An Advanced Catalytic Solvent for Lower Cost Post-combustion CO_2 Capture in a Coal-fired Power Plant

Award # DE-FE0012926

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Project Overview

Overall Objective: Address technical hurdles to developing an integrated process focused on a catalyzed solvent utilizing homogeneous catalyst.

Project Details

- **Benefit from multiple CAER technologies: solvent; catalyst, membrane, process**
- **Project cost:**
  - **DOE share:$2.97M**
  - **Cost share:$742K**
- **Period performance:** 10/1/2013 – 9/30/2016

Project Objectives

- Build towards low-cost CO_2 capture system via Integration of multiple CAER technologies
- To verify an advanced catalytic solvent with integrated membrane dewatering for solvent enrichment in our 0.1MW pilot plant (Proof of concept)

CAER	CMRG	SMG	WorleyParsons
• Project management • Catalytic solvent testing • ASPEN modeling	• Technical support	• PPE recommendation • EH&S analysis	• Front-end engineering support • TEA

Project Schedule and Milestones

	Previous work	Current Project				Future Development	
Yr	2011-2013	**2013**	**2014**	**2015**	**2016**	2017-2020	>2020
BP	-	**1**	**1/2**	**2/3**	**3**	-	-

Fundamental Development; Proof-of-Concept

Slipstream ~2 MWth

~20 MWe

Laboratory Validation and Scale-up

- **Solvent Optimization**
- Milestone: VLE and model regression

- **Membrane Enrichment**
- Milestone: 5% enrichment over 5hr

- **Catalyst Scale-up**
- Milestone: Develop method to produce 50g/batch

- *Milestone*: PPE recommendation & front-end engineering analysis

Parametric Testing on 0.1 MWth Unit

- **Catalyst Production**
- Milestone: 500g produced

- **Parametric Testing**
- Milestone: 100hr runs with and without catalyst completed

- **Membrane Enrichment**
- Milestone: 10% enrichment over 100hr and module design

Verification Testing on 0.1 MWth Unit

- **Verification Run**
- Milestone: 500hr verification run

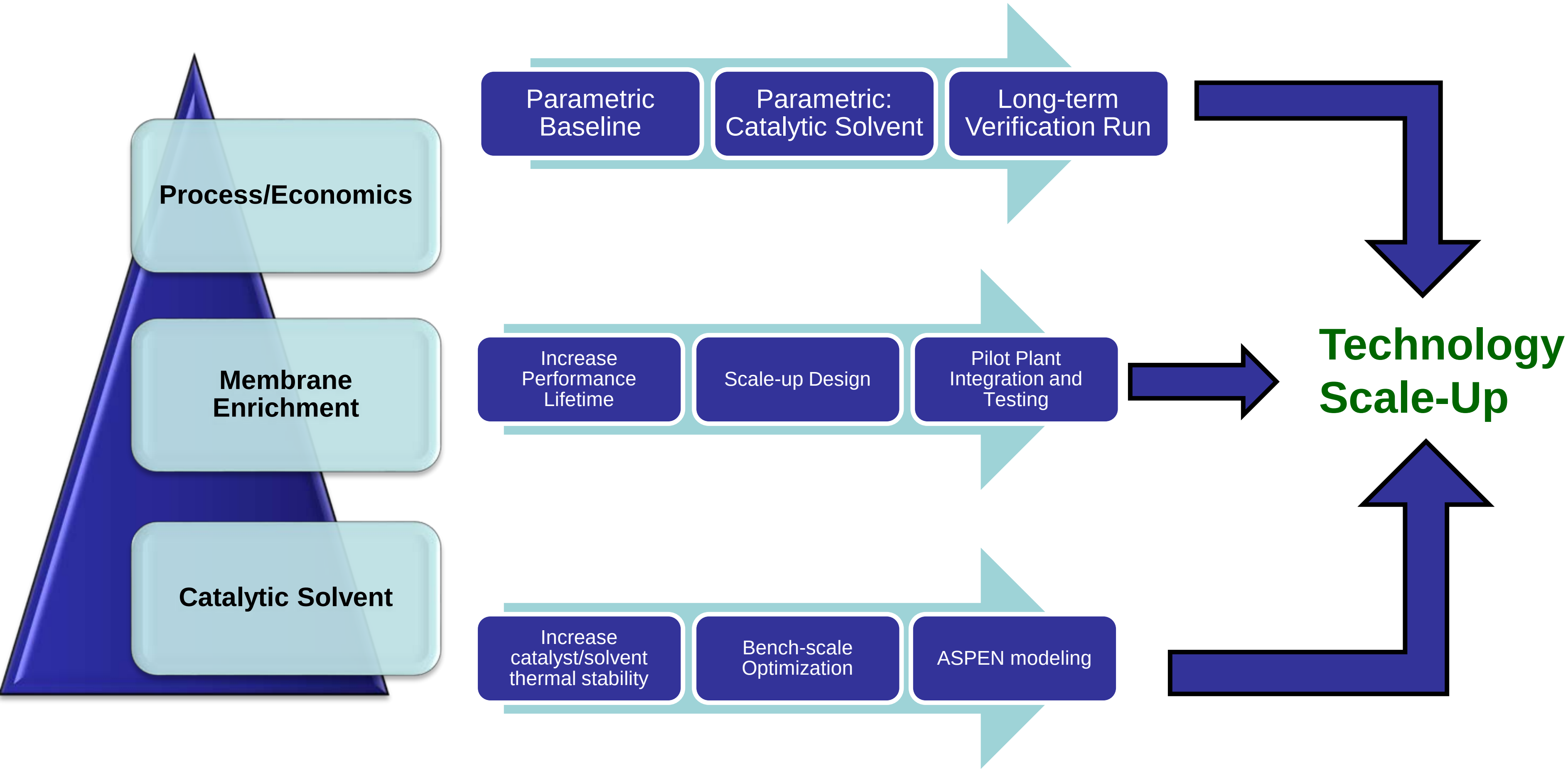
- **Membrane Enrichment**
- Milestone: Unit integrated and 20% dewatering observed

- **Techno-Economic Analysis**
- Milestone: TEA showing at least 20% reduction in energy cost compared to Case 12

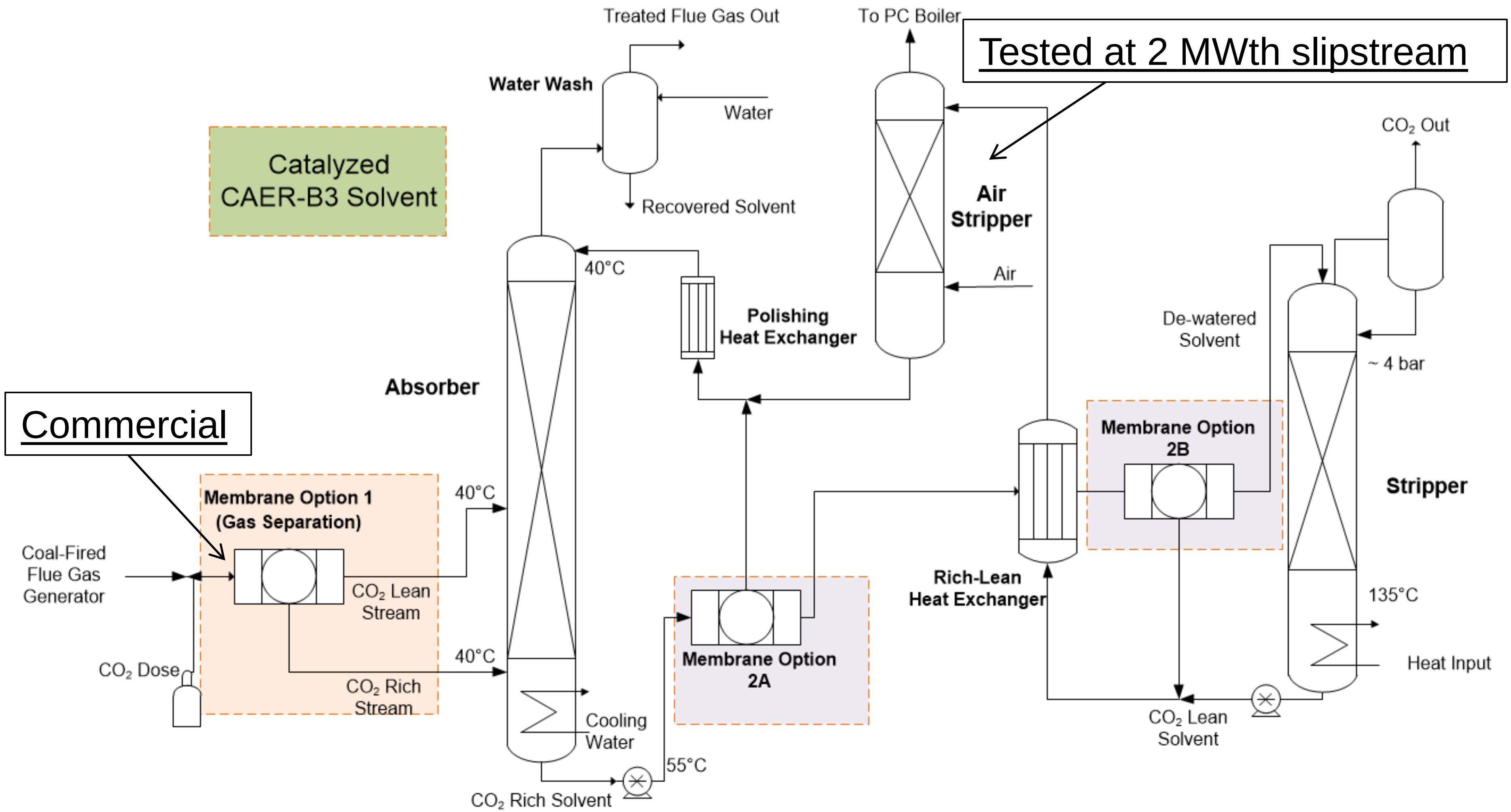
- **EH&S**
- Milestone: Favorable EHS assessment

Design and Work Plan

3-Prong Approach



CAER ad-CCS Process



Pre-absorber CO_2 enrichment and dewatered CAER-B3 used to lower the energy cost of CO_2 capture.

Catalytic Solvent CO_2 Capture

Advantages

- Potential for reduced capital cost for post-combustion CO_2 capture
  - Increased scrubber kinetics (smaller absorber)
- Potential for reduced energy consumption compared to reference case (MEA)
  - High α; cyclic capacity
  - High stripper temperatures/pressure
  - Less solvent make-up rate

Challenges

- Transition from lab- to bench-scale process under real flue gas conditions
- Solvent oxidation via catalyst addition
- Integration of multiple technologies

Technology Fundamentals

❖ k_{obs} impacts PFO calculation

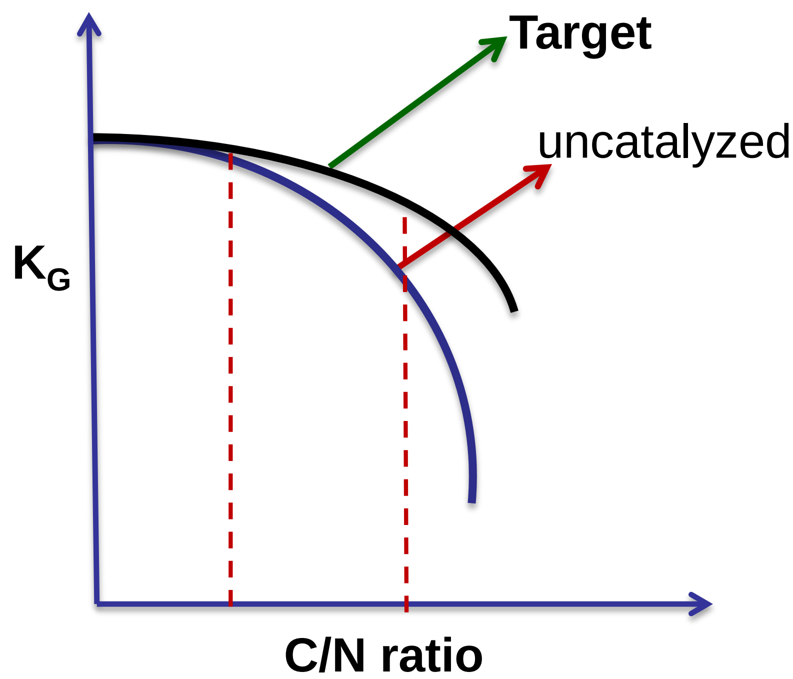
$$k_{obs} = k[amine] + k'[cat]$$

Pseudo first order approximation

$$k_{g,PFO}' = \frac{\sqrt{D_{CO2}.k_2.[amine]}}{H_{CO2}}$$

$$k_{g,PFO}' = \frac{\sqrt{D_{CO2}.k_{obs}}}{H_{CO2}}$$

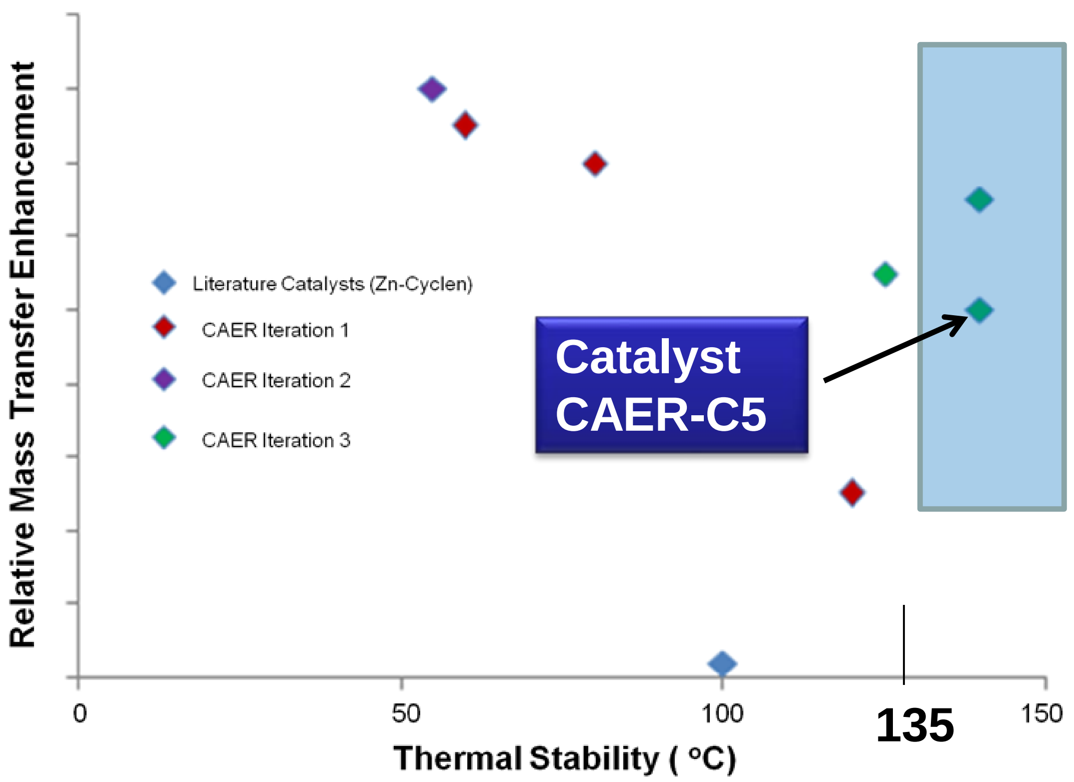
$$k_{g,PFO}' \alpha \sqrt{k_{obs}}$$



Higher the value of k_{obs} higher the mass transfer rate

Achieve rate enhancement at higher carbon loadings

Development Efforts: Catalysts



Improved Catalyst

- 10% rate enhancement in CAER-B3
- Retains activity after heating at 145 °C for 150h
- Simple catalyst preparation; suitable for scale-up

BP2 Activities

Task Number	Title	Description
7	Updated Project Management Plan for budget period 2.	Review and update PMP/SOPO
8	CAER catalyst Production	Production of at least 500 g of CAER catalyst
9	Parametric CAER-B3 investigation	100 hour parametric study on conventional PCC using CAER solvent without catalyst at bench-scale completed
10	Parametric catalytic CAER-B3 investigation	100 hour parametric study with catalyst and gas pre-concentration membrane at bench-scale completed
11	Membrane dewatering	Membrane shown to dewater CAER-B3 solvent by at least 10% over 100 hours in lab-scale single element testing
11	Zeolite membrane bench-scale test module design	Completed design for dewatering membrane test module for integration in 0.1 MWth bench-scale test unit

- BP2 has focused on testing in our 0.1 MWth unit
  - baseline testing, parametric catalytic solvent testing
  - short term degradation analysis
- Membrane improvement and module design for pilot integration

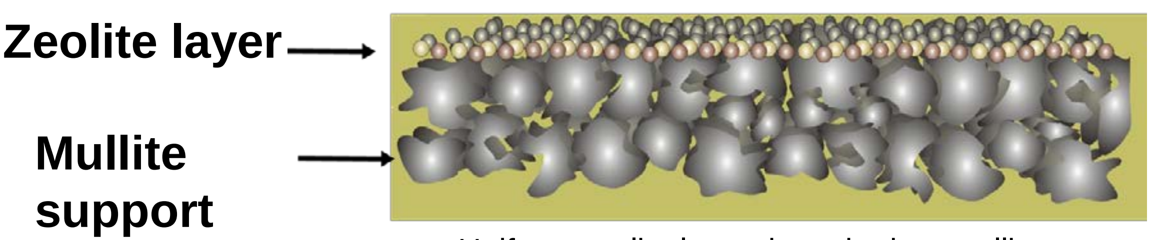
BP2 Milestones

Task #	Milestone	Description	Deliverable Date	Completion Date
7	Updated PMP for BP 2	Review and update PMP/SOPO	10/30/14	12/18/14
8	CAER catalyst production	Production of at least 500 g of CAER catalyst	12/31/14	12/17/14
9	Parametric CAER-B3 investigation	100 hr parametric study on conventional PCC using CAER solvent without catalyst at bench-scale completed	2/28/15	1/29/15
10	Parametric catalytic CAER-B3 investigation	100 hr parametric study with catalyst and pre-concentration membrane at bench-scale completed	8/15/15	
11	Membrane dewatering	Membrane shown to dewater CAER-B3 by at least 10% over 100 hr in lab scale testing	5/31/15	2/24/15
11	Zeolite membrane bench-scale test module design	Completed designs for dewatering membrane test module for integration into 0.1 MWth bench-scale unit	6/30/15	6/8/15

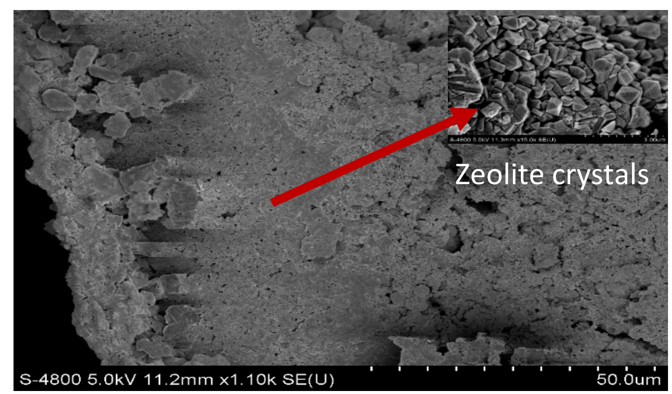
Success Criteria	
A minimum process energy operating condition established based on 100 hour parametric testing for the CAER catalyzed advanced amine solvent showing at least a 20% reduction in stripping energy compared to uncatalyzed CAER-B3 solvent.	80%
The validation to show the advantages of the CAER catalyzed amine to the uncatalyzed CAER advanced amine solvent verifying at least a 10% increase in overall mass transfer or 5% more rich solution at the CAER bench-scale evaluation.	80%
Zeolite membrane performance at the lab-scale maintains chemical and mechanical stability for 100 hour run verified.	100%

Previous Work

Scale (g)	Ligand Yield (%)	Ligand Purity (%)	Catalyst Yield (%)	Catalyst Purity (%)
1	> 90	> 90	50	> 90
5	> 90	> 90	86	> 90
20	70	> 90	77	> 90
50	> 90	> 90	81	> 90
100	> 90	> 90	92	> 90

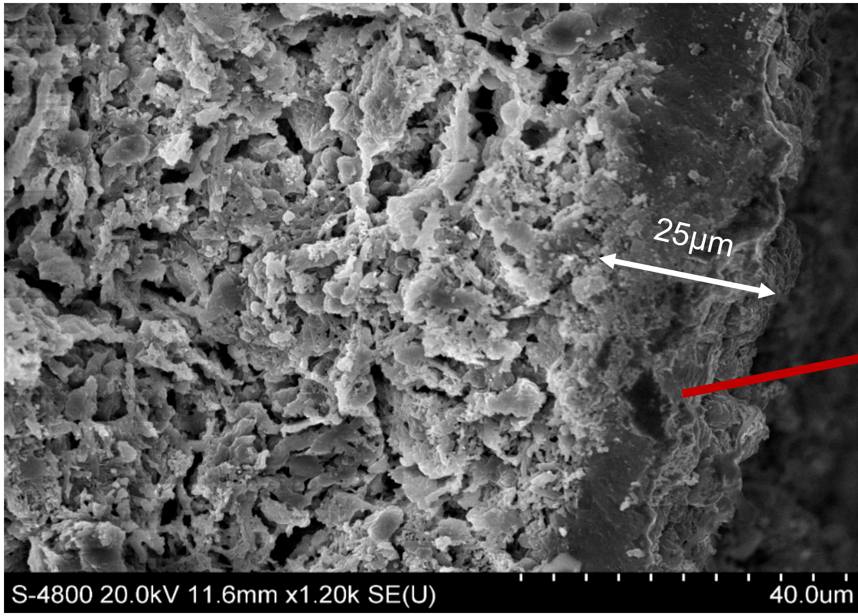


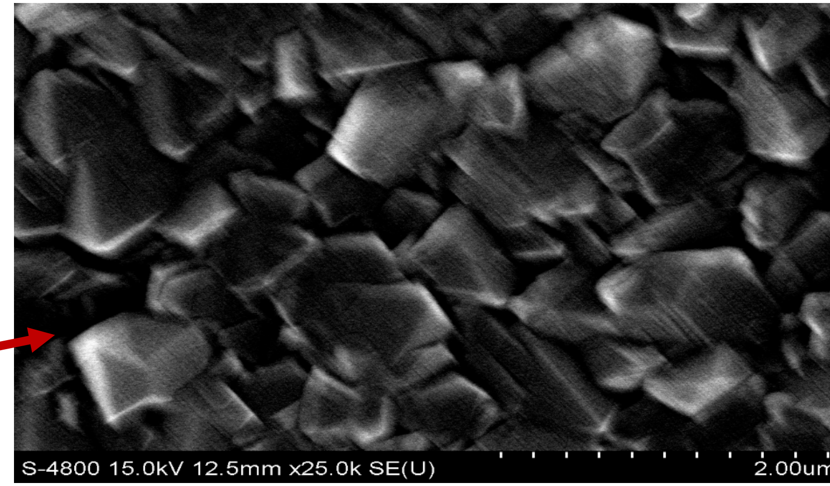
Uniform zeolite layer deposited on mullite support



Zeolite layer *ca* 50 -60 µm

Zeolite Membrane Characterization

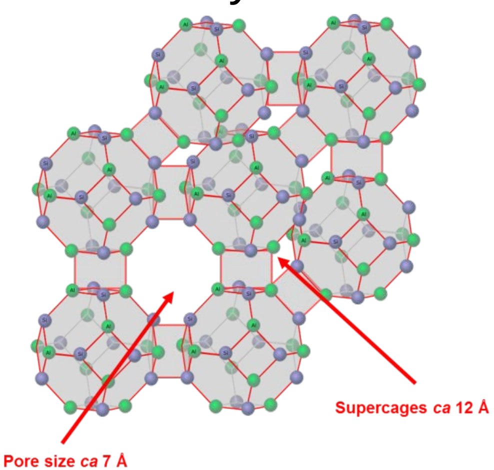




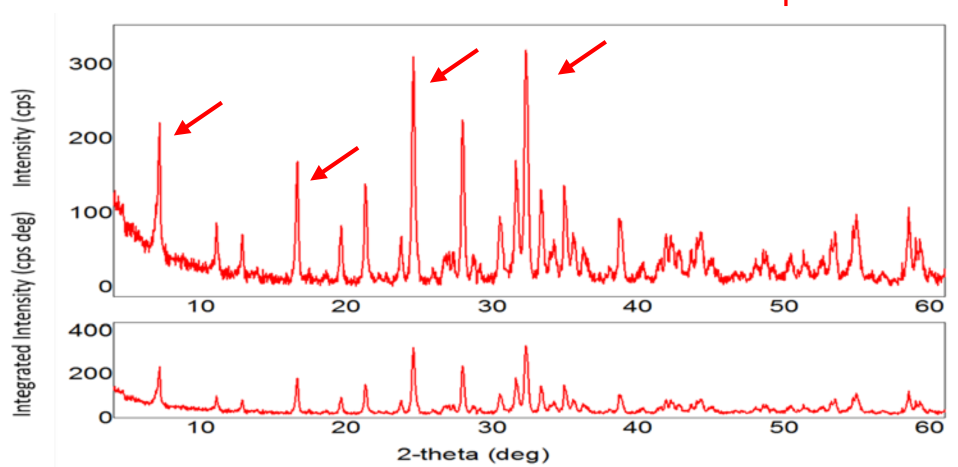
Y Zeolite crystals

Successful creation of ~25 µm crystalline zeolite layer

Y Zeolite layer *ca* 25-30 µm

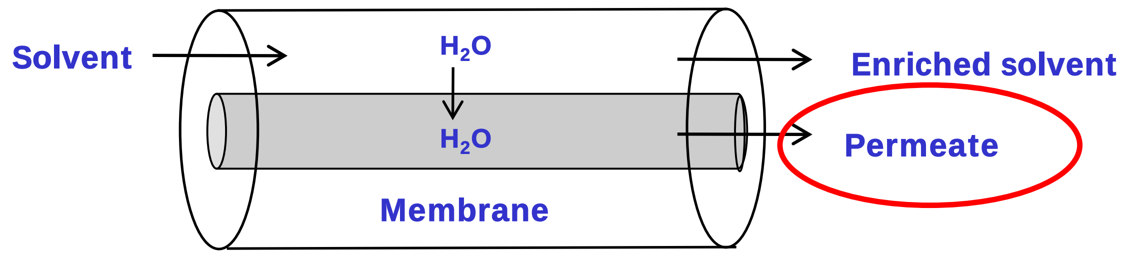


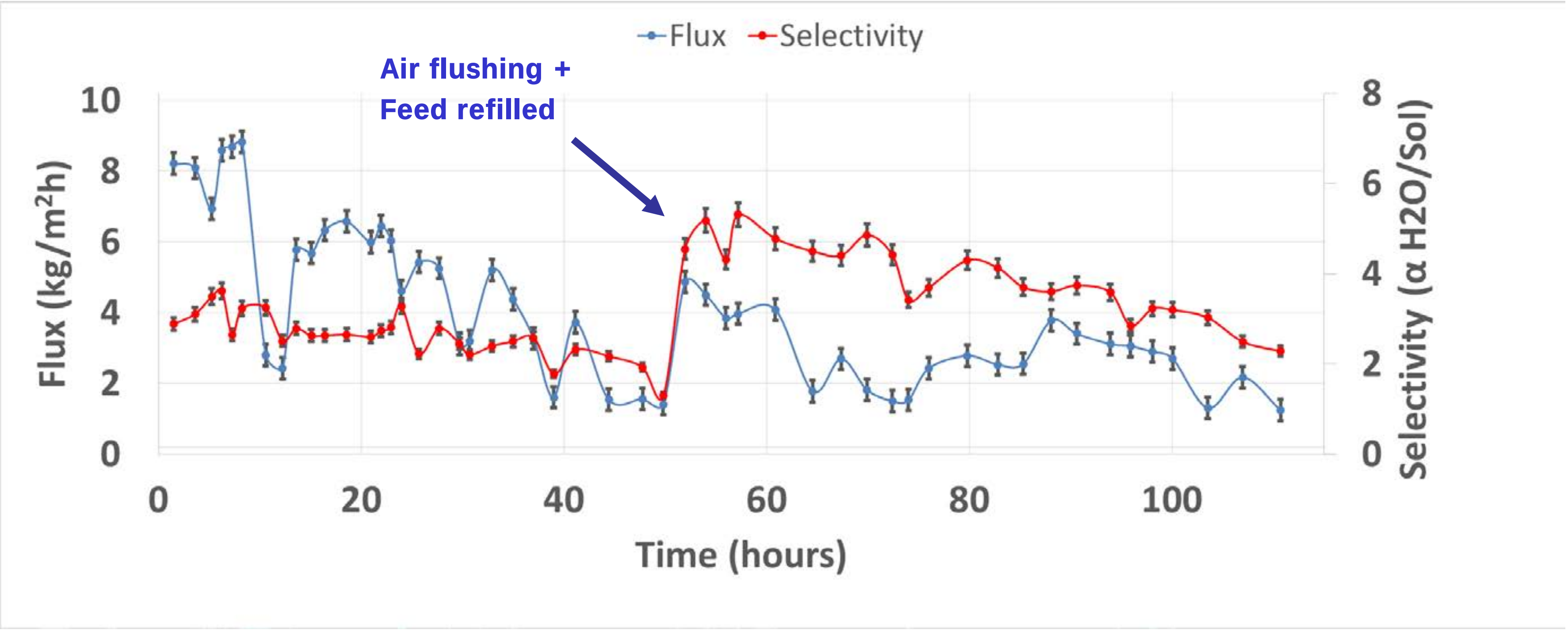
Characteristic Y zeolite peaks



Long term dewatering operation

Membrane: TMAOH/ 1.0 % seed solution /3 s deposition / 10h crystallization (100°C)
Conditions: CAER-B3 solvent α=0.4 , 100°C, 70 PSI, 20 mL/min





Zeolite Membrane Module

High packing density of separation area

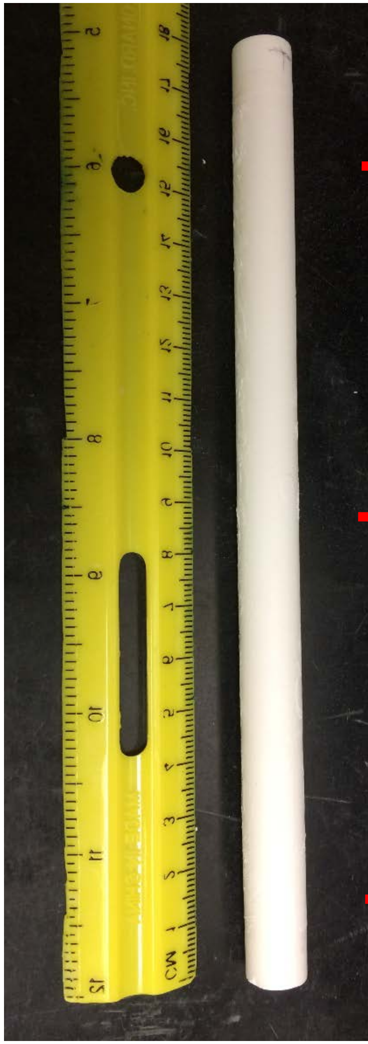
Values based on permeate flux of 10kg/m²h and flow rate of 40 mL/min

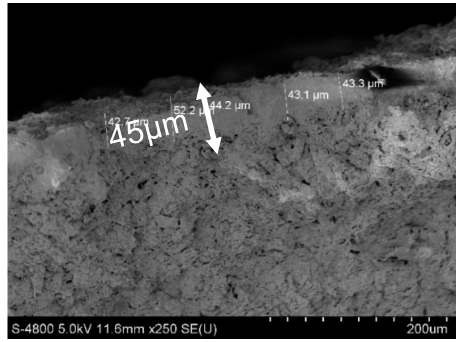
l= 10 cm
Active area of each membrane = 23.5 cm^2
Target Permeate flow rate = 200ml/min
Assuming 20% rejection= 91 membrane tubes

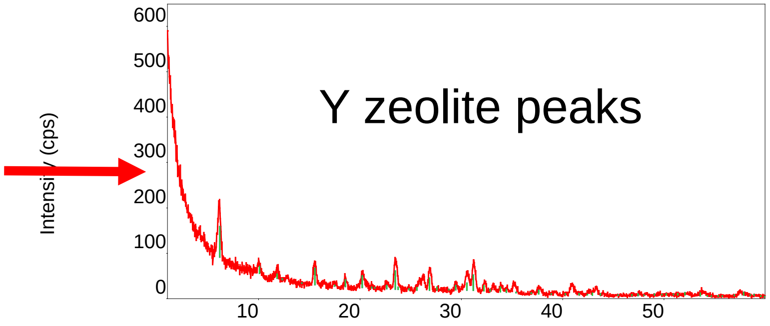
l= 18cm
Active area of each membrane = 48.7 cm^2
Target Permeate flow rate = 200ml/min
Assuming 20% rejection= 44 membrane tubes

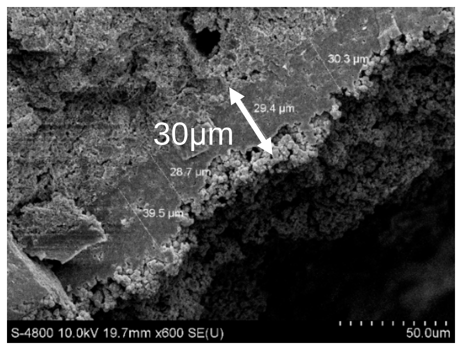
6 Tubes/Module

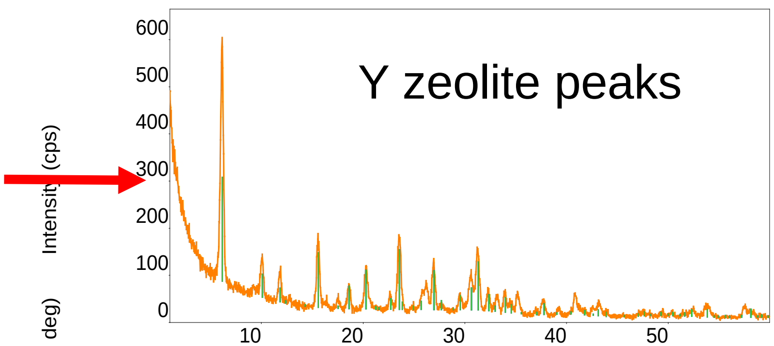
Long Membrane Synthesis

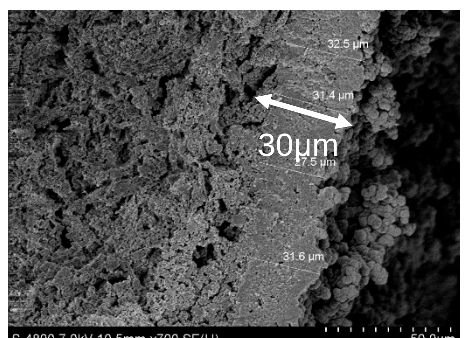


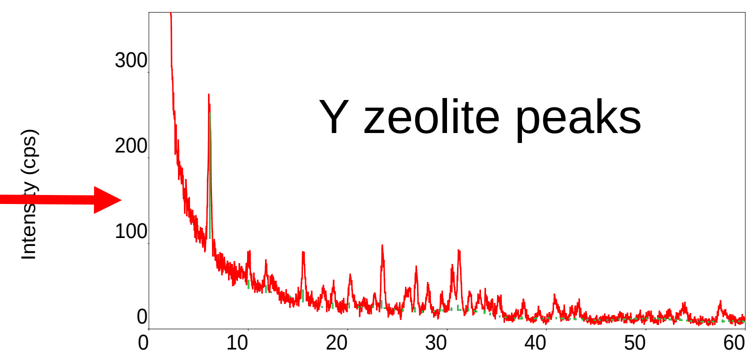




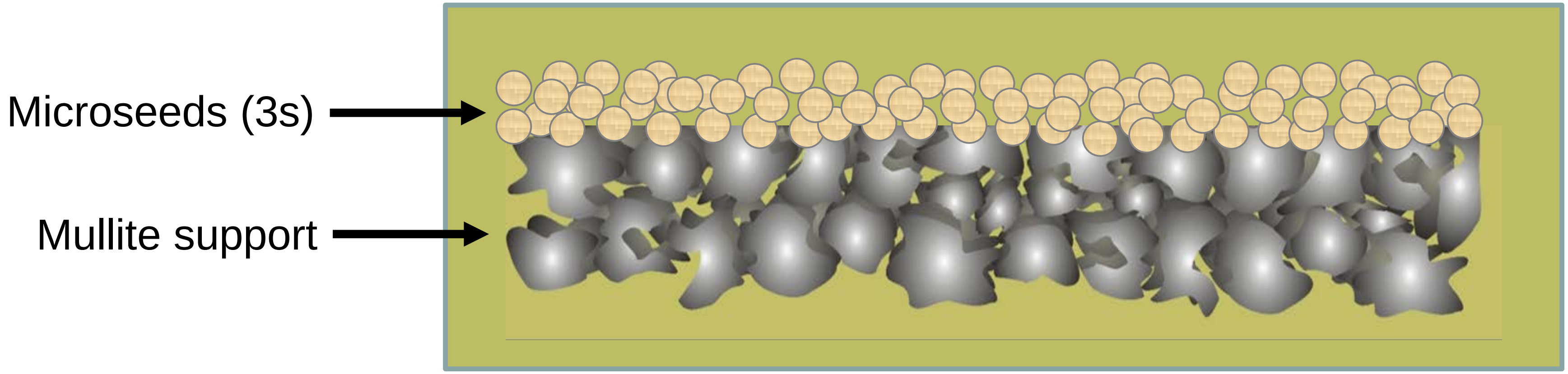




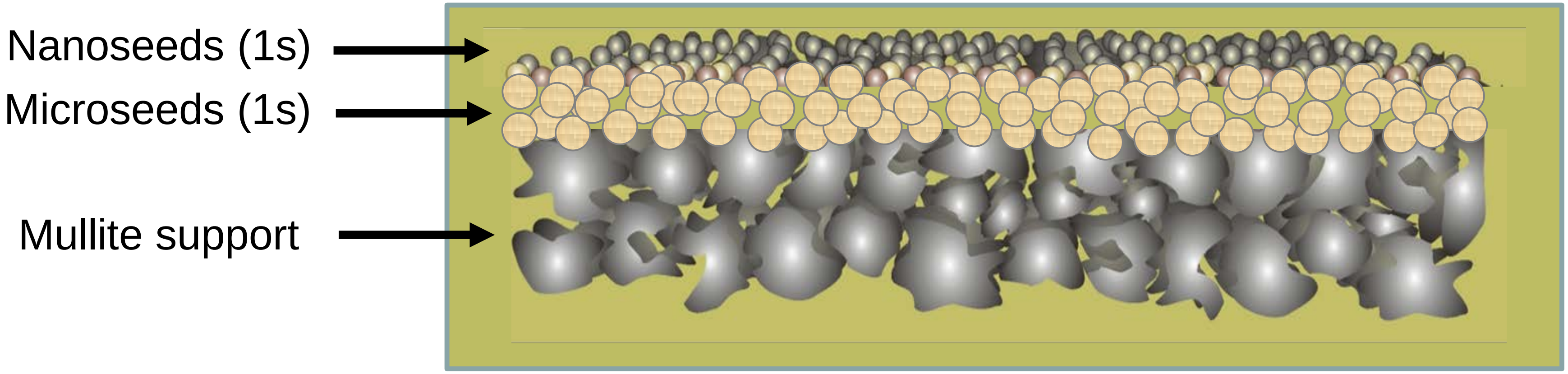




Membrane Improvements

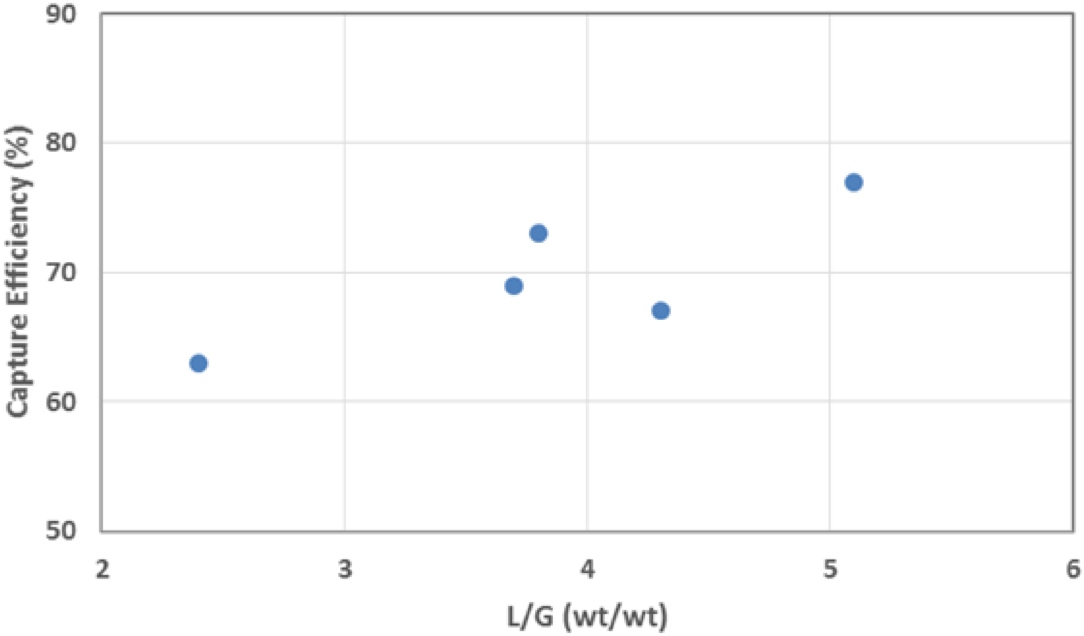


- Use of nanoseeds (OSU) towards the production of a defect-free membrane



- Ideal thickness 5-10 µm to produce higher flux

Bench-Scale CAER-B3 Testing



- Different L/G ratio from variation in liquid circulation
- Absorber inlet temperature (30, 40°C)
- Stripper pressure – (45, 55 psia)

CAER-B3 Performance

Experiments at liquid load of ~19 $m^3/(m^2.h)$ and stripper pressure of 45 psia, absorber inlet temperature of 40 °C.

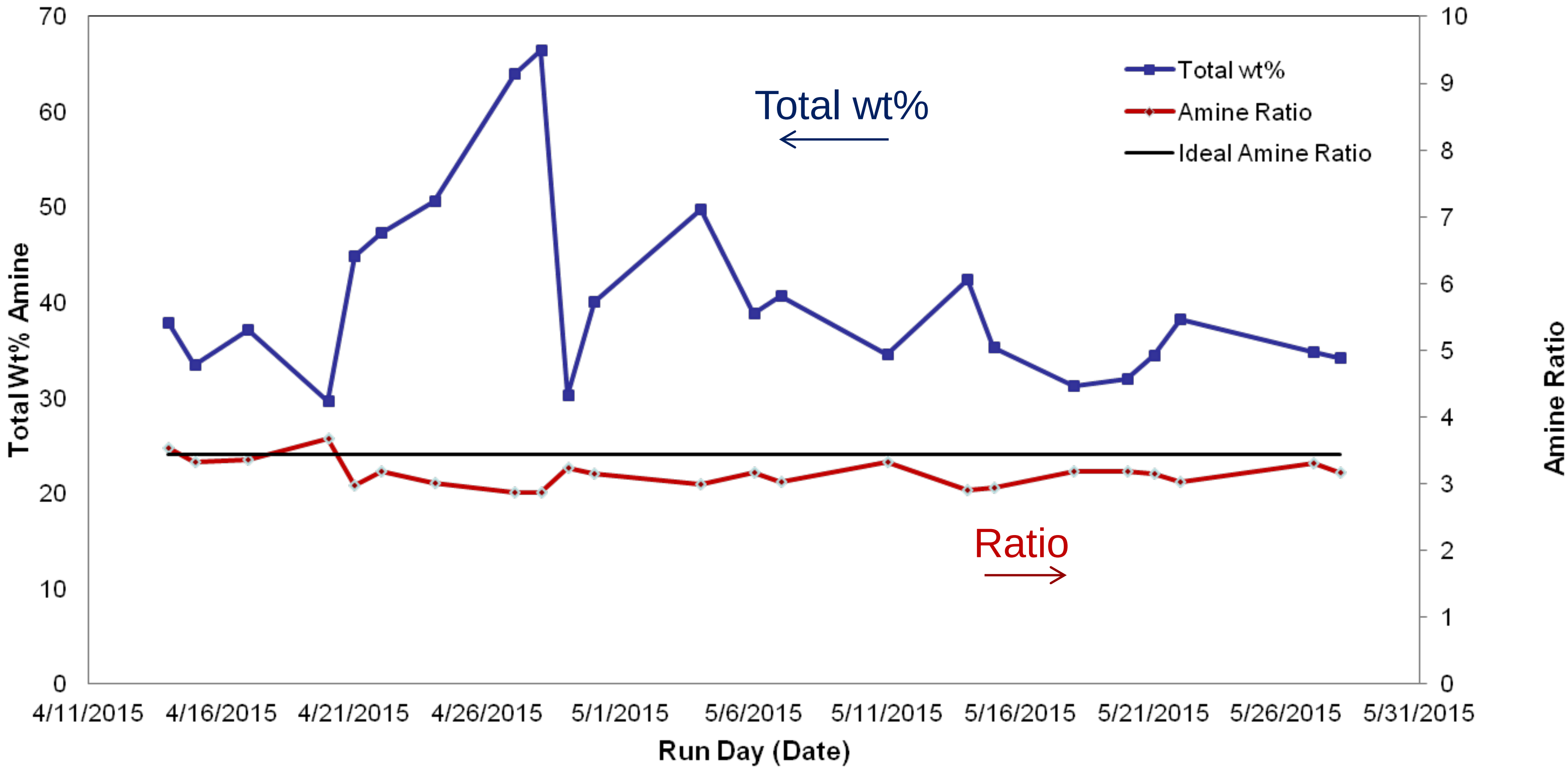
Baseline – No Catalyst Added

	Total amine wt%	Alkalinity (mol/kg)	Viscosity @ 40 °C (cP)	% Capture	Energy (Btu/lb CO_2)
April	29.7	5.34	4.67	81	2006
	66.5	7.04	12.84	76	1980
	40.2	4.88	3.76	81	2114
May	38.8	4.87	3.85	81	2007
	40.66	4.98	4.04	75	2135
	36.61	5.05	4.28	79	2107
	42.45	5.10	4.46	79	2085
	35.3	5.18	5.06	77	2034
	36.41	5.03	3.98	78	2005

Maintained similar capture for a range of varying relative concentrations of amines in blend

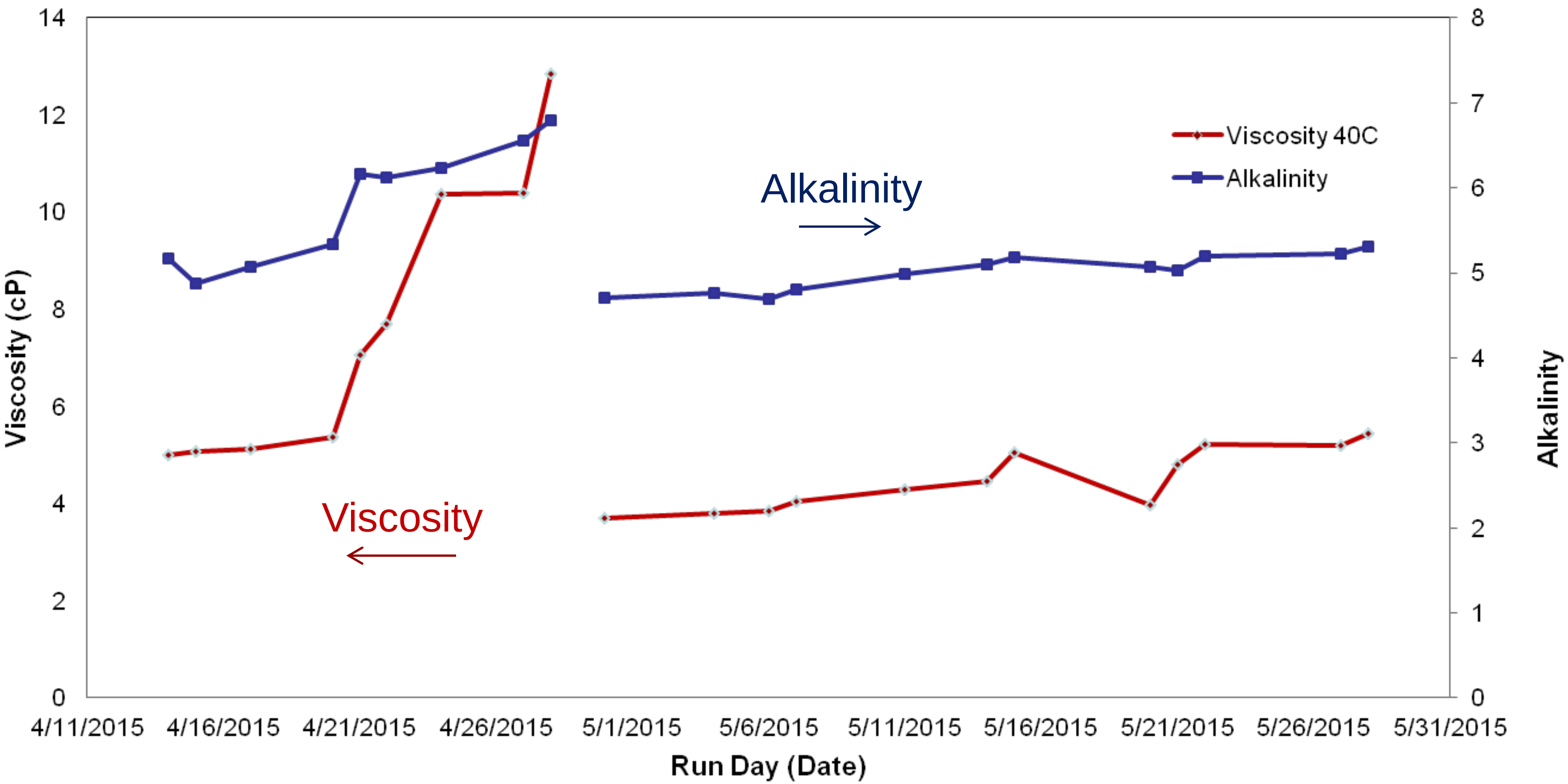
CAER-B3 Performance Tests

- Slow decrease in [amine]
  - ➢ most likely from aerosol emissions

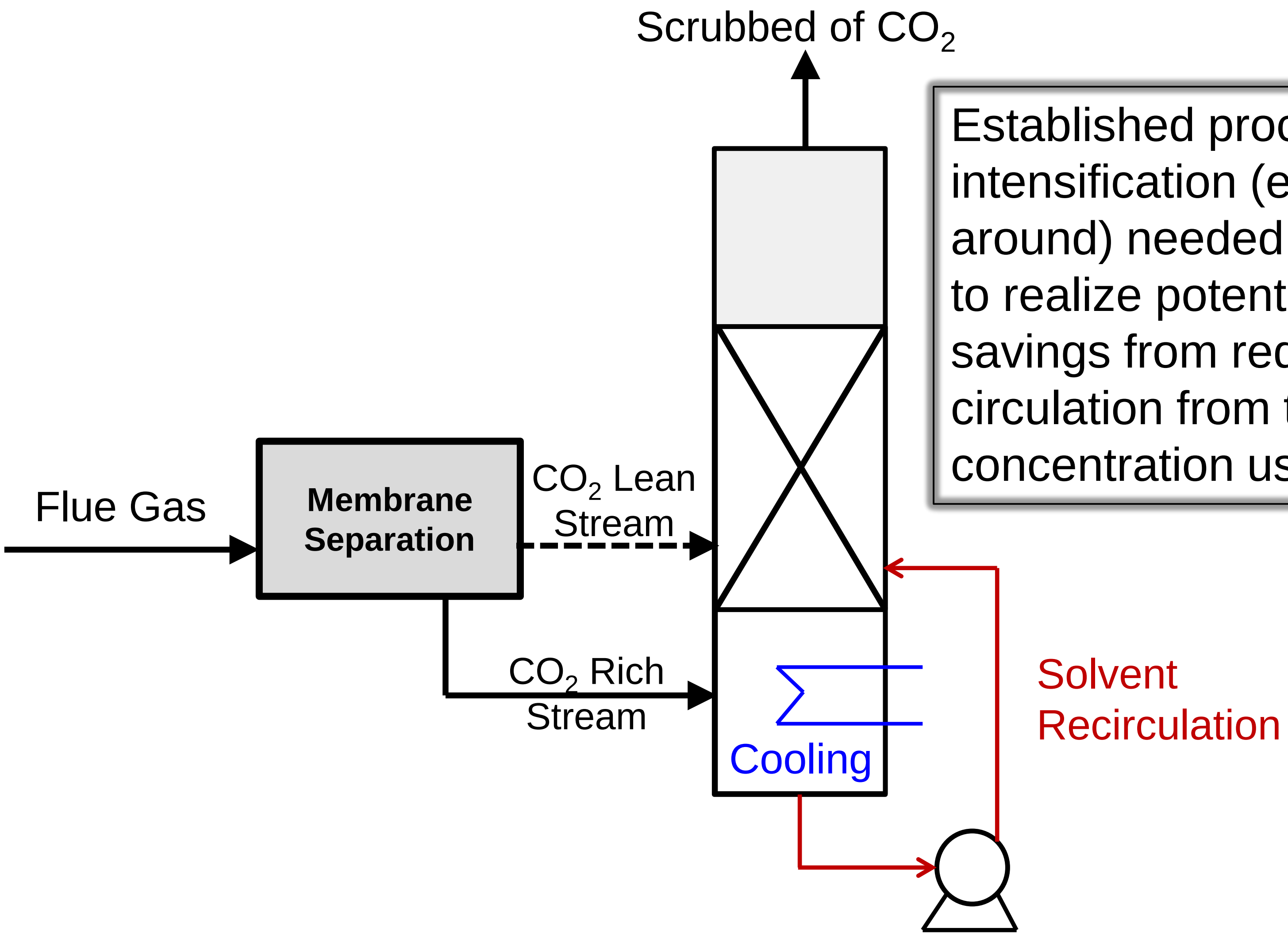


CAER-B3 Performance Tests

- Slow increase in alkalinity and viscosity



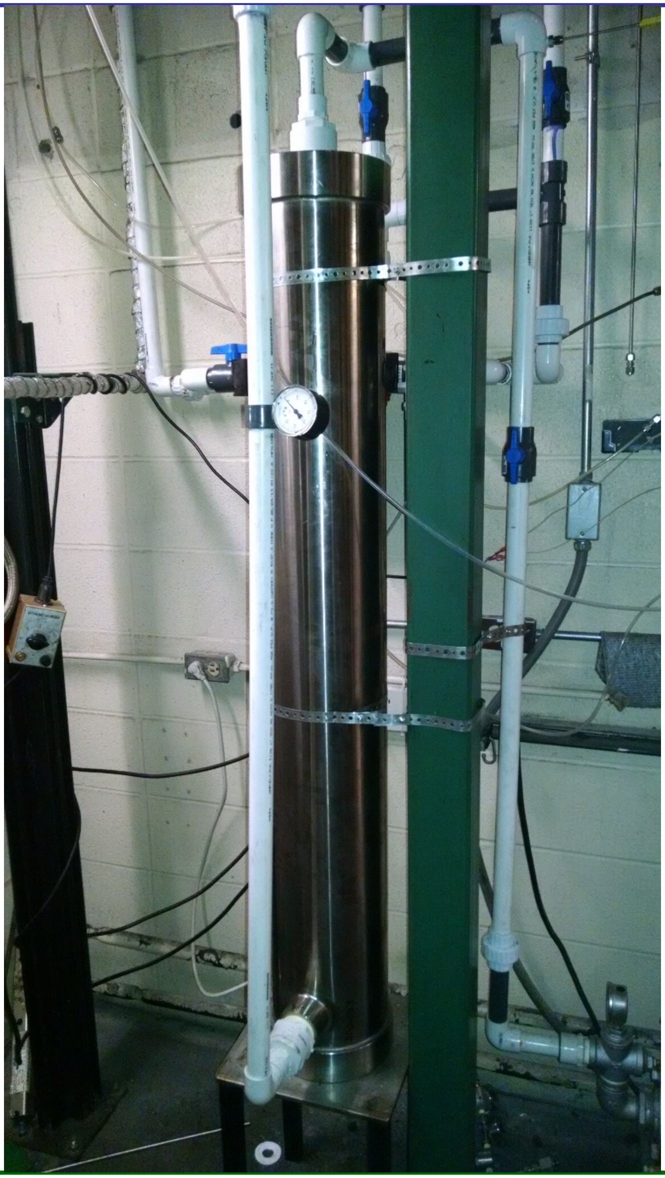
Membrane Integration



Established process intensification (e.g., pump around) needed with membrane to realize potential energy savings from reduced solvent circulation from the pre-concentration using CAER-B3

Membrane Installed

- Membrane successfully integrated with bench unit with accompanying vacuum pump and blower
  - Modified process
- Demonstrated CO_2 pre-concentration by a factor of ~2 obtainable in system



Membrane Integration

Run	L/G wt/wt	Liquid load $m^3/(m^2.h)$	Absorber LMTD (°C)	Stripper bottom temp. (°C)	Capture efficiency %	Energy (Btu/lb CO_2)
Ref 1	5.1	19	50	134	77	2091
Ref 2	5.3	19	47	135	81	2006
Membrane						
1	4.9	17.8	43	137	82	1650
2	3.8	13.6	41	138	80	1473
3	3.7	13.4	42	140	82	1515
4	3.1	10.8	42	140	88	1412
5	2.9	10.6	43	140	86	1465

Energy savings of ~25% could be obtained from the reduced L/G runs with the membrane.

Acknowledgements

The work presented here was made possible through funding by:

- The U.S. DOE/ National Energy Technology Laboratory
  - Project Award # DE-FE-0012926

- Carbon Management Research Group: Duke Energy, EPRI, LGE&KU, DEDI, AEP

DOE	CAER	CMRG	SMG	WorleyParsons resources & energy
• Lynn Brickett • José Figueroa	•Heather Nikolic • Kun Liu • Jesse Thompson • Brad Irvin	• John Moffet • David Link • Michael Manahan • Doug Durst • Talina Matthews • Abhoyjit Bhown • Curtis Sharp	• Clayton Whitney • Sarah Carty	• Mike Bartone • Vlad Vaysman


Thank You