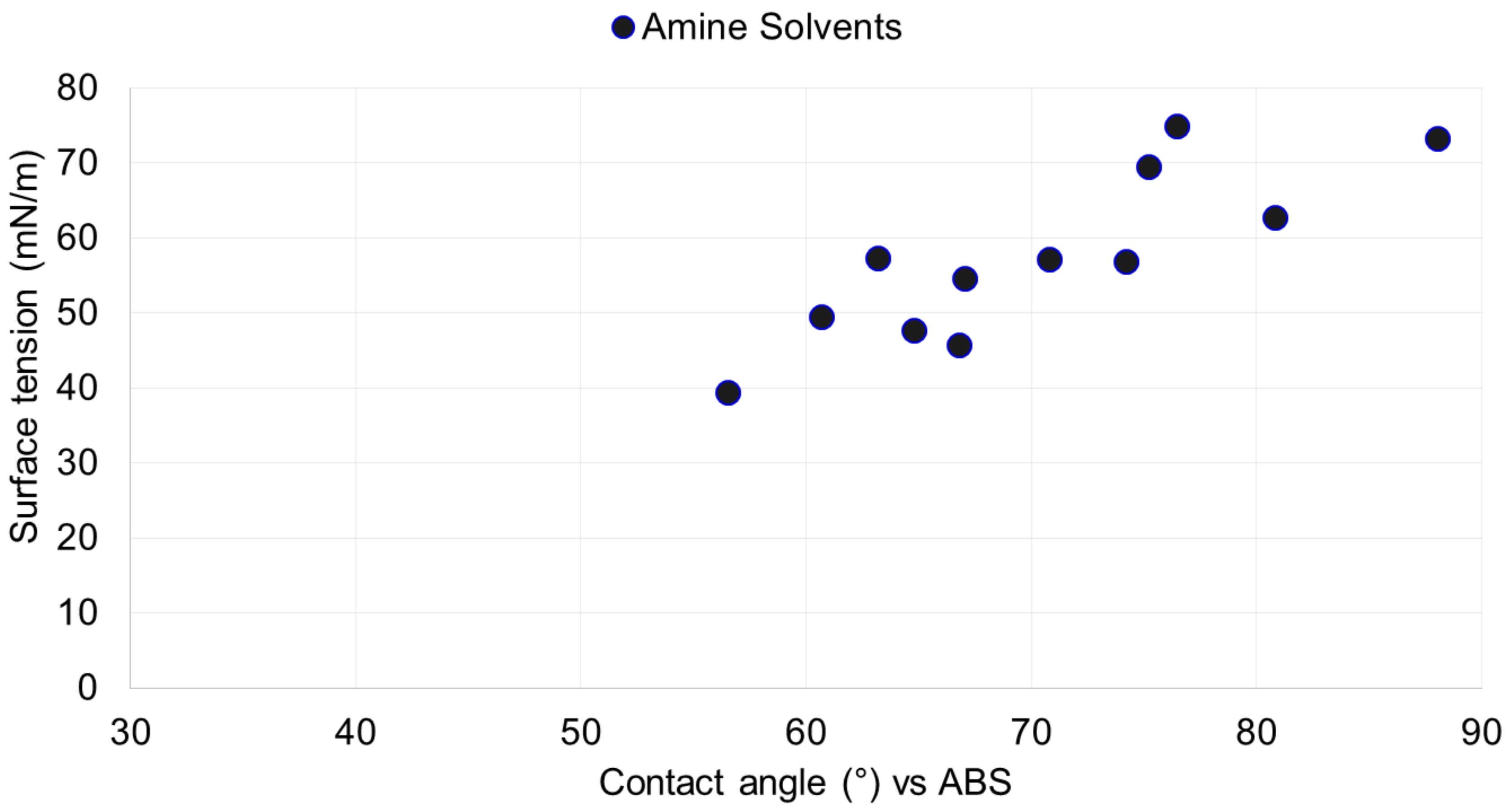


Mass Transfer Enhancement with Additives



Increased CO_2 mass transfer was observed as the result of micro-bubble/froth formation in solutions containing a small amount of surfactant-type additive

Modify Physical Properties of Amine Solvents



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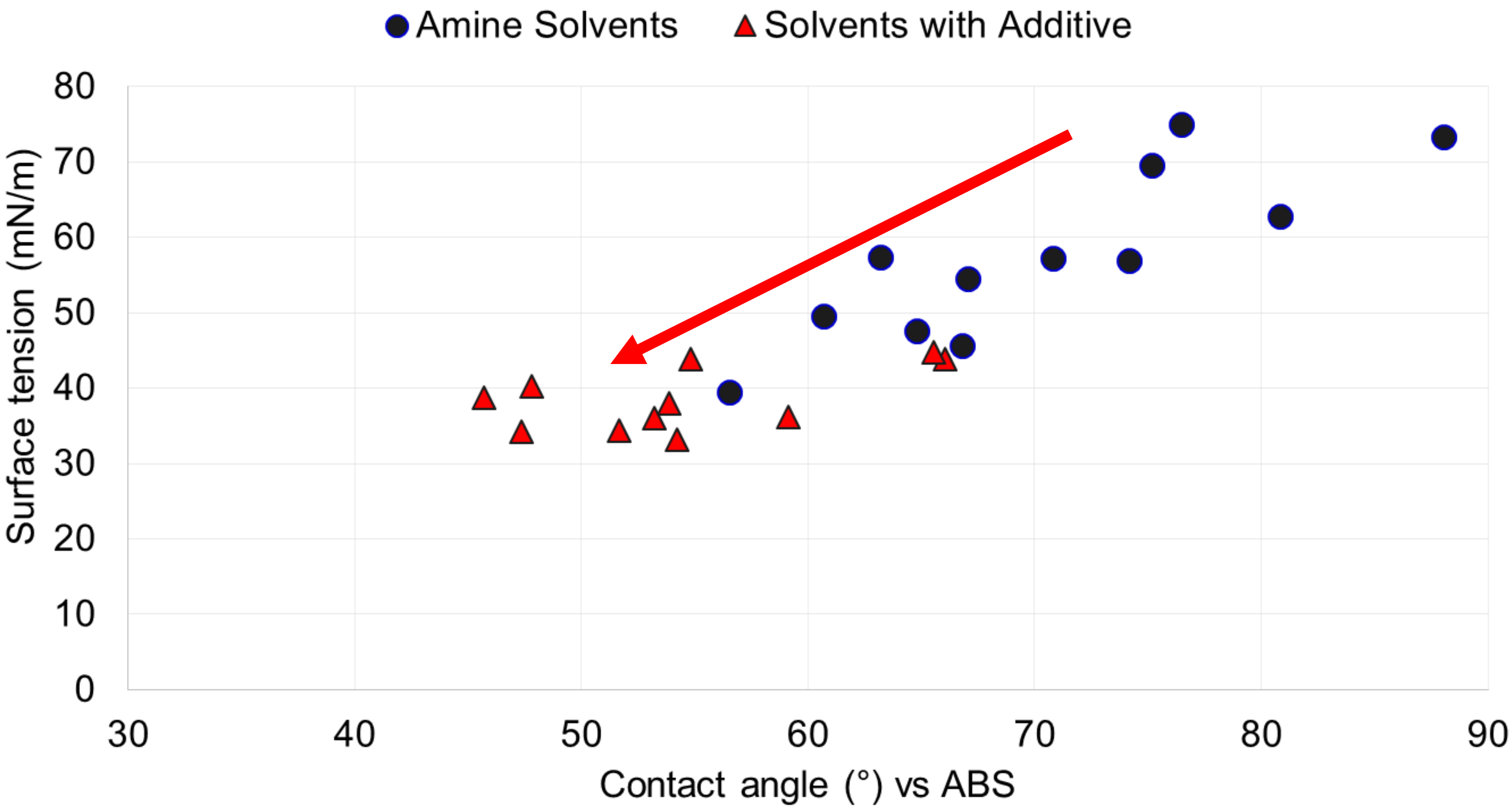
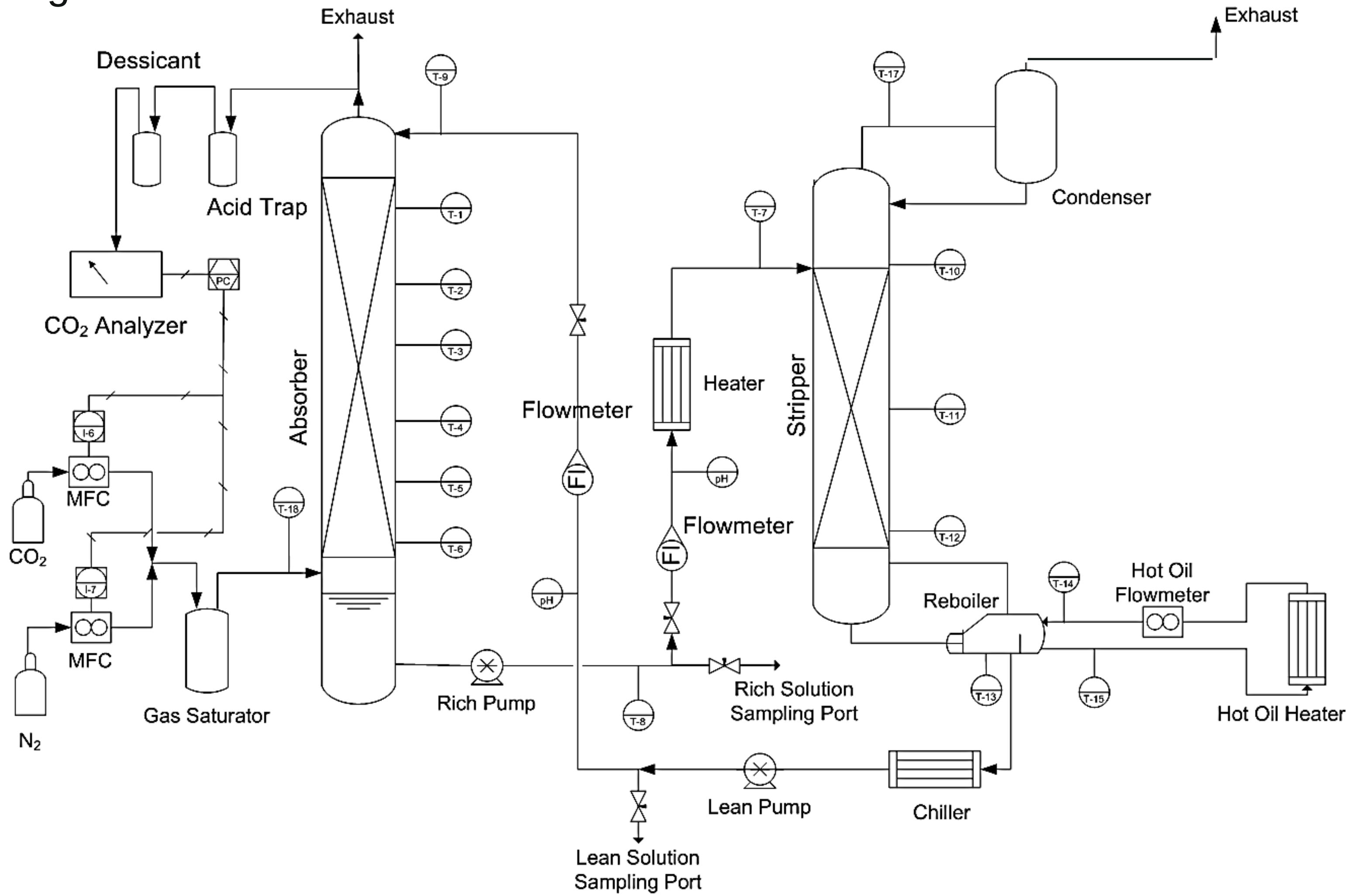


A very small amount of surfactant-type additive (< 0.1%) can be used to reduce the surface tension (ave. ↓30%) and contact angle (ave. ↓23%) of common amine solvents, helping to increase the wettability of these solvents on the hydrophobic polymer packing

Small-Bench Testing

Next steps: Fabrication of 3” diameter Dynamic Packing sections and installation into our small-bench CCS, followed by integrated solvent/packing testing in Phase II



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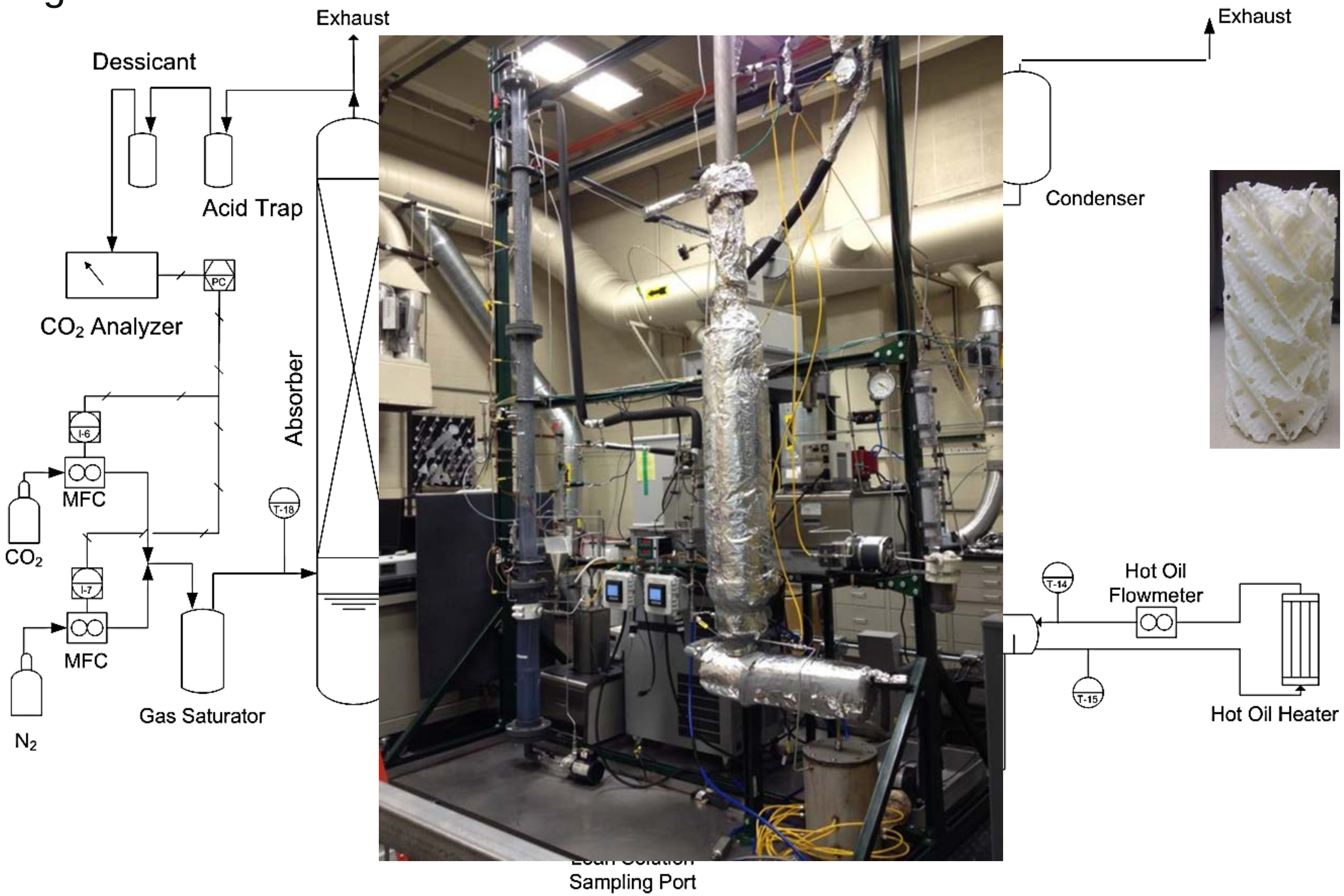
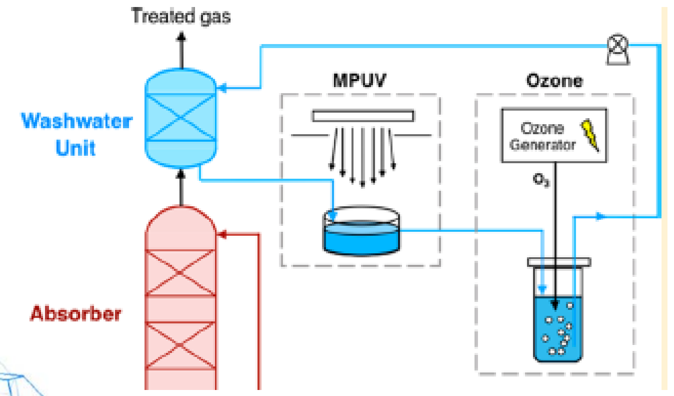
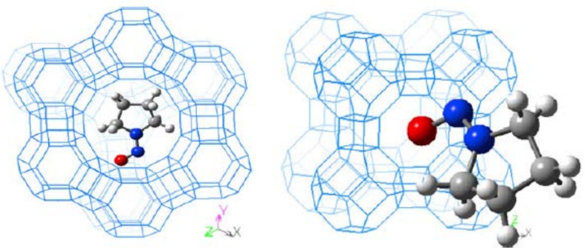


Nitrosamine Mitigtion

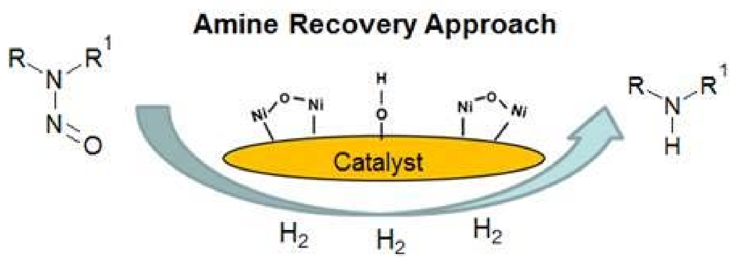
Photochemical Reduction (UV)
w/ Ozone treatment



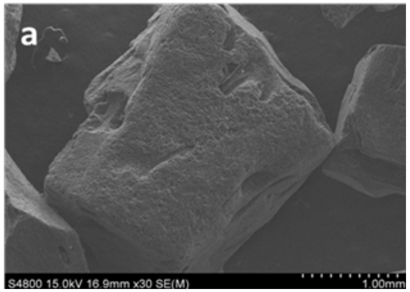
Zeolite Membrane



Catalytic Hydrogenation

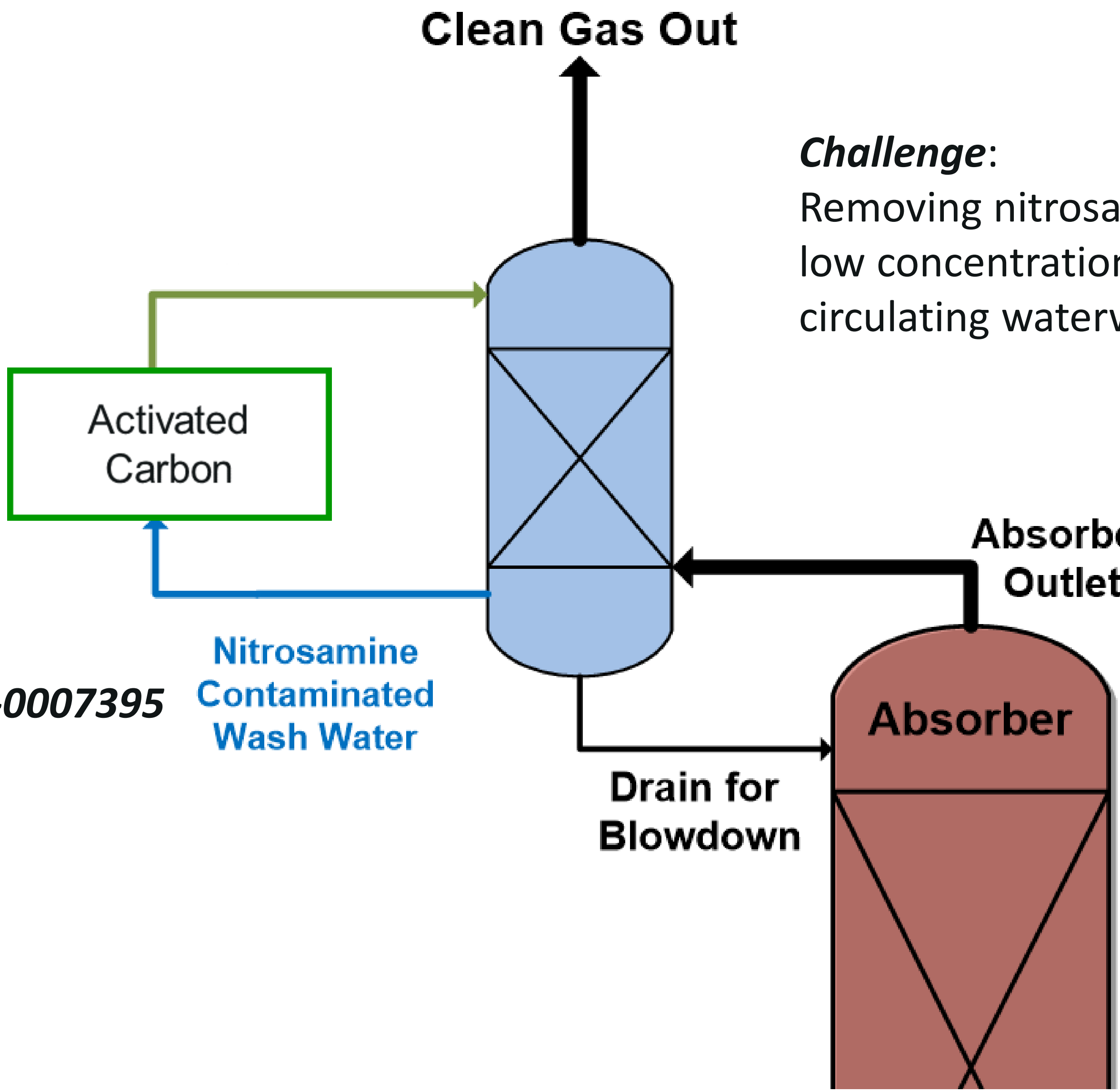


Activated Carbon Adsorption



Int. J. Greenhouse Gas Control. 2015, 39, 158; Environ Sci. Technol. 2015, 49, 8878; Environ. Chem. Lett. 2014, 12, 139; Environ. Sci. Technol. 2017, 51, 10913

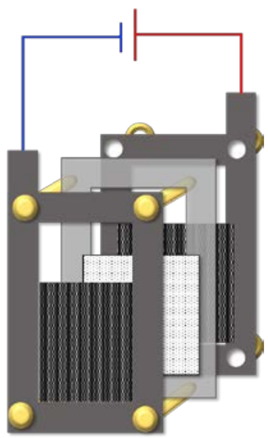
Nitrosamine Mitigation

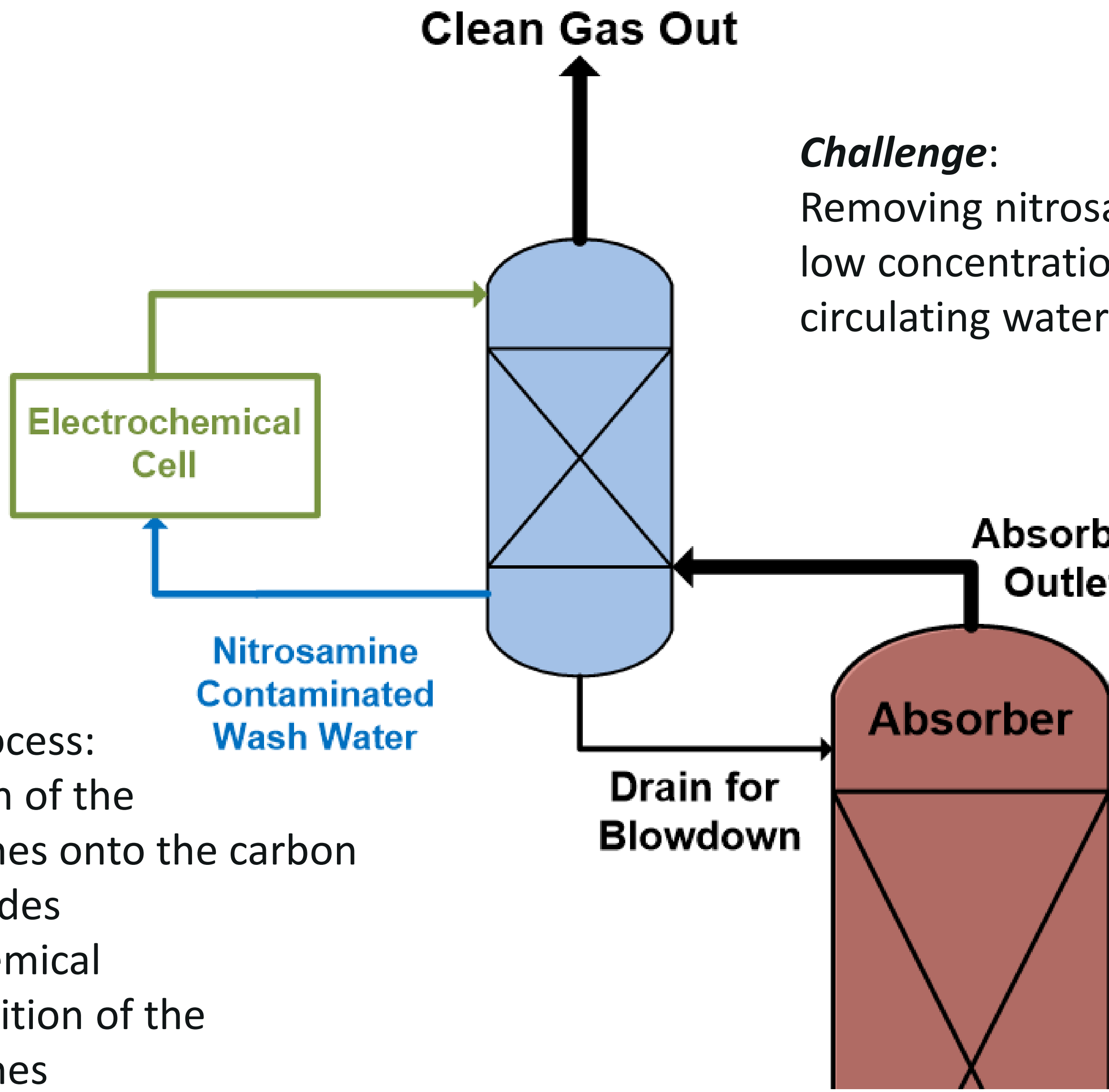


Challenge:
Removing nitrosamines at very low concentrations from the circulating waterwash solution

Part of DE-FE-0007395

Nitrosamine Mitigation





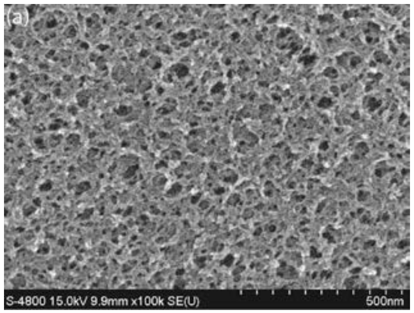
Challenge:
Removing nitrosamines at very low concentrations from the circulating waterwash solution

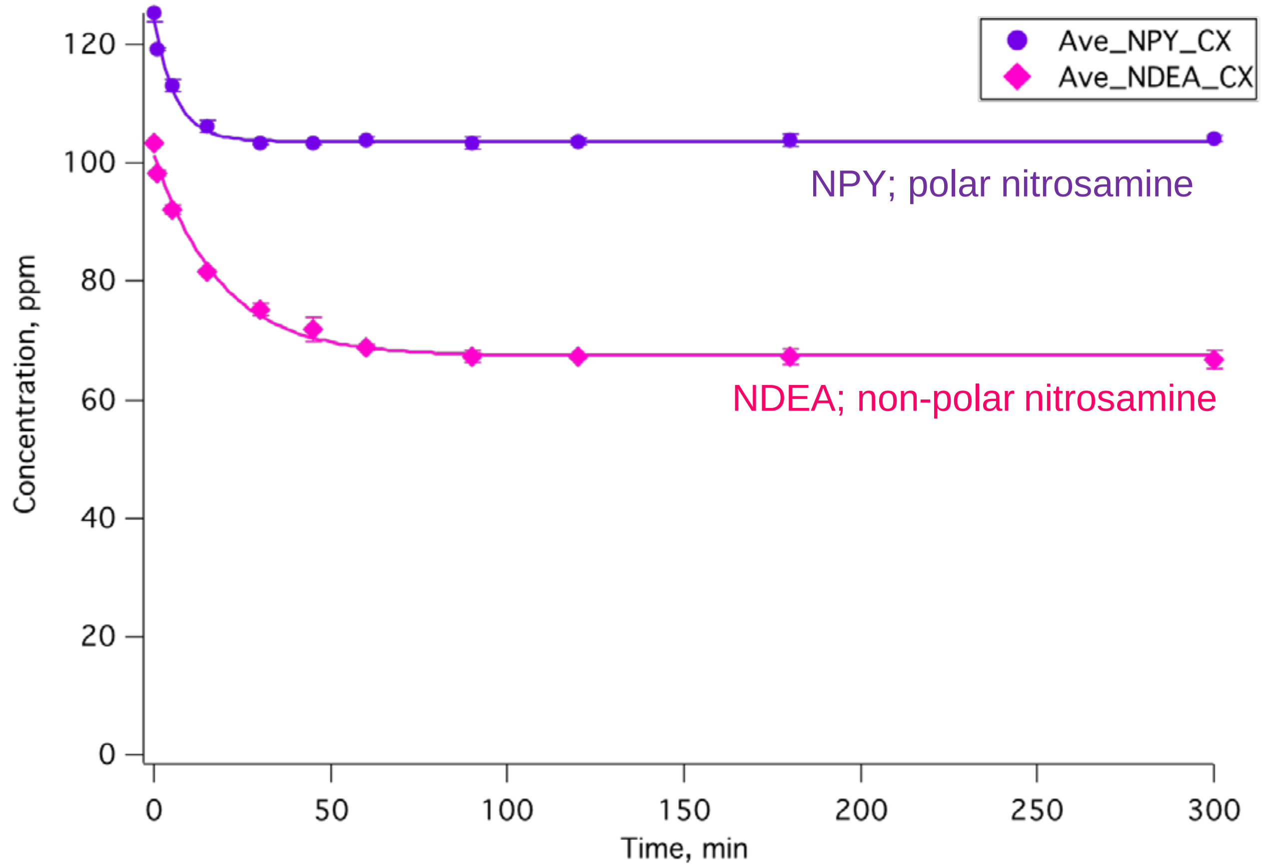
Two-step process:

1) Adsorption of the nitrosamines onto the carbon CX electrodes
2) Electrochemical decomposition of the nitrosamines

Current Progress– Nitrosamine Mitigation

Nitrosamine adsorption onto high surface area, high porosity, highly conductive Carbon Xerogel (CX) electrodes





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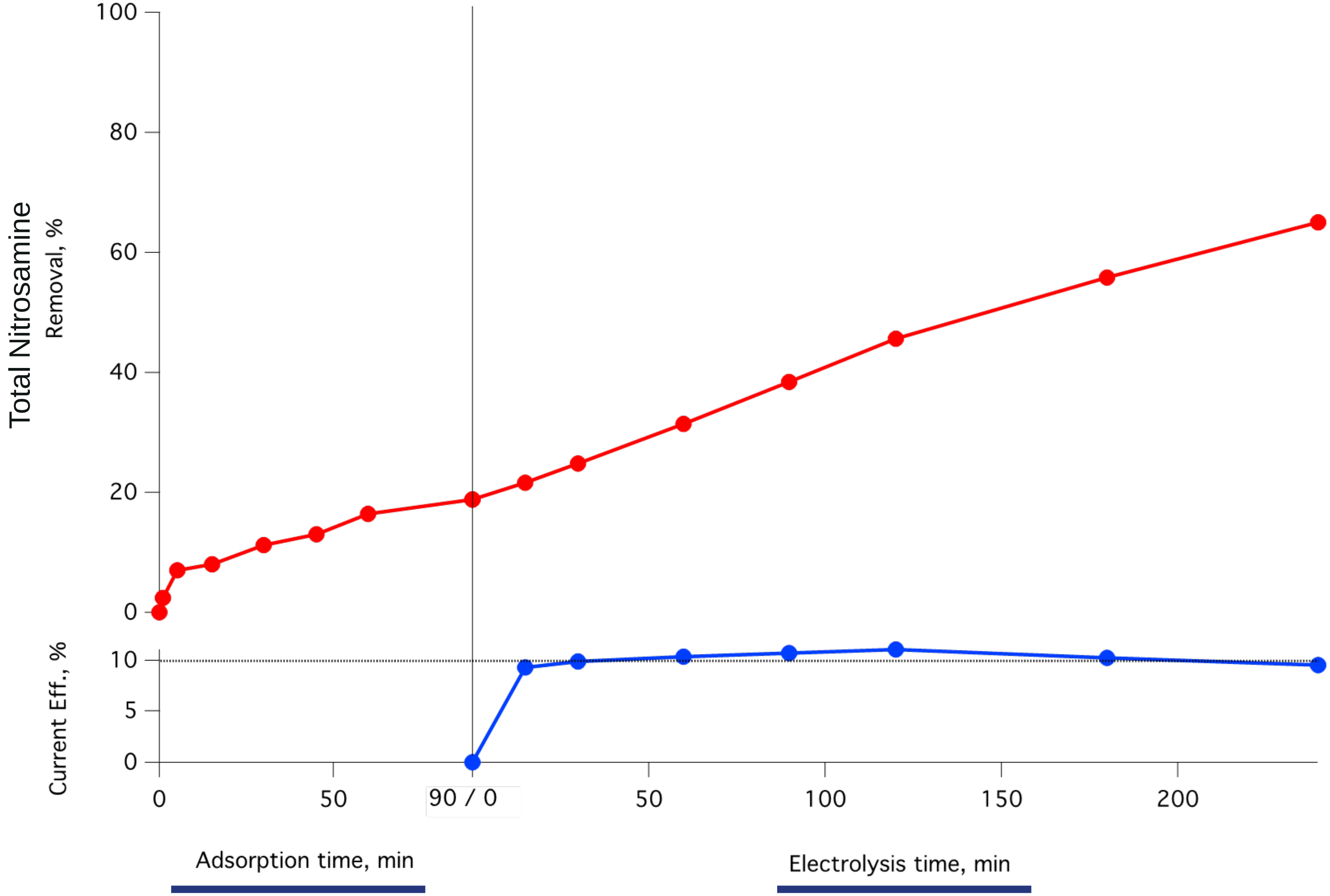
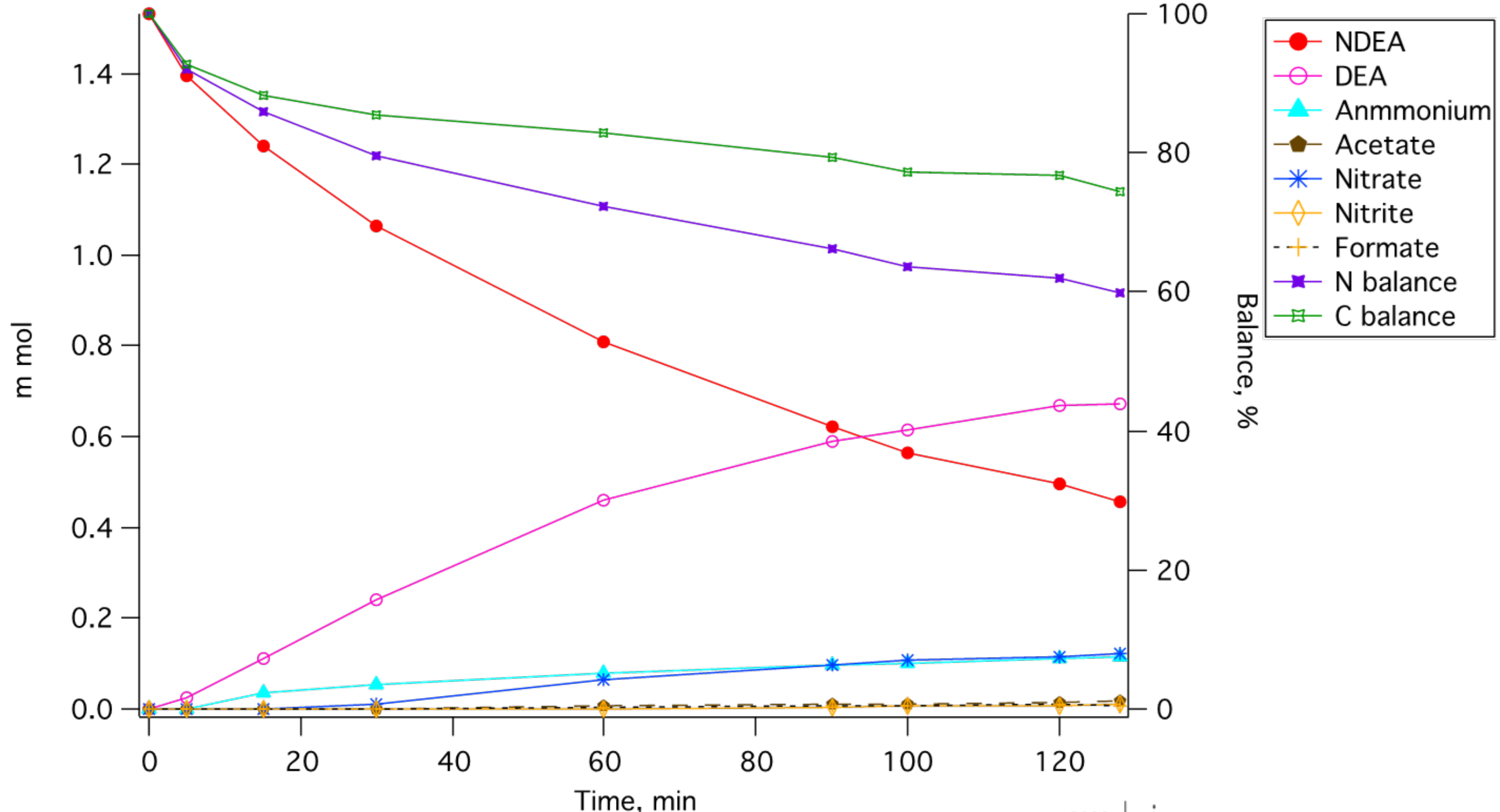
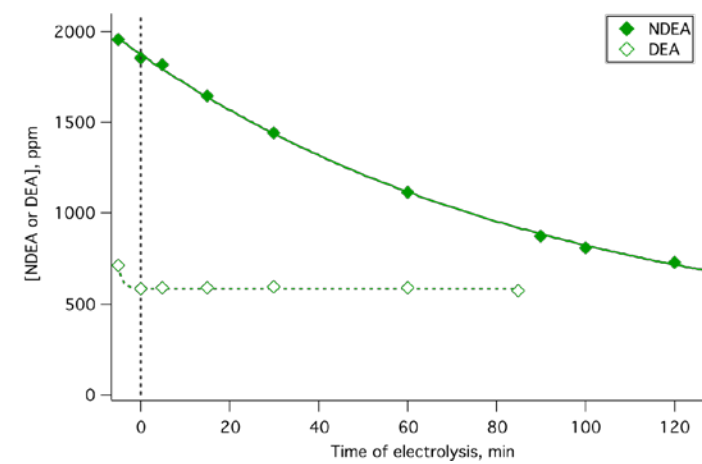


Target: >60% nitrosamine removal with a Faradic (charge) efficiency of >10% from a waterwash solution

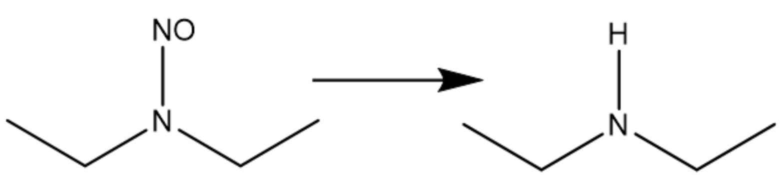
Surface modifications of the CX can be used to increase adsorption and/or electrochemical reaction rates

Current Progress– Nitrosamine Mitigation





Primary byproduct is regeneration of the parent amine through a reduction reaction



with minimal additional amine decomposition

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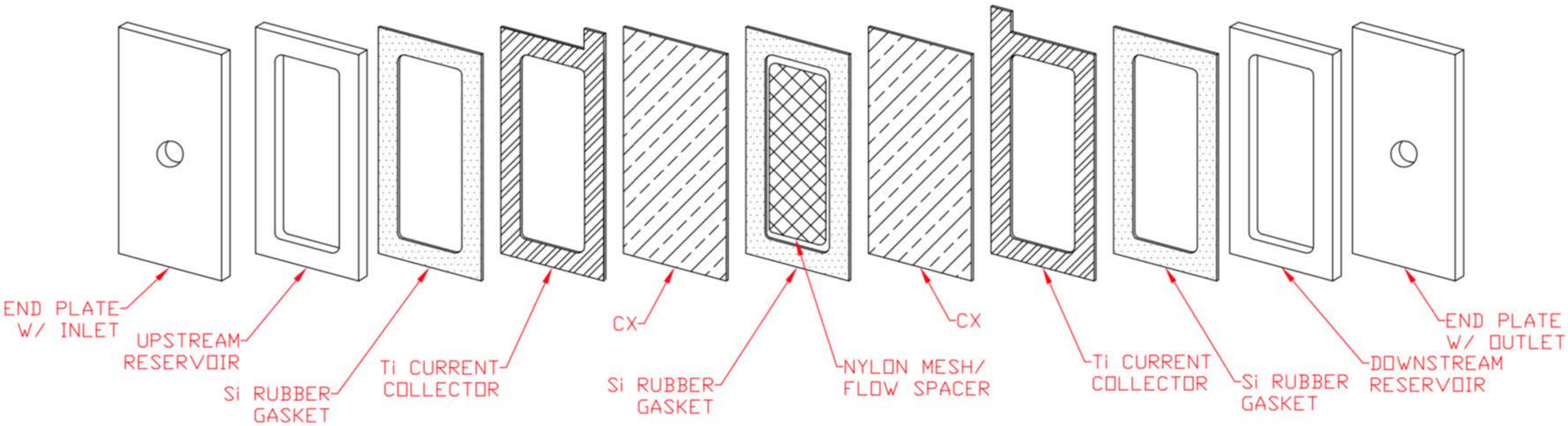
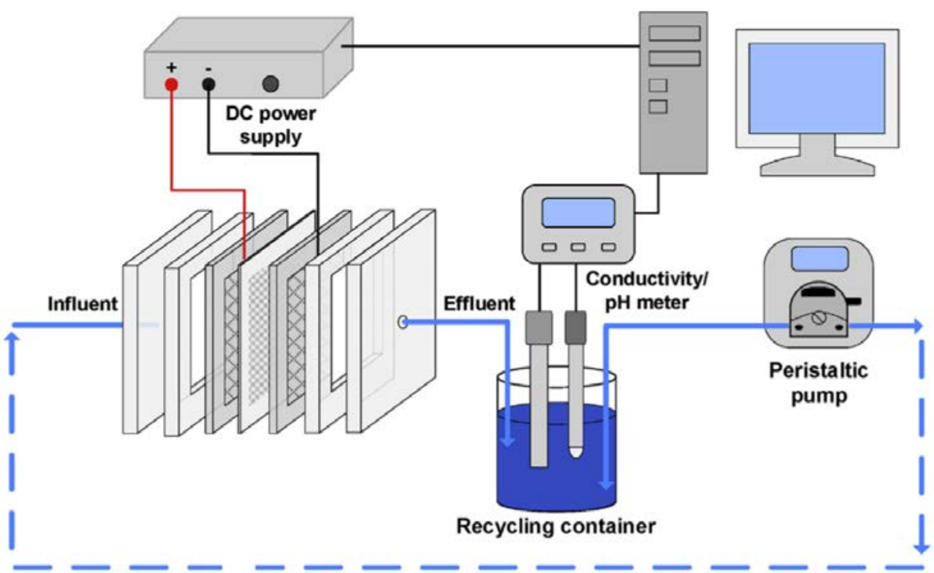


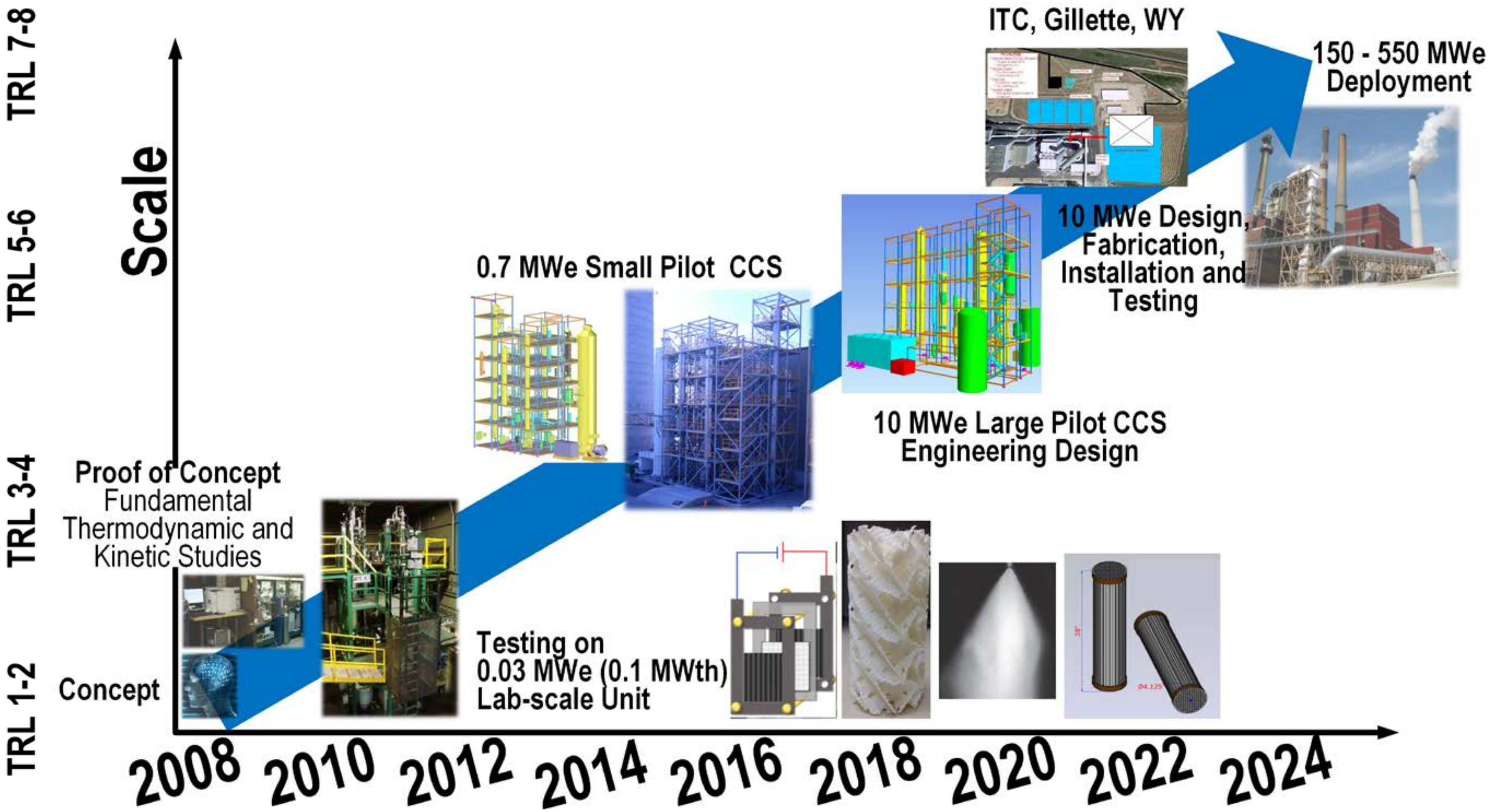


Next steps: Fabrication of flow-through cell and test using authentic waterwash collected at our 0.7 MWe Small Pilot CCS

Key Knowledge Gained

- 3D printed dynamic packing is a promising and potentially lower-cost alternative for amine CO_2 capture absorbers
- Amine solvent physical properties can be modified through the addition of additives to decrease surface tension and increase wettability on hydrophobic packing surfaces
- Nitrosamine decomposition can be achieved using an electrochemical treatment process.

Technology Development Pathway



Acknowledgements

- DOE-NETL: Andy Aurelio, José Figueroa, Lynn Brickett
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UK Center for Applied Energy Research

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