



# Advanced Low Energy Enzyme Catalyzed Solvent for CO<sub>2</sub> Capture

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# Project Overview

- Project participants



- Project duration: 24 months (initiated in Oct'2010)
- Funding:
  - Total Project: \$ 3,256,759
  - DOE funding: \$ 2,605,407
  - Akermin Cost share: \$ 651,352

# Akermin

- Founded in 2004 to commercialize patented enzyme immobilization and stabilization technology
  - Technology based on use of novel micellar polymers to immobilize and stabilize enzymes
  - Originally developed at St. Louis University, Akermin has exclusive, world-wide rights
- Akermin's technology can be applied to a variety of enzymes for applications requiring long enzyme life under harsh conditions
  - Focused on carbon capture opportunity (since 2009)

# Key Driver for Solvent-based CO<sub>2</sub> Capture: Energy Cost Minimization

- Most amine-based post-combustion CO<sub>2</sub> capture imposes an unacceptable energy demand on power plant due to energy required for solvent regeneration

Solvent	Heat of Reaction GJ/ton CO <sub>2</sub>
Monoethanolamine - H <sub>2</sub> O (MEA)	1.92
Diethanolamine - H <sub>2</sub> O (DEA)	1.93
Methyldiethanolamine - H <sub>2</sub> O (MDEA)	1.34
Potassium carbonate - H <sub>2</sub> O	0.64

- Carbonate systems offer potential for lower regeneration energy, but exhibit slow kinetics, requiring operation at high temperatures and pressures

# Akermin's Approach

- Enable the use of low energy carbonate solvents through enzyme-catalyzed formation of bicarbonate

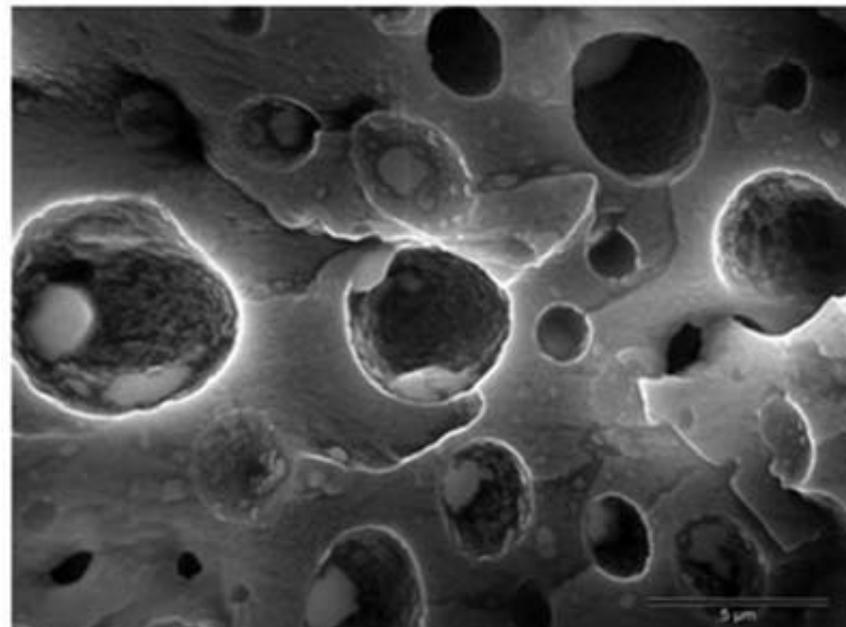


- Achieve kinetics comparable to benchmark amine systems
- Maximize operational lifetime by using immobilized and stabilized carbonic anhydrase
  - Initial system operational life-time goal of 6 months



# Benefits of Micellar Immobilization

- Hydrophilic domains of the micellar polymer minimize enzyme unfolding at elevated temperatures
- Encapsulation in a micellar polymer protects the embedded enzymes from high shear force
- High CO<sub>2</sub> permeability of siloxanes facilitates diffusion of CO<sub>2</sub> and products to and from enzyme active site
- Polymer films can be cast on a variety of contactor systems
- Immobilization keeps the enzyme in the absorber



CD-5-88A – PTA & Au Putter  
5000 x, 15 keV

09-23-2010\_MKH

Siloxane-based micellar polymer stained with PTA and coated with Au; 5000x magnification; scale bar = 5μm.



# Key Program Objectives

- Select the enzyme addressing anticipated operating conditions
- Optimize micellar polymer to achieve high enzyme loading and stabilization, minimize internal diffusion
- Develop detailed Aspen model of enzyme-catalyzed carbonate system and extrapolate to a power plant of 550 MWe (net)
  - Including mass and energy balances, electric power requirements and projected chemical and maintenance costs
- Build and test a closed loop bio-reactor capable of processing up to 500 SLPM of gas, the approximate equivalent of a 5 kWe power plant
  - Demonstrate operation over a 6 month period

# Developmental Challenges

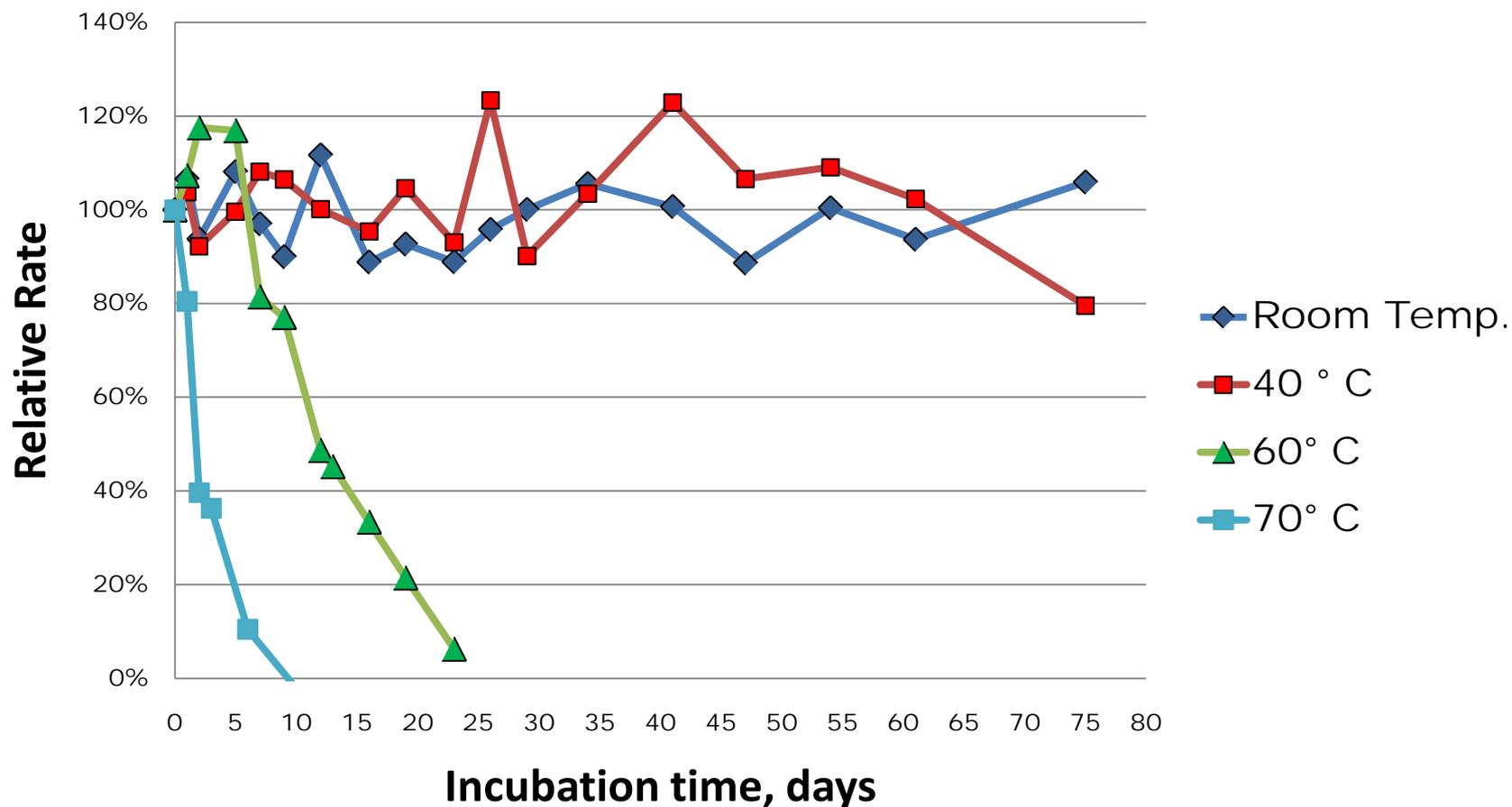
- Flexible, enzyme-independent immobilization technology
- Adaptable to a range of carbonate chemistries ( $K_2CO_3/KHCO_3$ , ammonium carbonate, MDEA, etc.)
- High physical enzyme retention and stabilization
  - 6-12 month lifetime under anticipated absorber conditions of 40 – 60°C, pH 9-11, high ionic strengths
- Tolerance to contaminants in flue gas
- Unique absorber design challenges
  - Heterogeneous catalysis in (3) phase system, complex mass transfer problem
  - Detailed modeling and bench-unit validation is needed

# Progress and Current Status

# Selection of Carbonic Anhydrase (CA) for CO<sub>2</sub> Capture

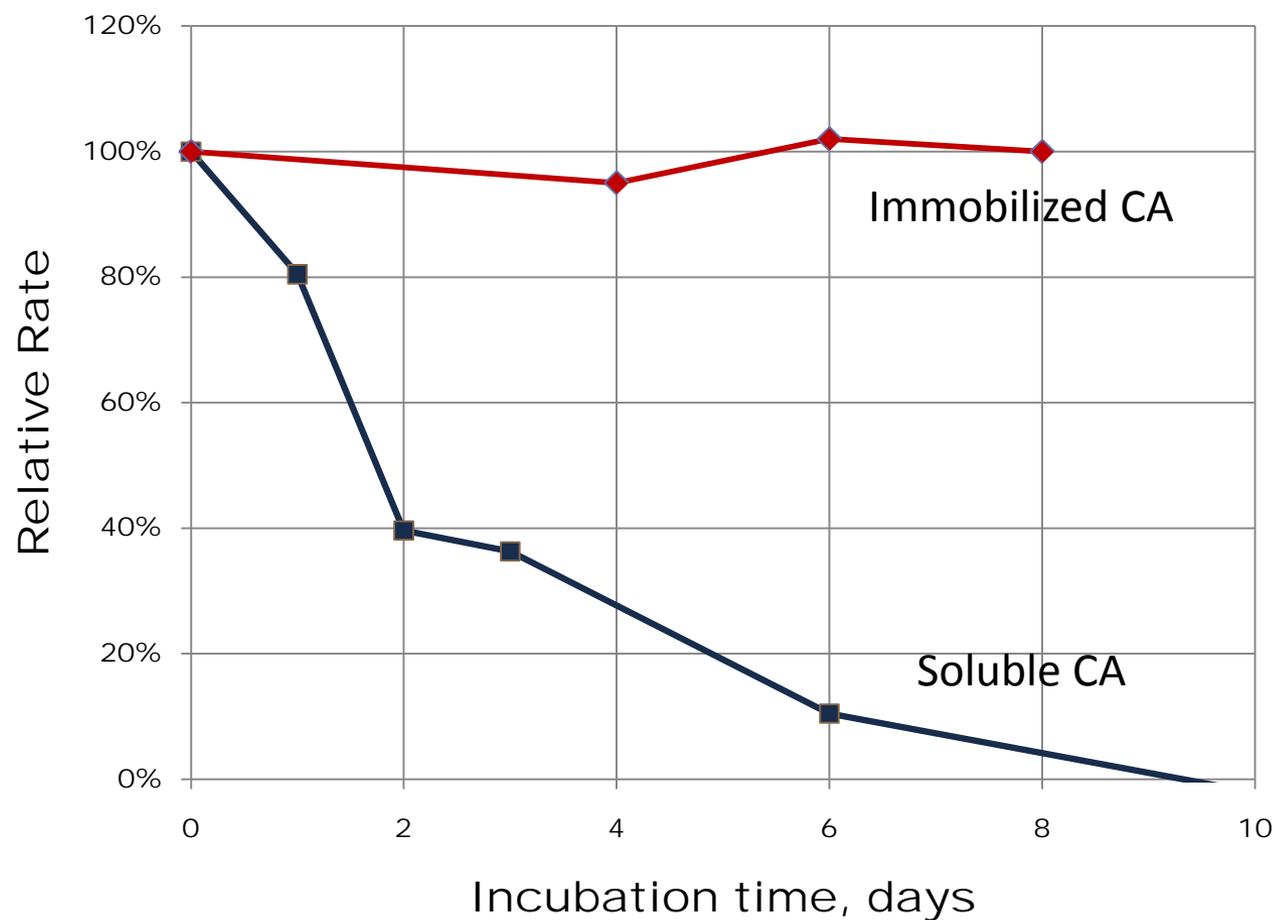
- CA catalyzes hydration of CO<sub>2</sub> to bicarbonate with  $k_{\text{cat}} = 10^6 \text{ sec}^{-1}$
- CA activity is expressed ubiquitously across all life forms
  - represent a family of structurally and genetically diverse enzymes
  - active sites of all CAs contains a single divalent metal essential for catalysis
    - Zn predominates, Fe, Cd, and Co are observed.
- Enzyme selected for this project is a recombinant thermostable CA developed by Novozymes
  - Highly active (~24,000 W&A units/mg protein)
  - Good expression (sample concentrations ~38 g/l)
  - Enzyme is secreted into the medium
    - Simplifies downstream processing, and purification

# Thermostability of Soluble Novozyme CA in 0.5 M $K_2CO_3/KHCO_3$ (pH ~10)



- Novozymes CA is a highly thermostable enzyme with  $T_{1/2} \sim 12$  days at 60 °C pH 10

# Thermostability of Soluble and Immobilized Novozyme CA in 0.5 M $K_2CO_3/KHCO_3$ (pH ~10) at 70 °C

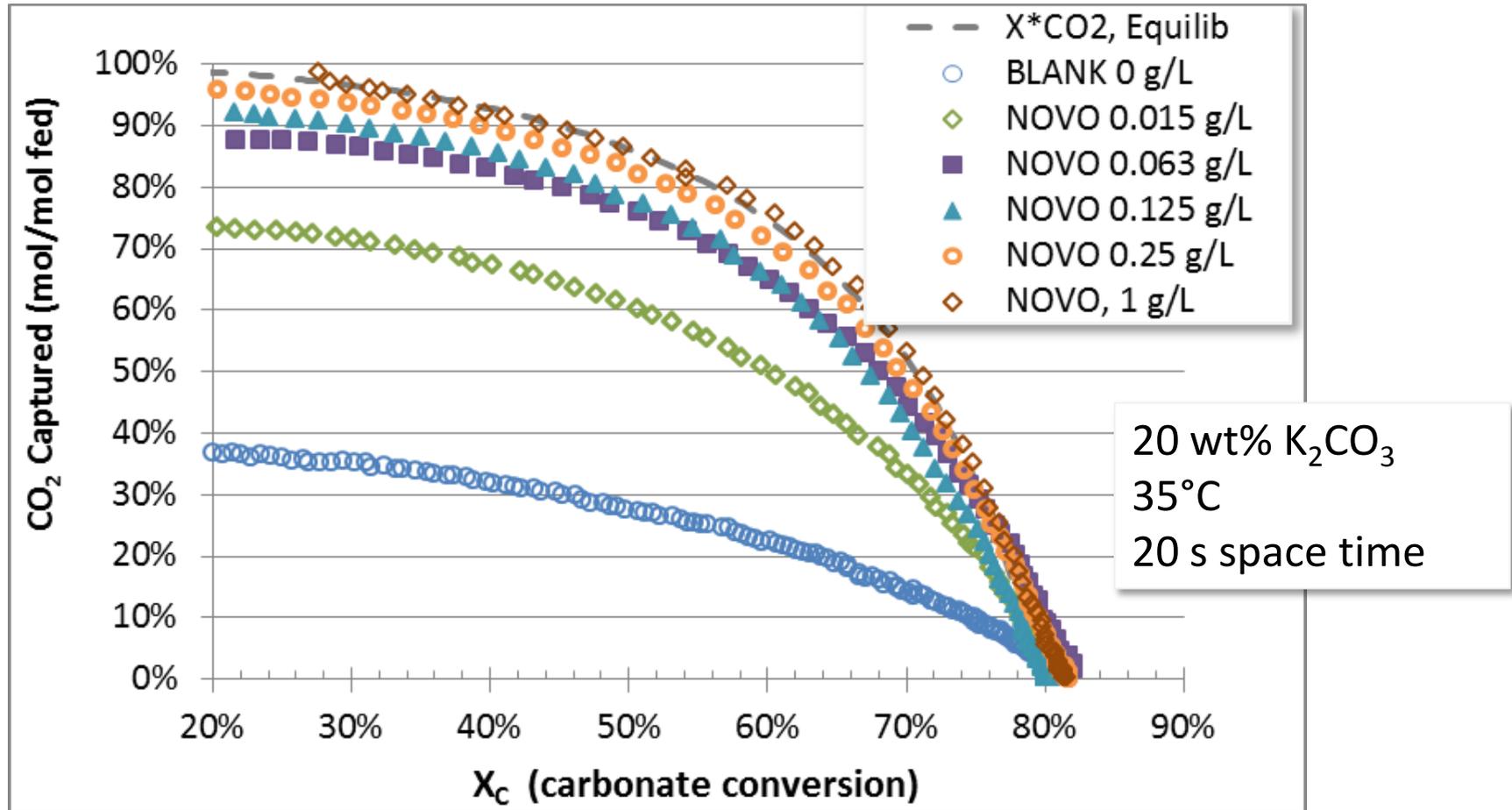


# CA Inhibition Studies

Contaminant	Anticipated Conc*	Soluble Product	IC50 (mM)	Activity Remaining (conc.)	Comments
NO <sub>x</sub>	~80 ppmv	Nitrate (NO <sub>3</sub> <sup>-</sup> )	----	49% (1 M)	
		Nitrite (NO <sub>2</sub> <sup>-</sup> )	----	75% (1M)	
SO <sub>x</sub>	~45 ppmv	Sulfate (SO <sub>4</sub> <sup>-2</sup> )	----	100% (250 mM)	Solubility limiting
		Sulfite (SO <sub>3</sub> <sup>-2</sup> )	----	100% (2.5 mM)	Background limiting
Chloride	< 1ppm	Chloride (Cl <sup>-</sup> )	----	123% (2 M)	
Heavy Metals	~1.2 ppbw	Mercury(II) (HgCl <sub>2</sub> )	0.13	14% (3 mM)	Solubility limiting
		Lead(II) (Pb(NO <sub>3</sub> ) <sub>2</sub> )	----	80% (0.002 mM)	Solubility limiting

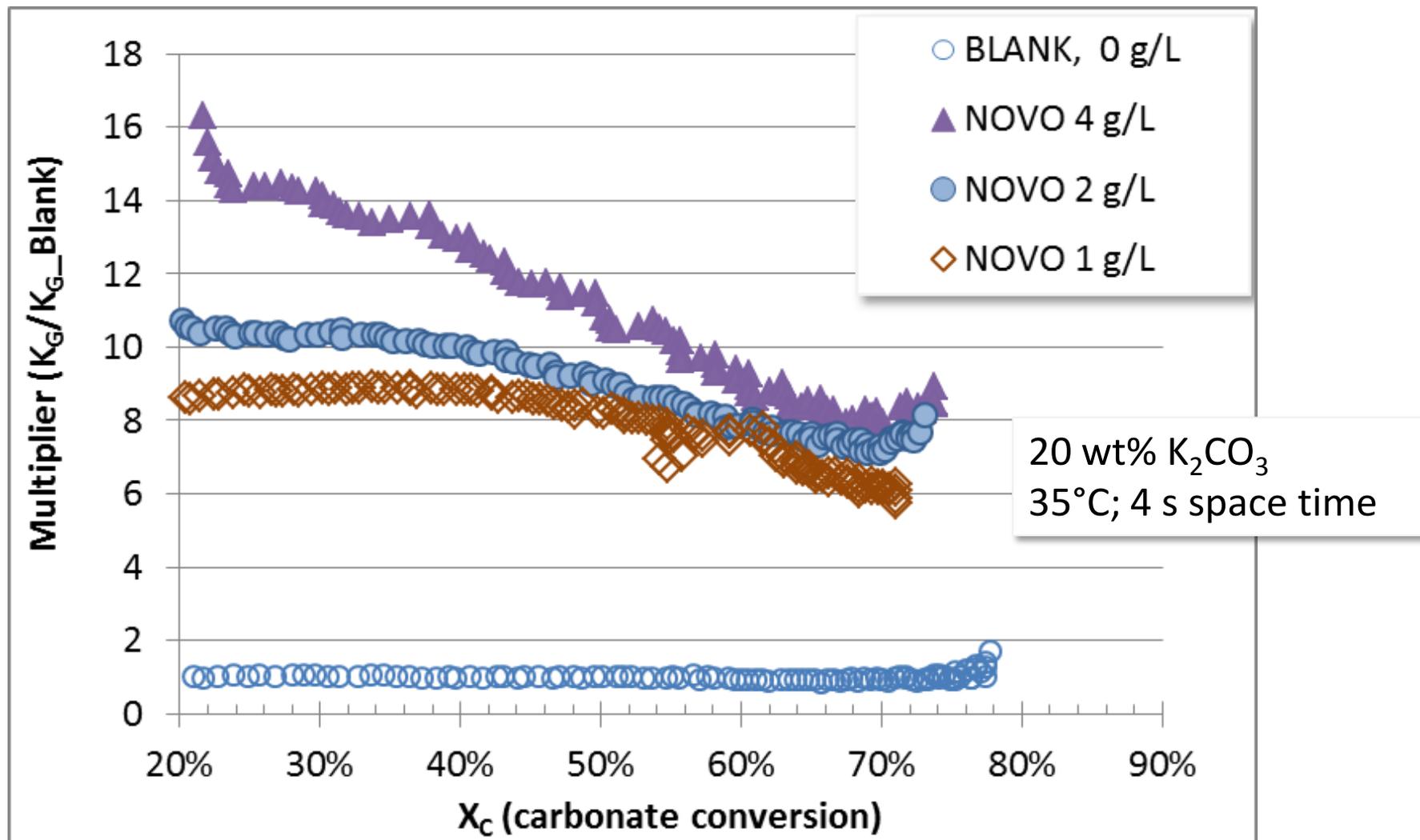
- Sulfate, sulfite, nitrate, nitrite and chloride - little or no inhibitory potency
- Potent inhibition by divalent metals in low ionic strength buffer.
- Poor solubility of carbonates and hydroxide salts of divalent metals in carbonate solutions might obviate CA inhibition at high pH

# Characterization of CA Performance in packed bed 1 L reactor (free enzyme)



- At low loading and 20 s space time >90% absorption is achieved with 0.125 g/l CA
- $CO_2$  absorption reaches equilibrium at ~ 80% carbonate conversion

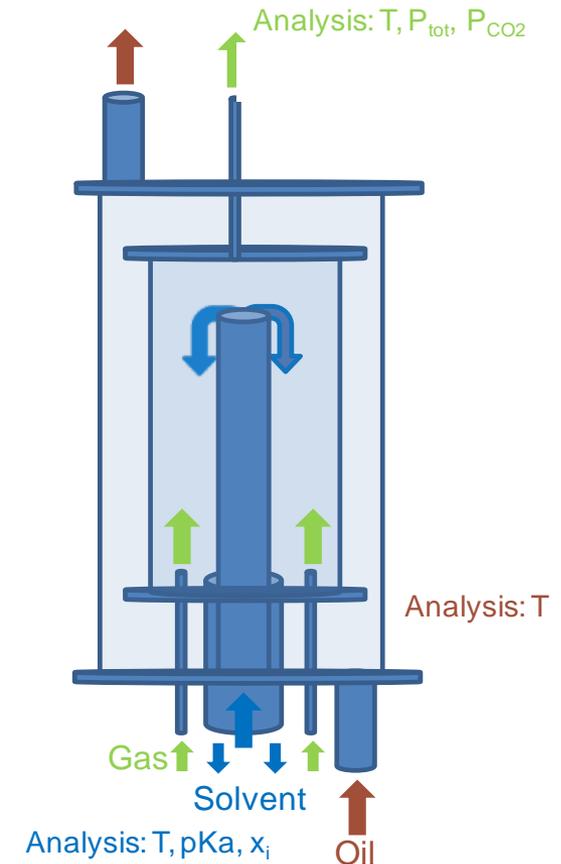
# Mass Transfer Coefficient ( $K_G$ ) for Free CA vs. Blank



# Effect of CA on Mass Transfer Coefficient: Wetted Wall Measurements

- Objective:
  - Measure  $\text{CO}_2$  flux (or overall mass transfer coefficient,  $K_G$ ) for a range of  $P_{\text{CO}_2}$
  - Calculate equilibrium and kinetics parameters to support system-level modeling
- Results:
  - Strong dependency on dissolved protein; less dependent on pH and temperature.
  - Measured value with no enzyme matched Aspen Plus

*Wetted wall information, observed and targeted  $K_G/K_{G, \text{blank}}$  data were incorporated into Aspen Plus*



17 wt %  $\text{K}_2\text{CO}_3$  solution; dissolved CA  
 $\text{CO}_2$ : 0%, 5%, 10%, 20%, and 30% (balance  $\text{N}_2$ )  
 $\text{CO}_2$  loading: 13% - 80%  
 $\text{K}_2\text{CO}_3$  to  $\text{KHCO}_3$  conversion (pH of 10.2 to 8.8)

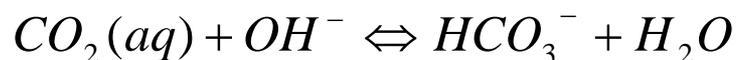
# Initial ASPEN Simulation Results for Enzyme-Catalyzed Potassium Carbonate ( $K_2CO_3$ ) System

# Initial Simulation Assumptions/Details

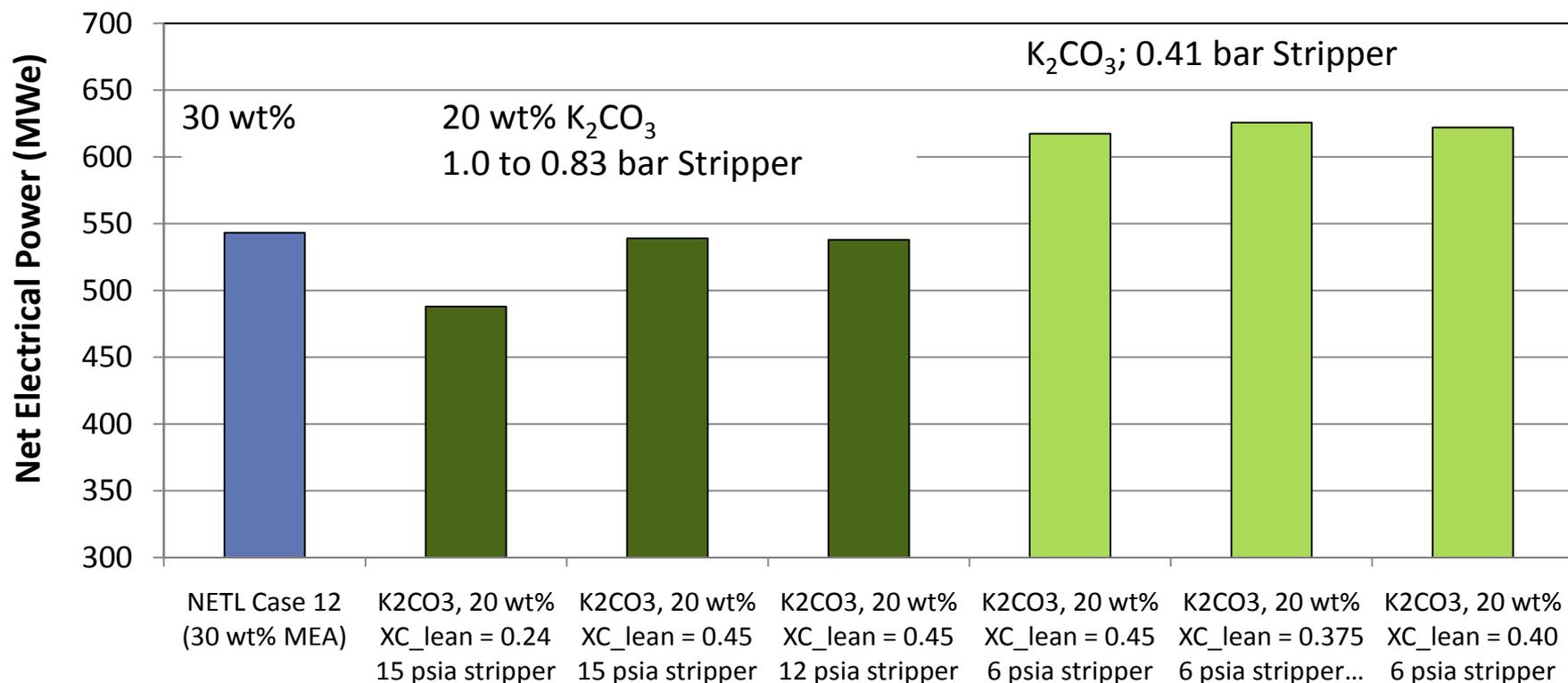
- NETL Case 12 flue gas rate and composition downstream of a wet limestone flue gas desulfurization unit & direct contact water cooler (same as MEA)

Flowrate (lbmol/hr)	210,160
Flowrate (lbs/hr)	6,323,430
Temperature (F)	90.1
Pressure (psia)	15.2
<i>Composition:</i>	
N <sub>2</sub> (mol%)	76.4%
H <sub>2</sub> O (mol%)	4.9%
CO <sub>2</sub> (mol%)	15.1%
O <sub>2</sub> (mol%)	2.7%
Ar (mol%)	0.9%

- 90% CO<sub>2</sub> capture
- ISO ambient conditions (sea level, 15 °C, 14.7 psia, 60% RH)
- Absorber: packed tower gas liquid contacting system
- Equilibrium simulation in stripper
- Compression of separated CO<sub>2</sub> to 2215 psia
- ASPEN model components: cooling tower, steam cycle, absorber/stripper, and CO<sub>2</sub> compressor.
- Enzyme effect simulated by adjusting activation energy for bicarbonate reaction:



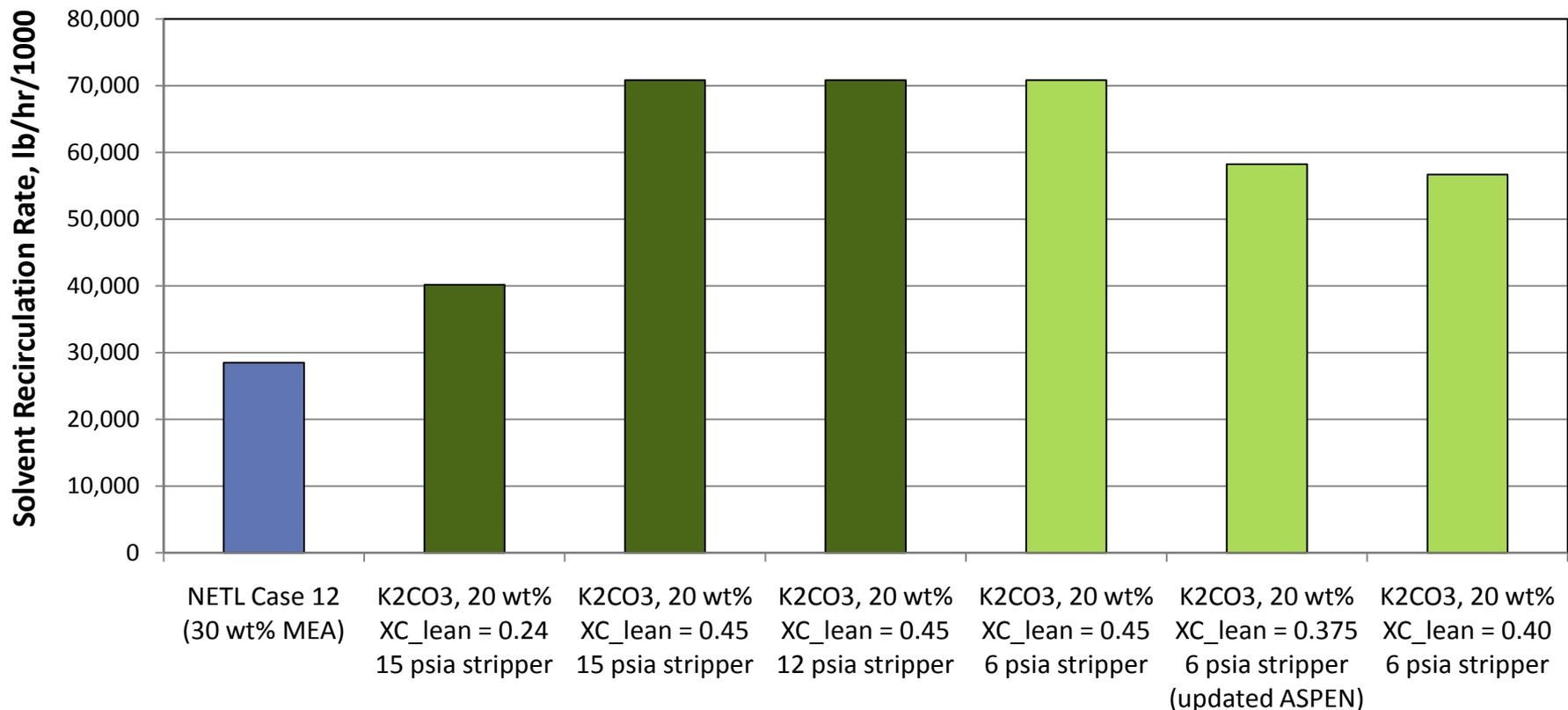
# Initial Simulation Data Comparison – Net Electric Power



## Key Observations:

- To exceed the net electric power of MEA **the lean loading is increased**, and stripper **pressure is reduced**
- Initial set of conditions was identified for potassium carbonate system exhibiting a **21% parasitic load compared to 31% for MEA** (including CO<sub>2</sub> compression energy )
- Increase of carbonate concentration from 20 wt% to 25 wt% had little impact on net electric power
- Absorber kinetics had little or no effect on net electric power (equilibrium effect only).

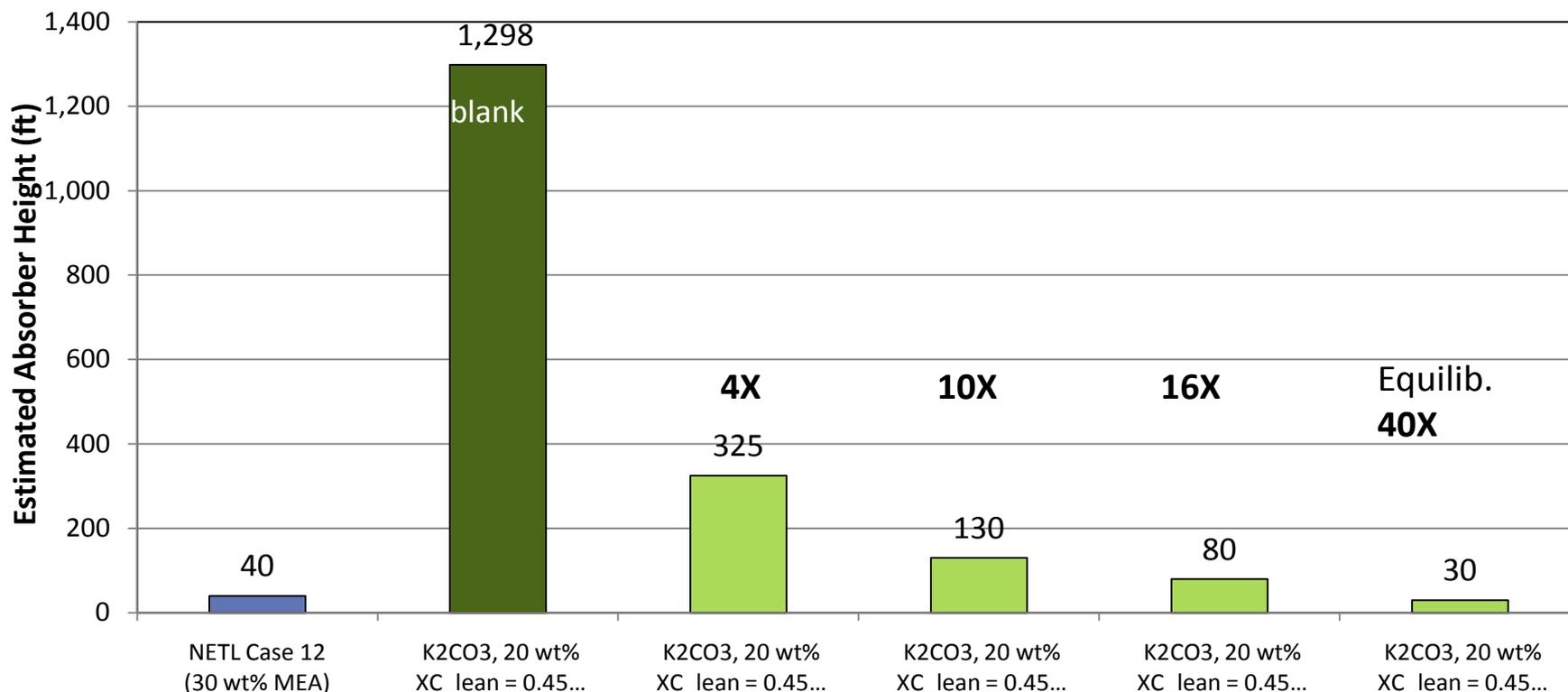
# Solvent Recirculation to Achieve 90% Capture



## Key Observations:

- Solvent recirculation increased with increases in lean loading
- Increased solvent concentration reduces solvent recirculation rate
- Recirculation rate is not affected by improved kinetics

# Simulation Data Comparison – Absorber Height



## Key Observations:

- Predicted absorber tower height for MEA is 40 ft; 100 ft is reasonable from an economic perspective
- A 10-15X multiplier in  $K_G$  (vs. blank) reduces absorber to ~100 ft for  $K_2CO_3$
- Tower height is roughly proportional to the multiplier in overall mass transfer coefficient; impacts capital cost

## Conclusions Based on Initial Modeling

- A positive impact on net electric energy was predicted with higher lean loading levels.
- Operating the stripper under mild vacuum conditions yielded energy efficiencies that outperformed MEA. Combined efficiency ~33% better than MEA.
- $K_2CO_3$  with no kinetic enhancements would require an absorption tower 30 times taller than NETL's MEA reference case.
- $K_2CO_3$  with a kinetic enhancement of ~10X on an overall flux basis reduces the absorber tower height considerably, placing it within a competitive range.

# Future Activities

- Optimize micellar polymer
- Perform the long-term enzyme stability studies
- Design and commission a bench-scale closed loop carbon capture system
- Refine CAPEX and OPEX calculations
- Experimentally determine regeneration energy for  $K_2CO_3$  under various operating conditions of the desorber
- Operate unit for 6 months to establish robust data set for system operating costs

# Key Team Members

## AKERMIN:

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Andrew Jones, PM

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