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

Award # DE-FE0012926

Power Generation Group
Center for Applied Energy Research
University of Kentucky Research Foundation

Executive Summary

- Project tasks for budget period 1 are completed
- Targets/milestones are met and we are requesting to conclude the BP1 activities

Task Number	Title	Description	Planned Completion Date	Actual Completion Date	Verification Method
1	Updated PMP	Review and update PMP/SOPO	10/30/13	12/5/13	PMP file
1	Kickoff Meeting	Kickoff meeting with NETL program managers and support team	11/14/13	12/4/13	Presentation file
2	VLE data collection	Solvent kinetic data collected for modeling including: no less than 30 data points collected for VLE regression verification	6/30/14	5/31/14	Quarterly report
2	Modeling data collection	Completion of mass transfer and kinetic data collection on CAER-B3 solvent	9/30/14	7/31/14	Quarterly report
3	Gas Membrane-CO_2 enrichment	Completion of MTR module installation for higher CO_2 loadings and lower stripper energy costs shown in 30 wt % MEA system in 0.1 MWth bench-scale test unit	9/30/14	8/20/14	Quarterly report
3	Polymeric Membrane Dewatering	Examination of alternative polyamide membranes from TriSep for post scrubber solvent enrichment	9/30/14	9/30/14	Quarterly report
4	Catalyst Synthesis	Methodology developed for synthesis of > 50 g/batch of catalyst.	1/31/14	1/31/14	Quarterly report
4	Mass transfer enhancement	At least 5% enhancement in mass transfer verified compared to the uncatalyzed	9/30/14	8/26/14	Quarterly report
5	Front-end engineering assistance	Technical support and input from WP received regarding cost of chemicals, membrane, and flow diagram reviewed.	7/31/14	8/4/14	Quarterly report
6	Assessment for PPE requirement	Completion of preliminary health and safety analysis on proposed solvent	4/30/14	4/25/14	Topical report

Lessons Learned

- The impact of catalyst impurity could be significant – the foaming issue
- There is need to further understand the role of catalyst in primary amine-based solvent which we will work on further in BP 2 at no additional cost to DOE
- The parameters for synthesis of an effective zeolite membrane layer are sensitive for optimization. Small synthesis changes produce large performance variance.

Project Overview

Project Details

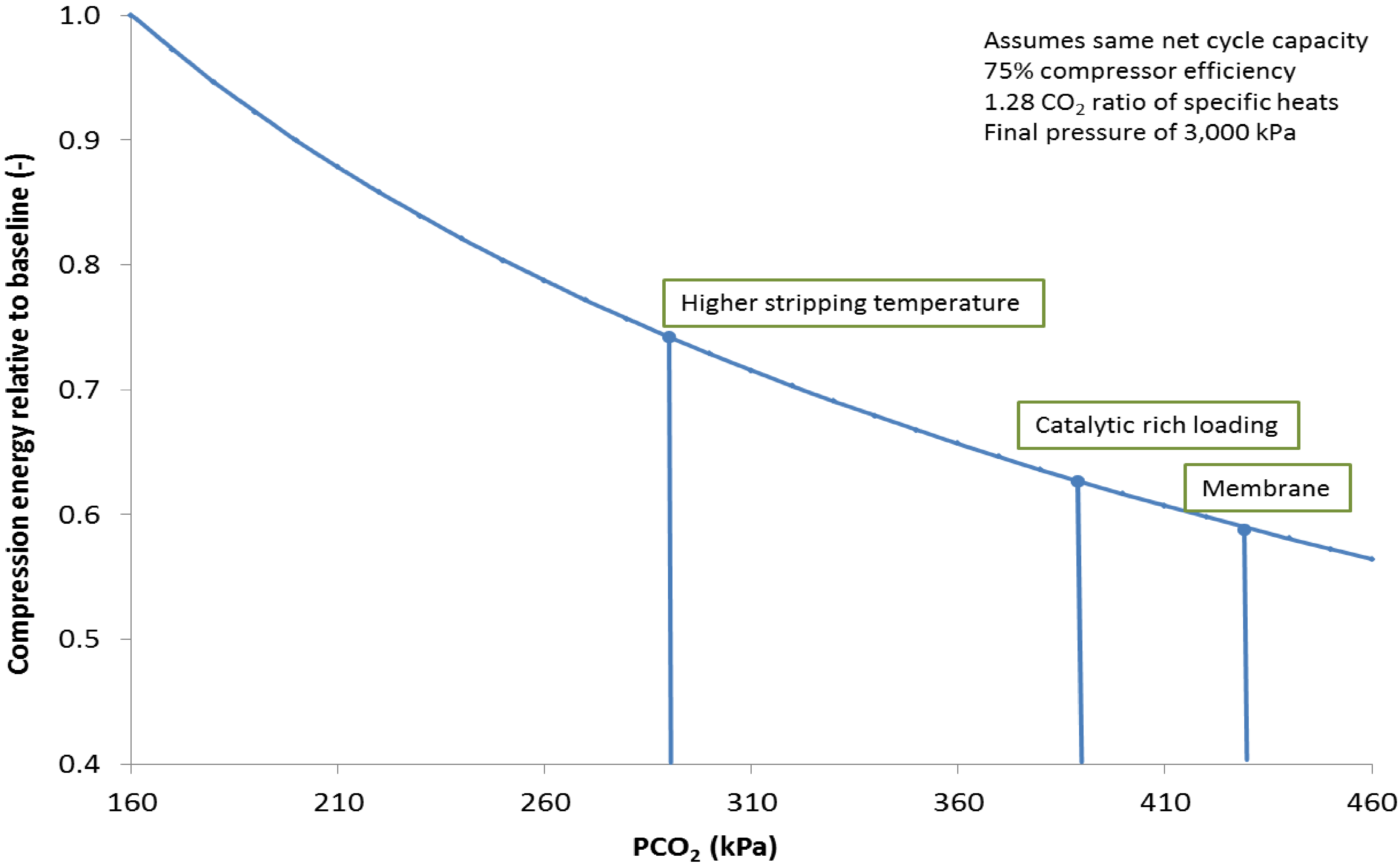
- **Benefit from multiple CAER technologies: solvent; catalyst, membrane, process**
- **Project cost:**
    - **DOE share:$2.97M**
    - **Cost share:$742K ($500K from CMRG)**
- **Period performance:** 10/1/2013 – 9/30/2016

Project Objectives

- Develop a 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 Center for Applied Energy Research	CMRG	SMG	WorleyParsons resources & energy
• Project management • Catalytic solvent testing • ASPEN modeling • Membrane synthesis	• Cost-share • Technical support	• PPE recommendation • EH&S analysis	• Front-end engineering • Techno-Economic Evaluation

Anticipated Benefits



Overall 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 of concept by CAER

pilot ~0.7MW

~20 MW

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: Favorable TEA

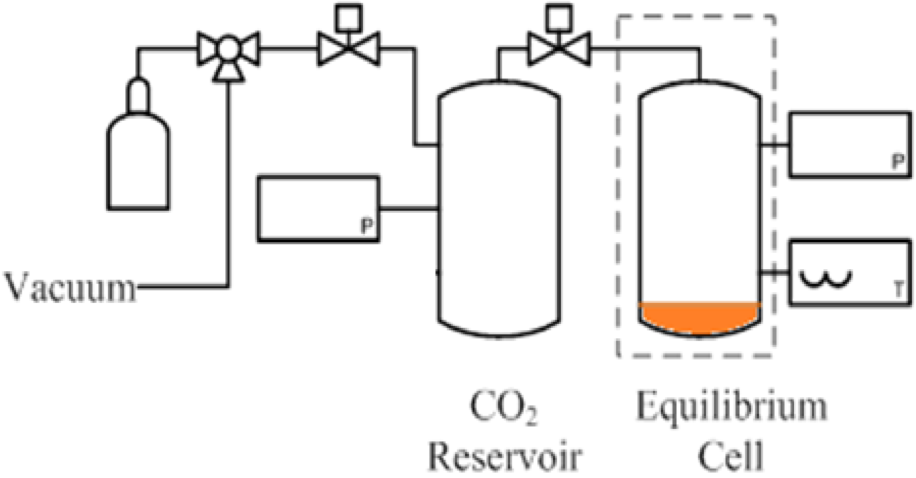
- **EH&S**
- Milestone: Favorable EHS assessment

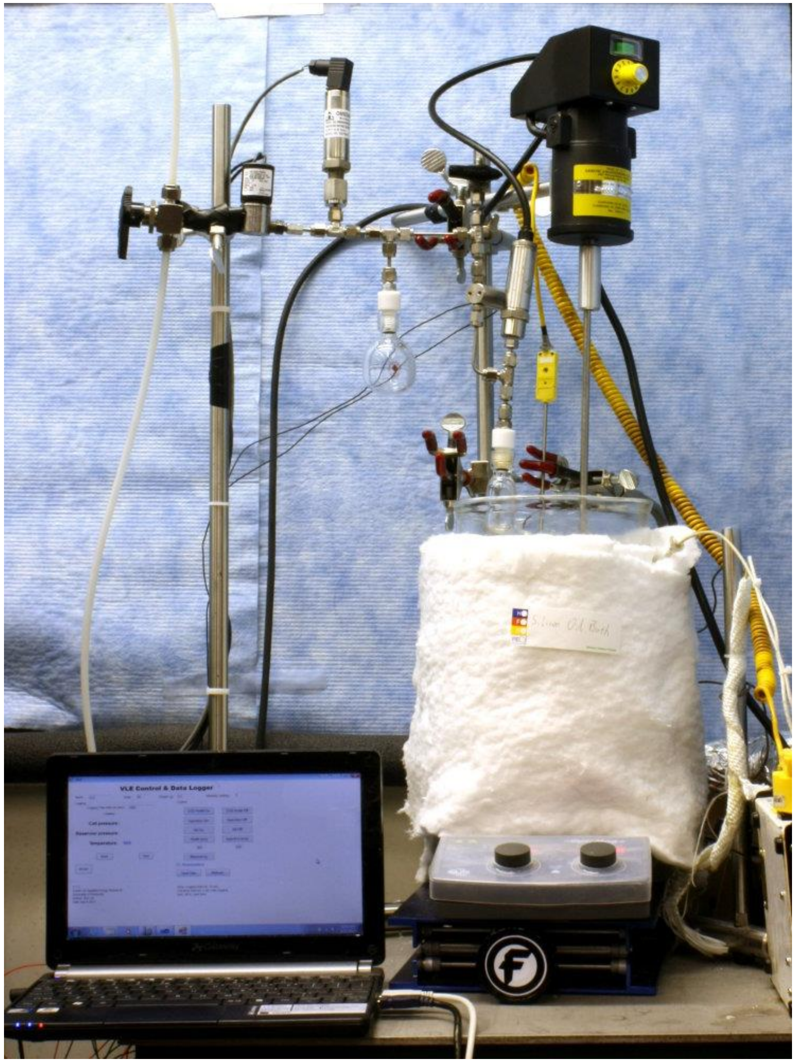
BP1 Schedule and Status

- Task 1 – Project Management and Planning
  - On-going and dynamically adjusted
- Task 2 – Collection of Physical Properties and Solvent Optimization
  - Required VLE data and regression completed
  - Mass transfer enhancement optimized vs. catalyst loading
  - Effects of flue gas contaminants on catalyst and solvent performance
- Task 3 – Carbon Enrichment Performance Evaluation with Selected Solvent
  - Indicated opportunities for net efficiency improvement vs. Case 10
- Task 4 – Catalyst Scale-up
  - Method developed to synthesize >50g of catalyst in a single batch
  - Repeatability of method verified
  - Constructed bench-scale absorber and host rig with vacuum stripper
- Task 5 – Front-end Engineering Analysis
  - Catalyst and solvent parameters, and PFD of the process was delivered to WP
  - Parameters and information needed for the full TEA in BP3 identified
  - Preliminary enzyme replenishment rate established for bench-scale
  - Initial Commercial Assessment Completed
- Task 6 – Assessment for PPE Requirement
  - Preliminary report received from SMG and no concerns identified; standard PPE is recommended

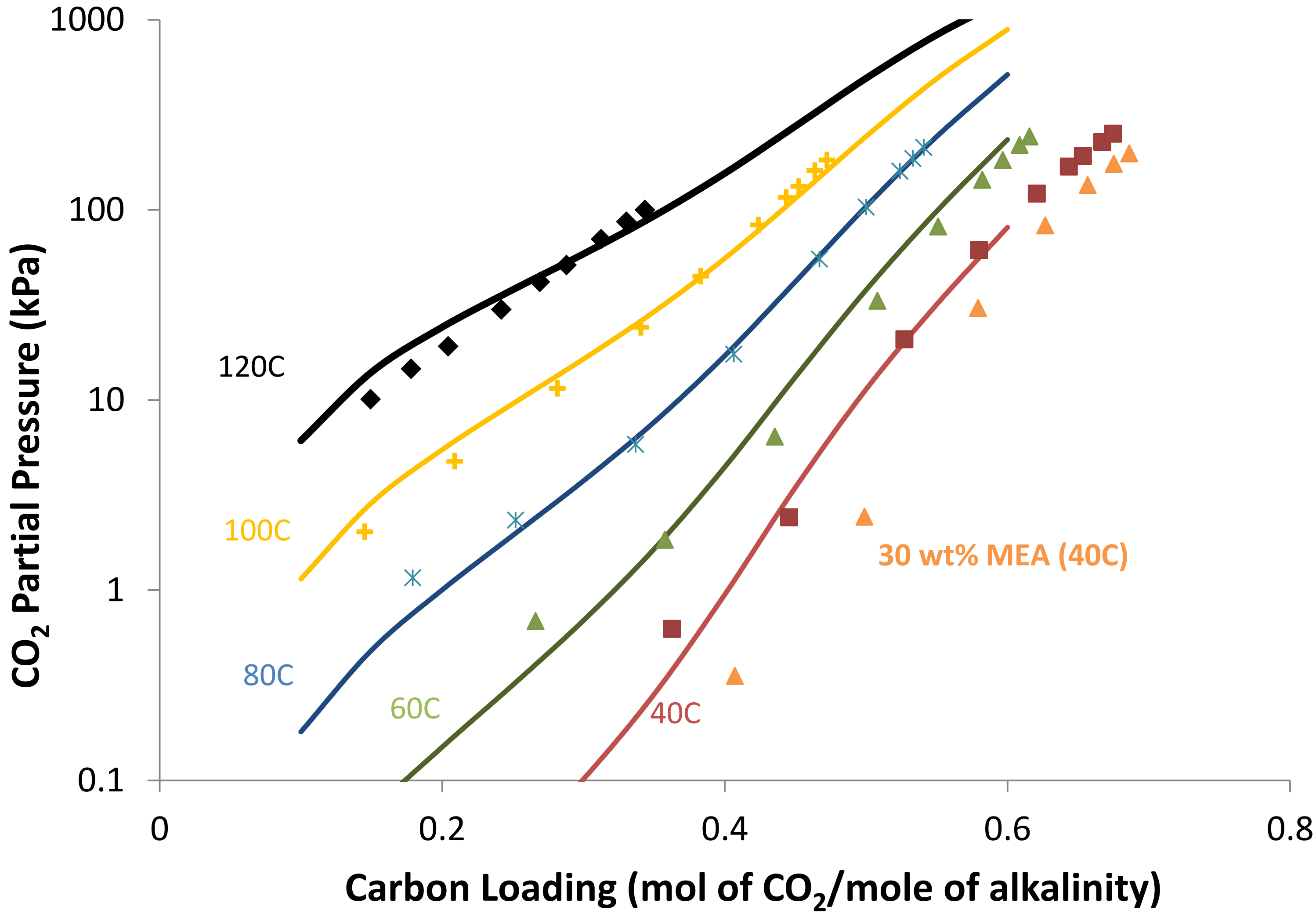
Task 2. Collection of Physical Properties and Solvent Optimization

- Pressure range of 0-350 kPa (0.03% linearity)
- Temperature control of ±0.1 °C
- Small sample size (~1 ml)
- Full automation setup

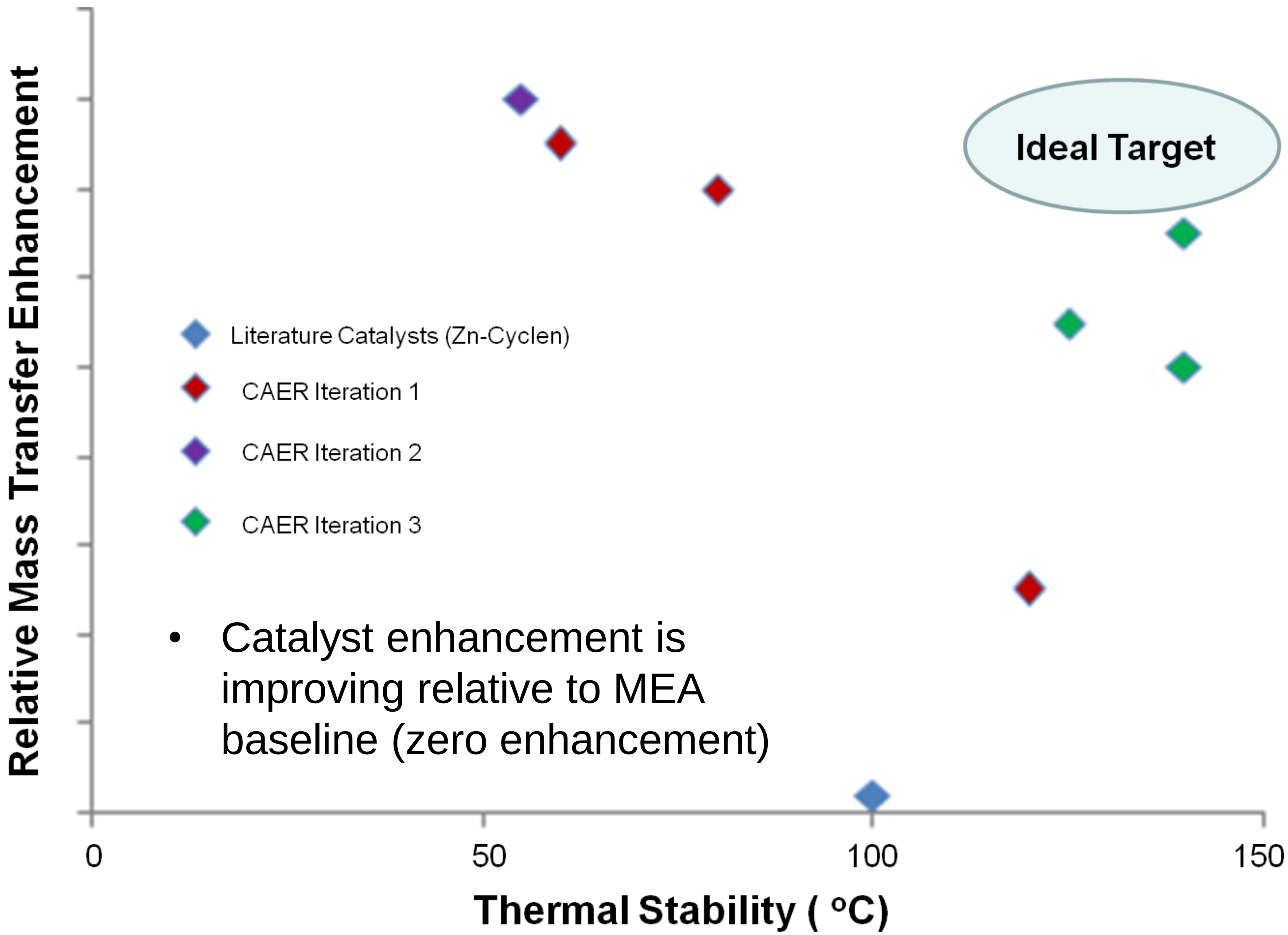




CAER-B3 VLE and Thermodynamic Regression Results



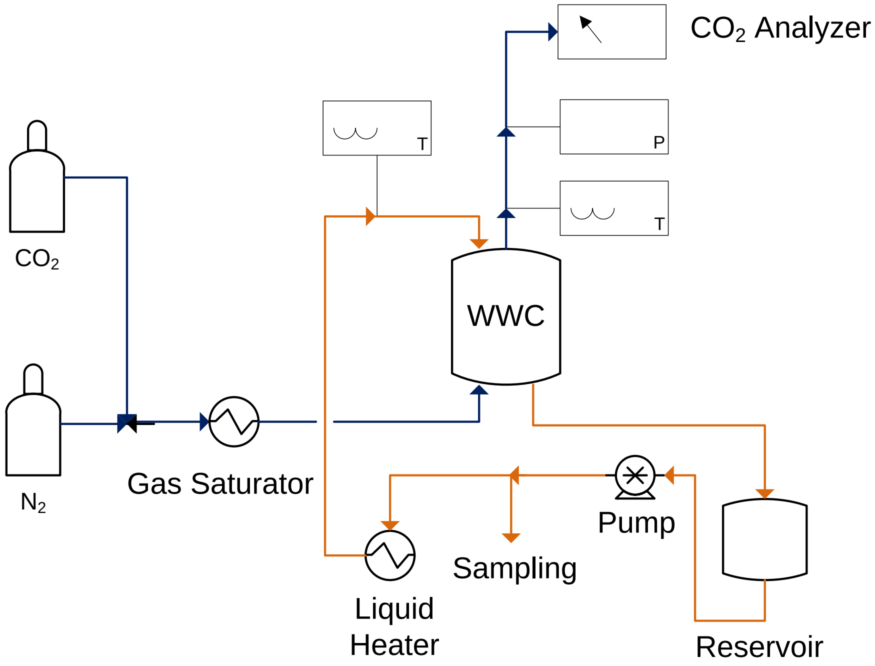
Catalyst Selection/Development

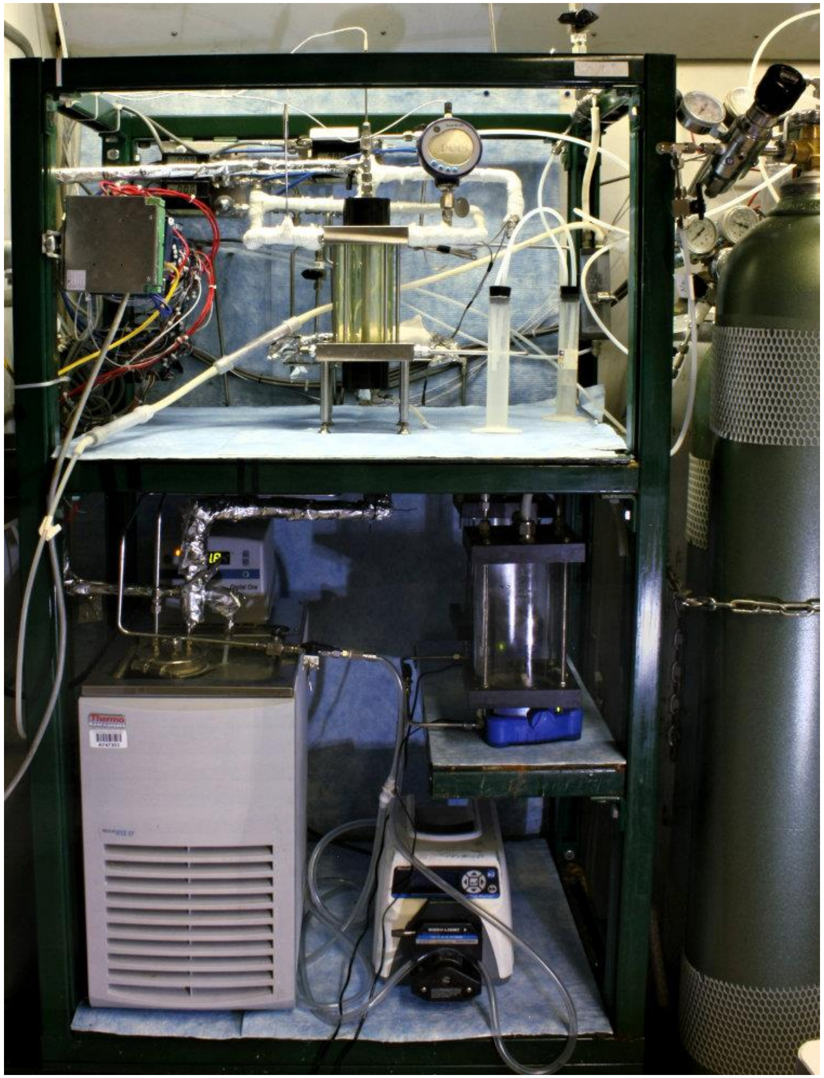


- Catalyst enhancement is improving relative to MEA baseline (zero enhancement)

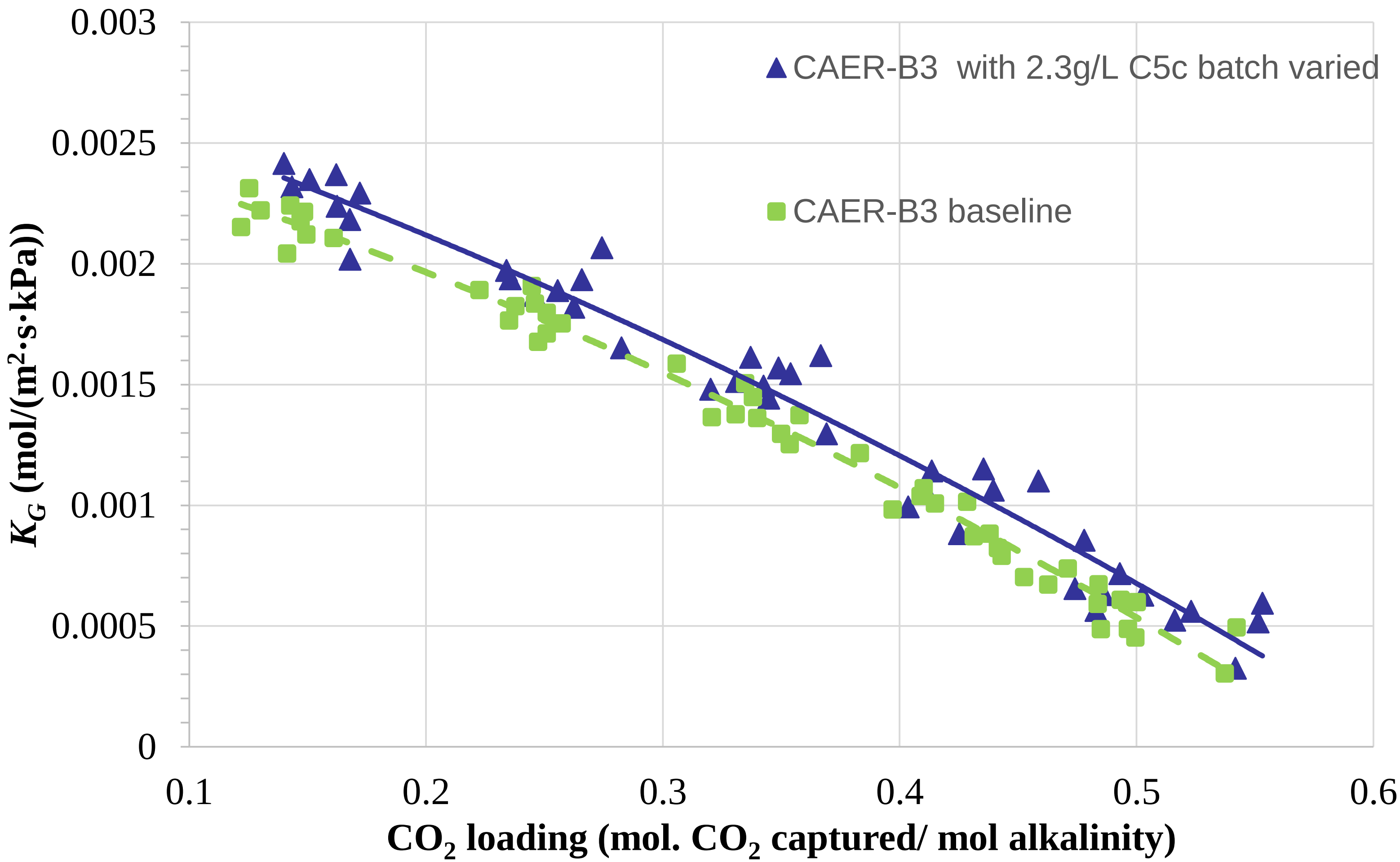
Wetted-wall Setup

- Well-defined surface area for accurate mass transfer coefficient measurement
- Simulated flue gas conditions in scrubber (40 °C, 2% - 14% CO_2 conc.)





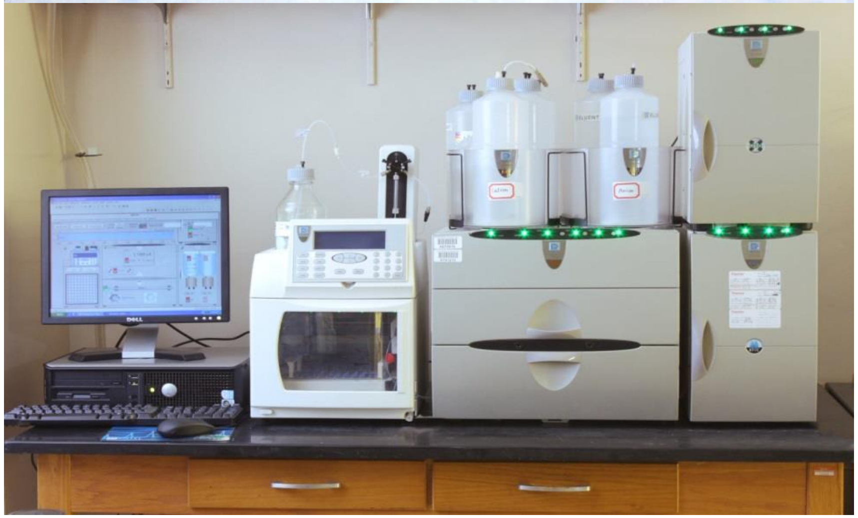
Mass Transfer Enhancement



- 10% improvement from baseline solvent to the catalyzed CAER-B3 at 0.35 C/alk.

Oxidative Degradation Experimental Setup

- Test condition: 80 °C, 12% CO_2 balanced with air
- Test time: ~200 hr
- Ion Chromatography System (IC) for amine loss determination



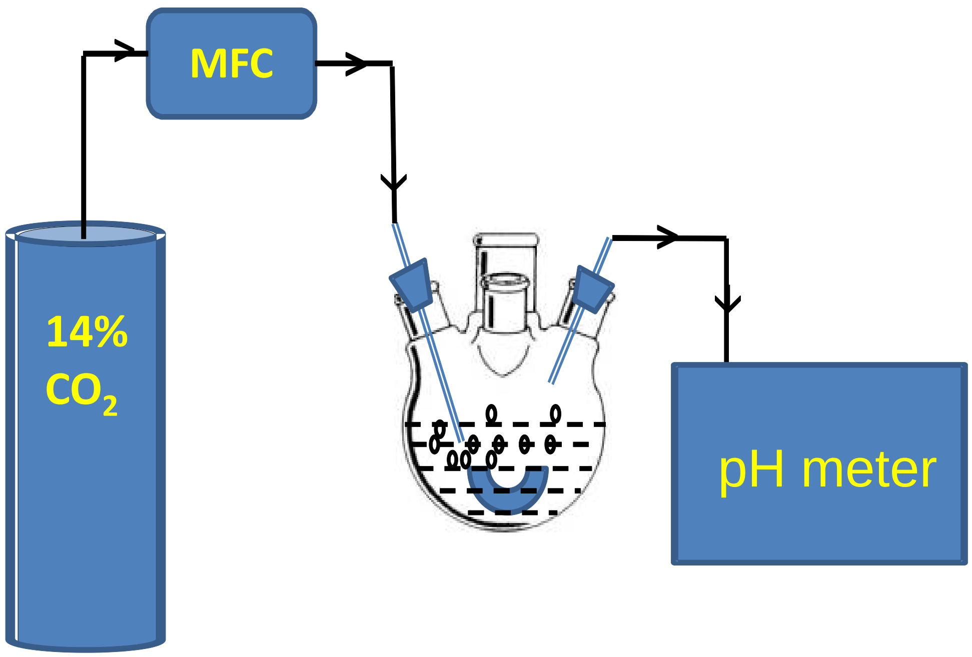
Degradation

Solvent	Overall amine loss (%)
CAER B3 + C5c oxidative, 80°C, 288 h	13.2
CAER B3 + C5z oxidative, 80°C, 288 h	7
[redacted]	[redacted]
CAER B3 + C5c thermal,145°C,1week	18.8
[redacted]	[redacted]

- *C5c selected for better catalytic performance than C5z*
- *Oxidative results show similar percent loss as MEA*
- *Less thermal degradation*

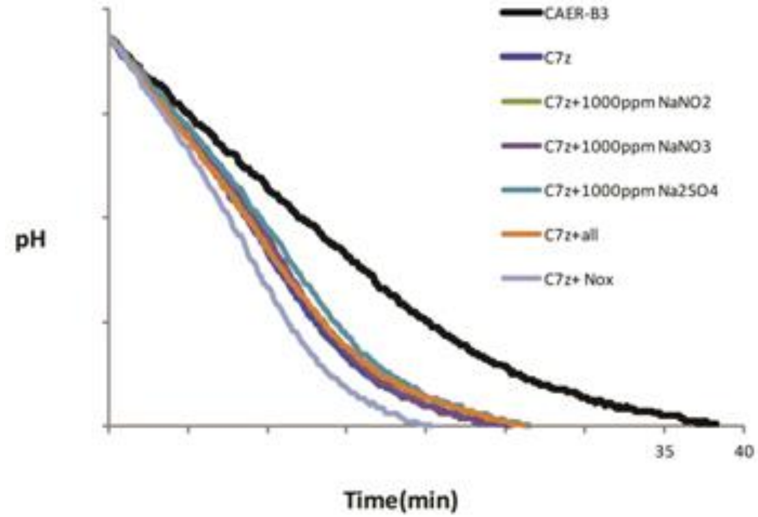
Evaluation Method for Flue Gas Impurity Effects

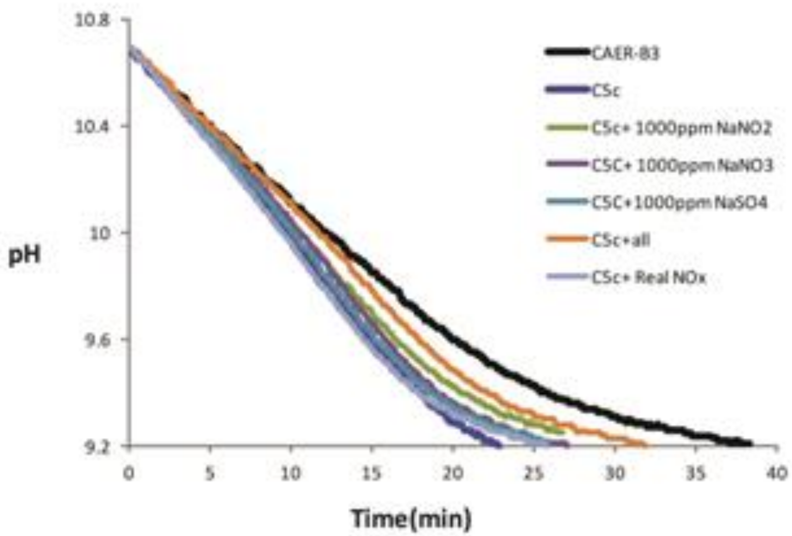
- pH drop method for quick mass transfer evaluation
- NO_x and SO_x are simulated by $NaNO_2$, $NaNO_3$ and Na_2SO_4

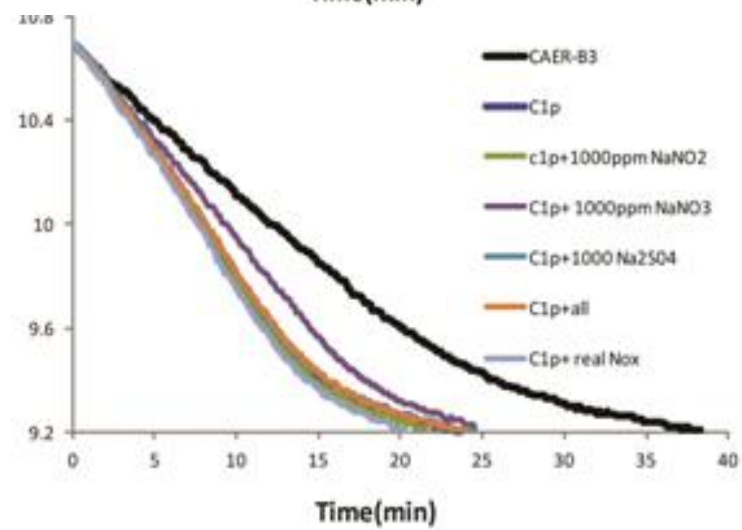


NO_x and SO_x Effects

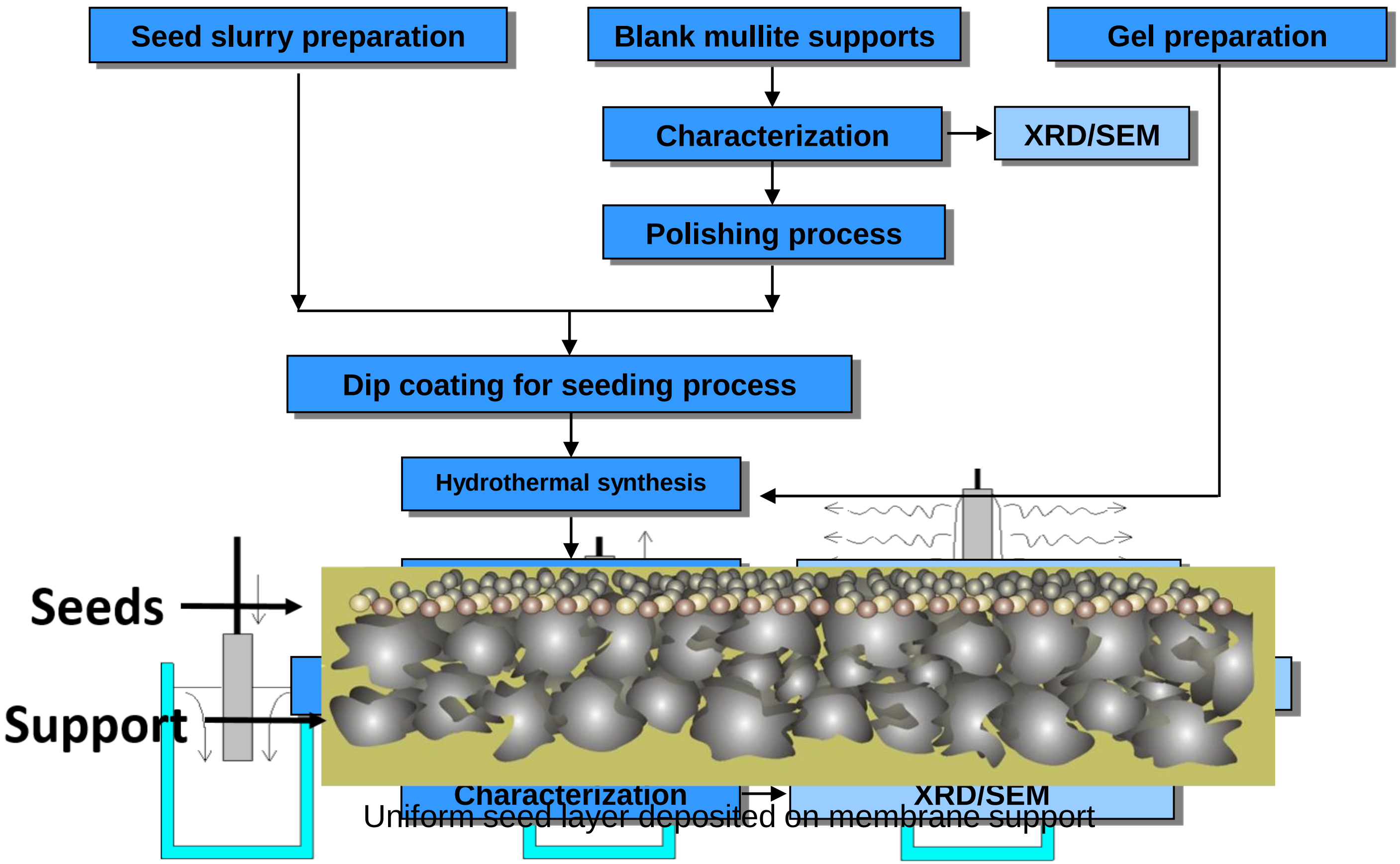
- Minor effect from NO_x and SO_x species
- C5c shows nitrite sensitivity
- Testing at concentrations of 1000 ppm of NO_x or SO_x







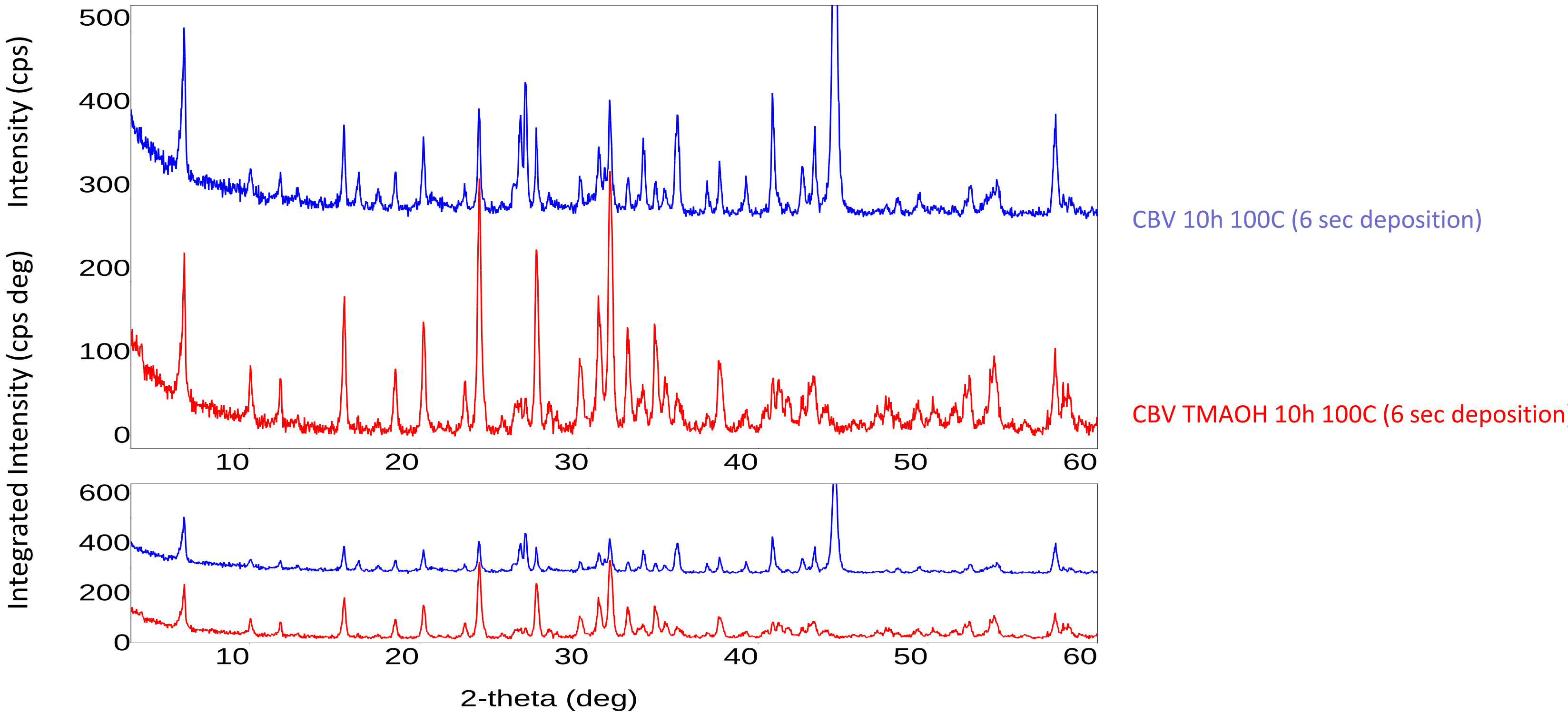
Task 3. Solvent Enrichment
3.1: Zeolite Solvent Enrichment



Uniform seed layer deposited on membrane support

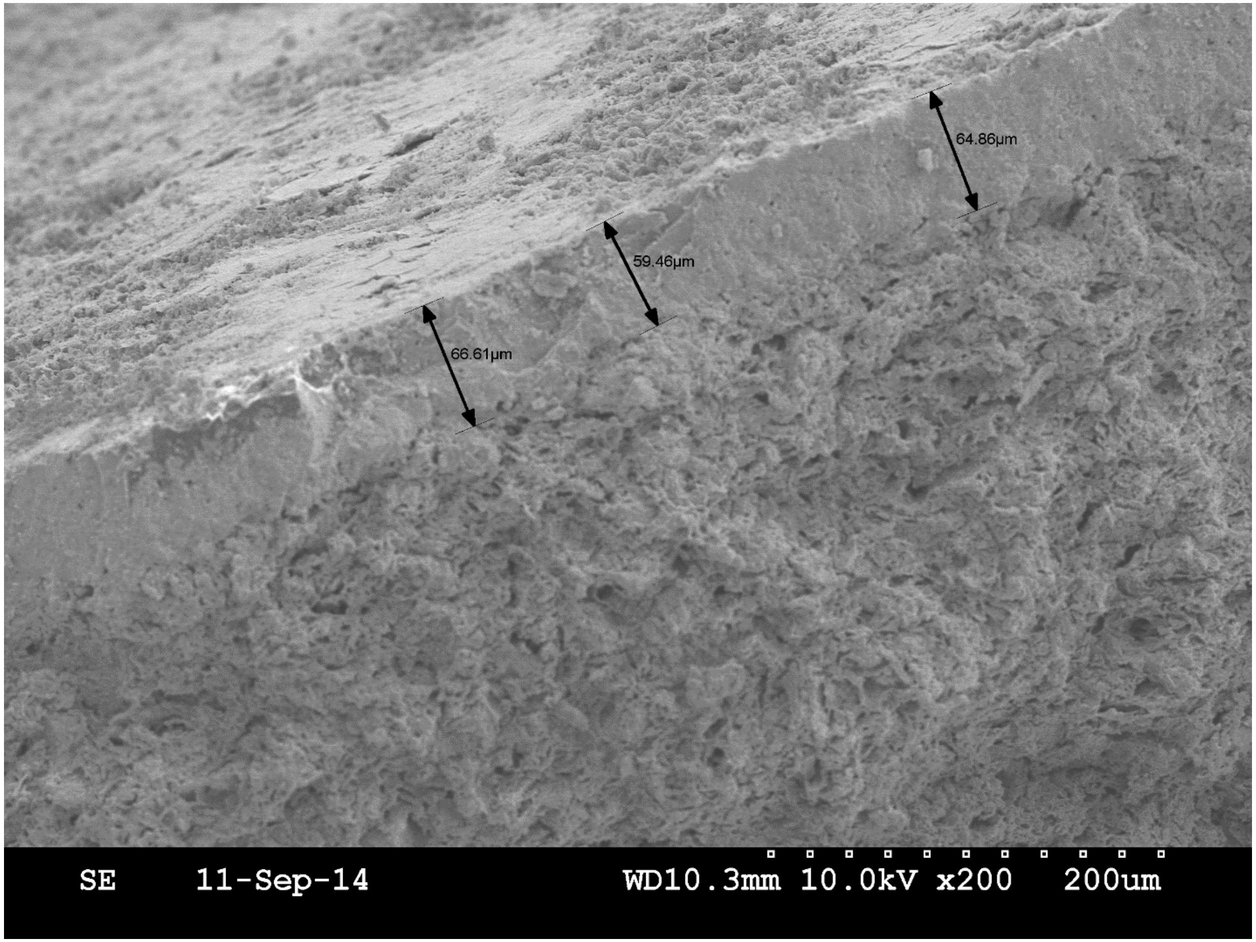
Dip coating process

Characterization of Membrane Layer



(Peak at ~45 degrees due to Fe sample holder)

The Cross-section of Membrane Layer



- Cross-section / 10 h crystallization
  + 6 s seed deposition time (3% wt)

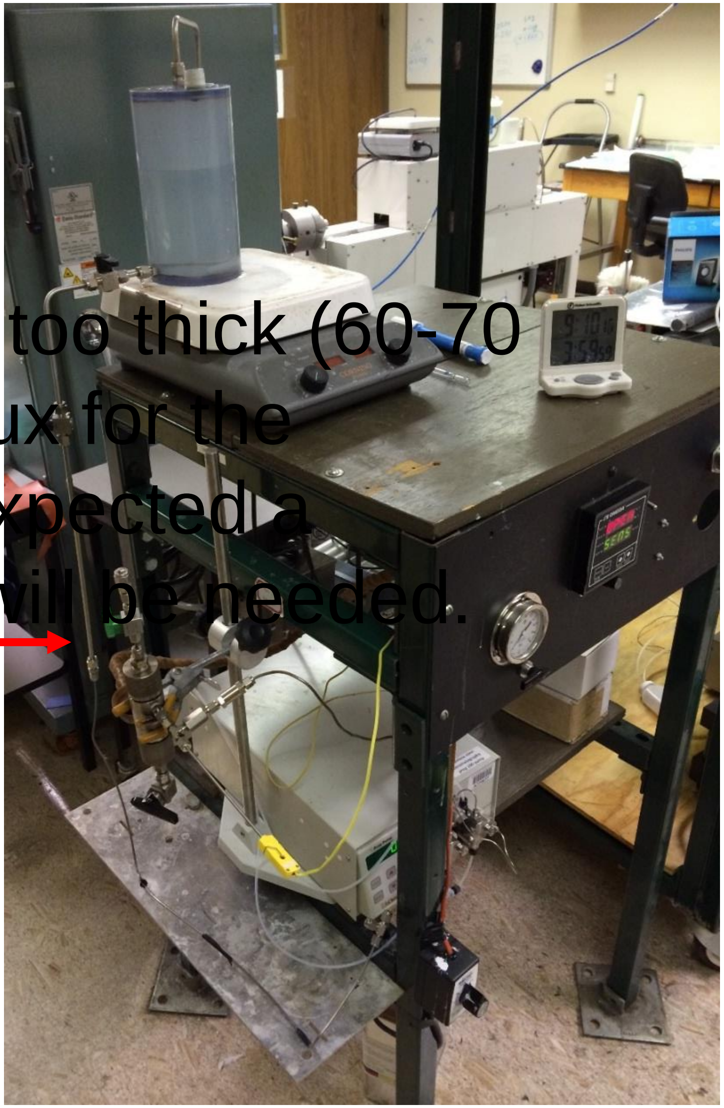
Zeolite layer *c.a* 60-70 μm

Evaluation setup

Membrane reactor

The initial zeolite layer is far too thick (60-70 microns) to yield sufficient flux for the enrichment operation. It is expected a thickness of 20-30 microns will be needed.

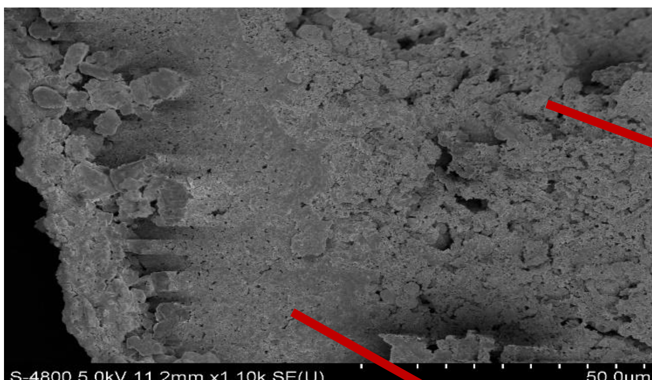
Zeolite membrane

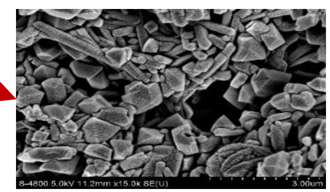


Seeding Modification yield Improvement (1)

1.0 % seed solution /6 s deposition / 10h crystallization (100°C)
Conditions: 30% amine (0.4 carbon loaded), 100°C, 70 PSI, 30 mL/min

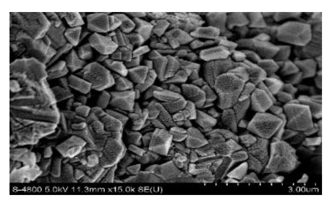
Time (hours)	Flux (kg/(m^{2}h)	Rejection rate (%)
1.00	0.44	75.0
2.00	0.00	0.0





Interface Zeolite crystals and mullite

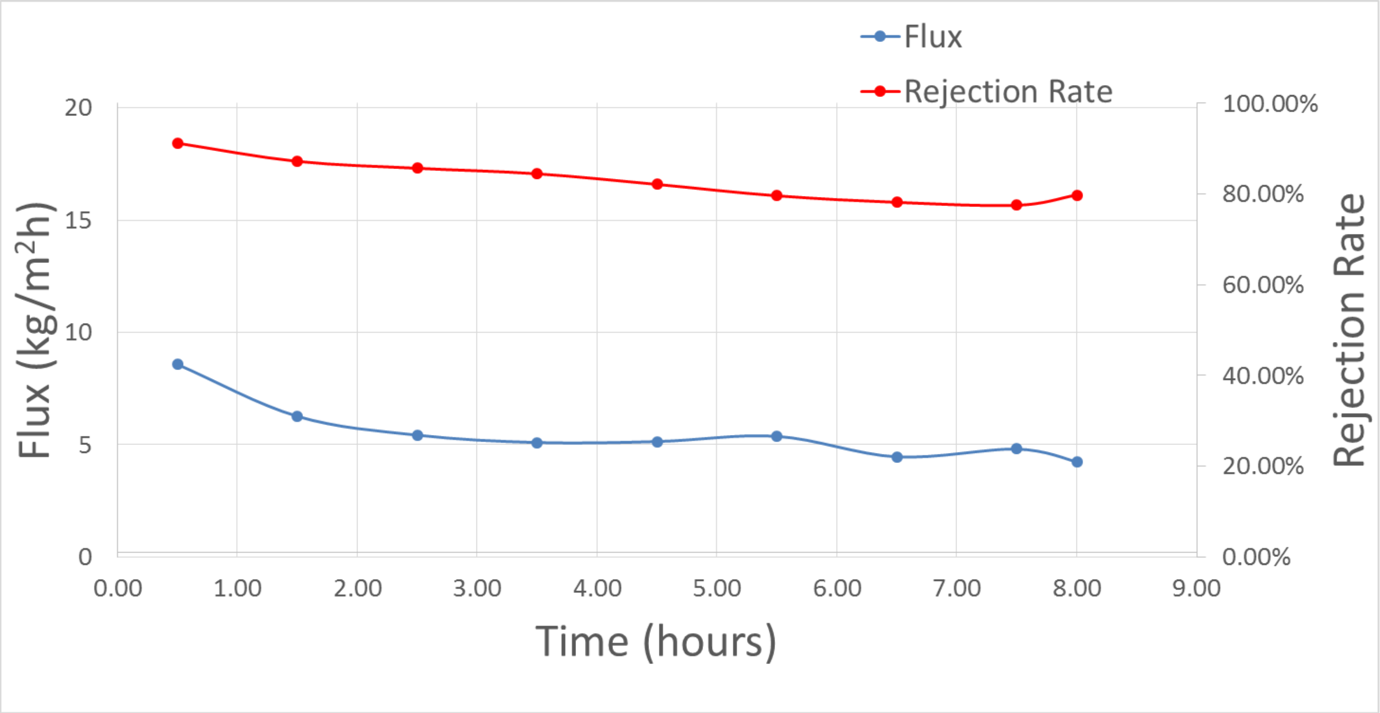
Zeolite layer *c.a* 45-50 µm

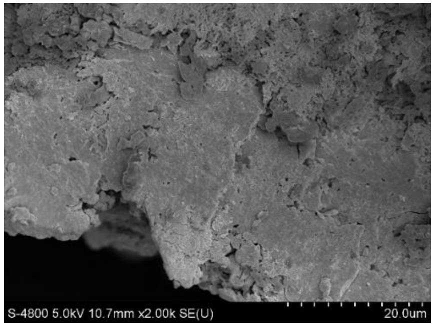


Zeolite crystals

Seeding Modification yield Improvement (2)

1.0 % seed solution /3 s deposition / 10h crystallization (100°C)
Conditions: 30% amine (0.4 carbon loaded), 100°C, 70 PSI, 30 mL/min





Zeolite layer *c.a* 25 µm

Vastly increased flux by using a ~25 µm vs. ~50 µm membranes

As Alternative to Zeolite Membrane -Polymer Membrane-

Time / hr	Pressure / psi	Percent Amine Rejected
0.5	500	-
1	600	-
1.5	700	-
2	800	30.8
2.5	900	33.4
3	1000	35
3.5	1100	37
4	1200	38.6

- Polymer membranes acquired from a commercial vendor including ACM2 and X20 were both examined for post scrubber solvent enrichment. A minimum pressure of 800 psi was required.

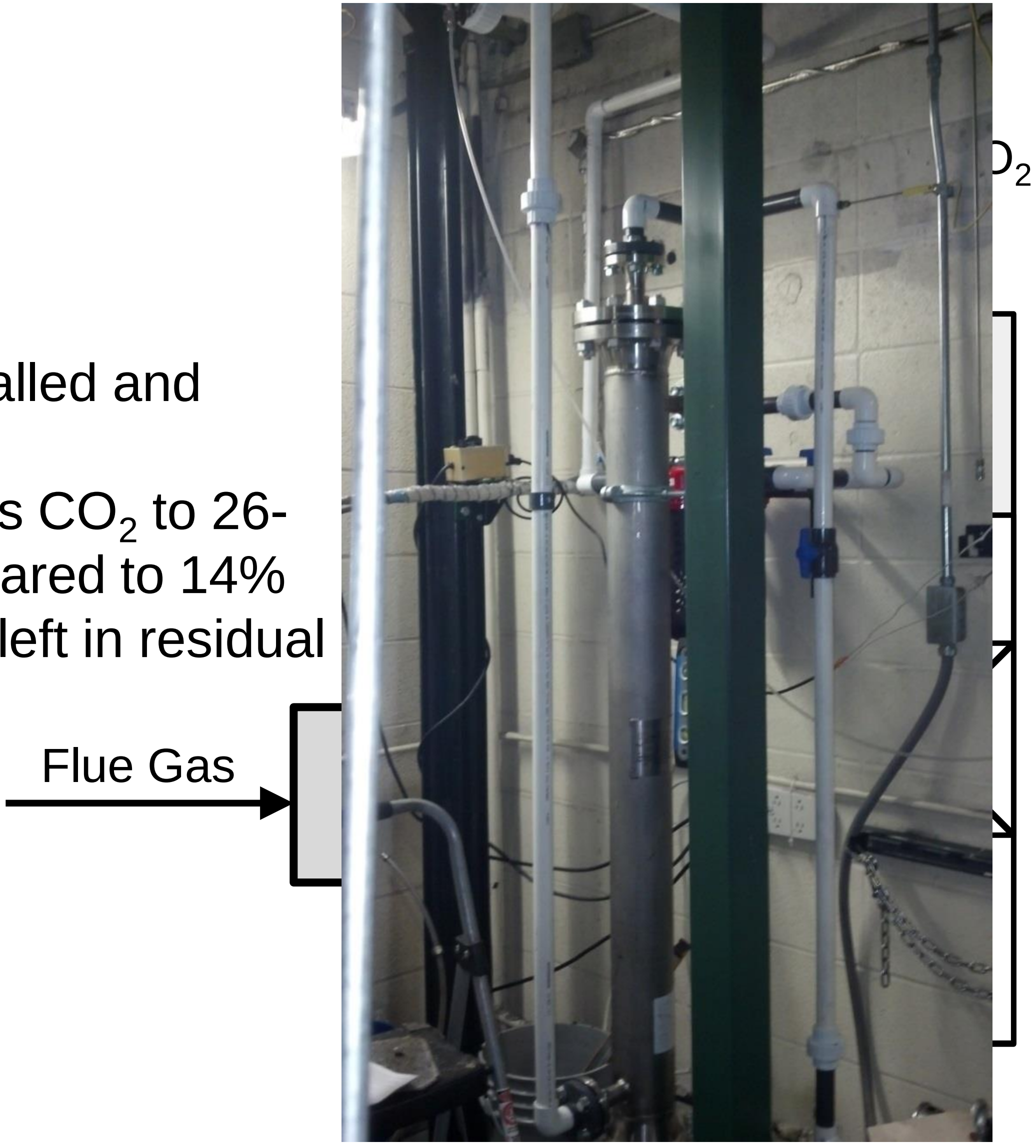
Energy Cost for Zeolite and Polymer Membrane

- Zeolite Membrane
  - Pressures from 60-150 psi are necessary
  - Energy cost for pressurizing a liquid from 20→150 psi is: 0.28 kW/(ton/hr)
- Polymer Membrane
  - Pressures from 800-1200 psi are necessary
  - Energy cost for pressurizing a liquid from 20→1200 psi is: 2.7 kW/(ton/hr)

Not pursuing the RO membrane due to high operating pressure.

Task 3.2 Pre-absorber CO_2 Enrichment

- MTR membrane is installed and commissioned
- Membrane concentrates CO_2 to 26-30% at permeate compared to 14% with approximately 7% left in residual



Platform for Pilot Experiment

Commissioning

Expt	Feed CO_2 (%)	Perm. CO_2 (%)	Residue CO_2 (%)	L/G (wt/wt)	Stripper bottom. temp. (°C)	% Capture	Energy Btu/lb CO_2
M1	14	28	n/A	5.2	133	81	1594
M2	14	28	10	5.1	133	85	1590
Ref	14	-	-	5.6	133	88	1644

Liquid Analysis

Expt	Alkalinity (mol/kg)	Lean Ldg (mol/kg)	Rich Ldg (mol/kg	Lean C/N	Rich (C/N)
M1	5.10	1.58	2.17	0.33	0.44
M2	5.10	1.49	2.18	0.29	0.44
Ref	5.64	1.74	2.14	0.33	0.42

Task 4. Catalyst Scale-up

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

- Large scale synthetic method of CAER catalysts validated
- Able to produce catalyst at high purity at scales needed for pilot testing
- Simple isolation with no purification
  - Collection via precipitation and filtration

Task 5. Front-end Engineering Analysis

Front-end Engineering

- Information needed for TEA identified from WP

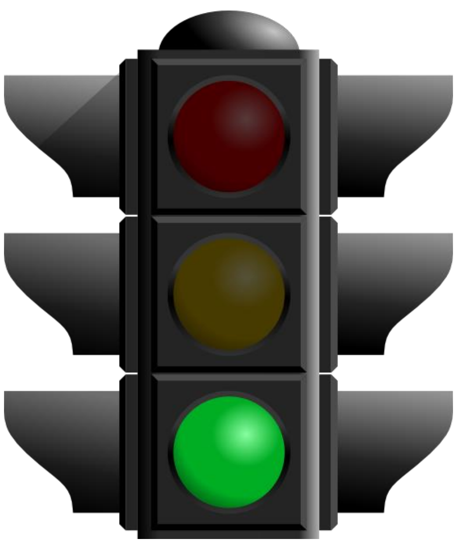
#	Questions/Comments
1	Please specify the pollutant limits for the feed gas entering the absorber (i.e. NO_2, SO_2, particulate, Hg)
2	Please indicate the corrosive nature of the solvent. For example, would 316 stainless steel be a suitable material of construction for all equipment and piping that is in contact with the solvent?
3	Is there a solvent recovery column downstream of the CO_2 absorber? (As shown in Figure 1: Current process flow description of the "Info to WP for Task 5.docx" file)
4	Please provide a heat and material balance around any piece of equipment that WorleyParsons will size (e.g. columns, heat exchanger, pumps, etc.)

Catalytic Solvent Commercial Availability

- All components are commercially available
- Available at scale
  - Mtons/yr
- Estimated catalyst cost of ~$250-350/kg
  - Catalyst charge~1kg/MW

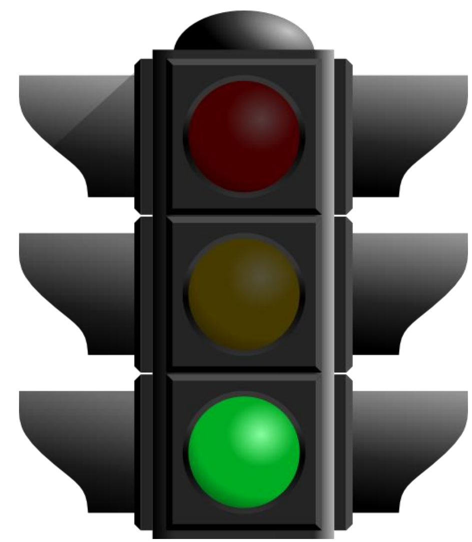
Task 6. PPE Assessment

"… evaluation did not identify any unusual or significant health or safety concerns that should delay or preclude conducting this research…"

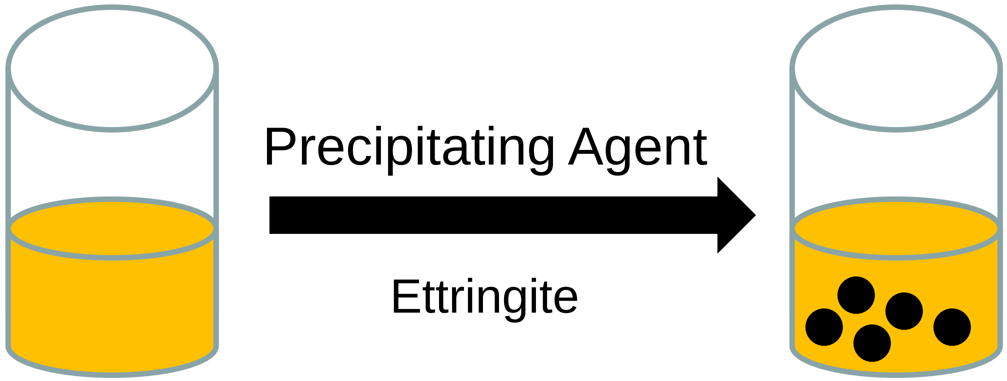


Clayton T. Whitney, Vice President, CHMM
Sarah A. Carty, MPH
SMITH MANAGEMENT GROUP

Issued March 31, 2014



Se Removal



- Solvent "A":
  - 30 wt% ethanolamine
  - 5.0 mg/L sodium selenate
  - 1000 mg/L sodium sulfate
  - pH = 10.8

Solvent "B3":

- 5.0 mg/L sodium selenate
- 1000 mg/L sodium sulfate
- pH = 10.9

Achieved Se reduction to 1.43 mg/L (ppm)

Budget and Expenditure

Budget Period 1	10/1/13 – 9/30/14		
	Baseline Cost Plan	**Estimated Incurred Cost**	**Unobligated Balance**
Federal Share	$888,922	$829,159	$59,763
Non-Federal Share	$222,322	$207,381	$14,941
Total	$1,111,244	$1,036,540	$74,704

- Down-scope of initial TEA & EHS led to BP 1 savings
- Part of savings was already applied in BP 1 to Task 3 (membrane)
- Request unobligated balance be carried to BP 3 for detailed TEA

Conclusions

- Developed robust catalysts
  - shown to maintain enhancement after heating at 145 °C for 100 hr
  - Negligible effect from NOx and SOx components
- VLE and regression obtained
  - Data will feed into ASPEN modeling for TEA
- Membrane enrichment
  - Further tune the zeolite thickness to balance the flux and rejection rate
  - Adjust the operating parameters to match with high inlet CO_2 concentration

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 without catalyst at bench-scale completed
10	Parametric catalytic CAER-B3 investigation	100 hour parametric study with catalyst at bench-scale completed
11	Membrane test module design	Membrane test module design completed
11	Membrane dewatering/enrichment	Membrane shown to dewater CAER-B3 solvent by at least 10% over100 hours or pre concentration achieved with 10% increased carbon loading

- BP2 will focus 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

Budget Requested

- BP 2 budget: DOE $740,078/ cost share $185,133
- BP 2 dates: October 1, 2014 – June 30, 2015

CAER CENTER FOR APPLIED ENERGY RESEARCH

Acknowledgements

UK

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Thank You