Advanced Enzyme-Catalyzed CO$_2$ Capture in Low-Energy Solvents

Alex Zaks, Ph.D.

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AKERMIN, INC.

• St. Louis-based biotechnology company
• Developing next generation cost and energy efficient, environmentally benign systems for CO₂ capture
• Technology based on integrating an enzyme within a proprietary biocatalyst delivery system which permits:
  • Use of low energy solutions of carbonates
  • Incorporation into a traditional chemical absorption process
PROJECT OVERVIEW

• Project participants

• Project duration: 33 months (initiated in October 2010)

• Funding
  Total Project: $4,749,469
  DOE Funding: $2,909,678
  Akermin Cost share: $1,839,791
PROJECT OBJECTIVES

• Engineer Bench-Scale Carbon Capture System
  — ~5 kWe (500 SLPM flue gas)

• Demonstrate 90% CO₂ capture from flue gas in a bench-scale unit in the presence of biocatalyst and potassium carbonate

• Characterize rate enhancement of biocatalyst

• Demonstrate tolerance to flue gas impurities

• Evaluate impact of external conditions on process performance

• Demonstrate CO₂ capture on flue gas for duration of 6 months

• Generate process data to further refine simulation models

• Model and evaluate the capital and operational costs for full-scale coal-fired power plant
CARBONIC ANHYDRASE

• CA accelerates hydration of CO₂ to bicarbonate:

  \[
  \text{CO}_2 + \text{H}_2\text{O} \xrightarrow{\text{CA}} \text{HCO}_3^- + \text{H}^+
  \]

• Akermin explored numerous CAs for CO₂ capture
• CA developed by Novozymes is top candidate
  – Highly active
  – Resistant to major impurities in flue gas
  – Thermostable
  – Resistant to high pH (9.5-10.5)
  – High expression level, few impurities

Active site of CA

\[k_{\text{cat}} = 10^6/\text{sec}\]
TECHNOLOGY FUNDAMENTALS

Basic unit design for CO₂ capture incorporating biocatalyst

**Biocatalyst delivery system**

- FLUE GAS
- 45 °C ABSORBER
- **K₂CO₃/KHCO₃ lean solution**
- ID FAN
- PUMP

**105 °C STRIPPER**

- VAPOR
- LIQUID
- **“LEAN**

**CONDENSER**

- ADVANCED CO₂ COMPRESSION

**PRODUCT CO₂**

**PRODUCT GAS**

- STEAM
- CONDENSATE

**Akermin Inc. (2011)**
THERMOSTABILITY OF FREE CARBONIC ANHYDRASE

Room Temp.  40 °C  50 °C  60 °C  70 °C  80 °C

0.5 M K₂CO₃/0.5 M KHCO₃, pH 10.0

T₁/₂ ~ 110 days at 40 °C
T₁/₂ ~ 60 days at 50 °C
T₁/₂ <1 day at 80 °C
CHARACTERISTICS OF BIOCATALYST DELIVERY SYSTEM

• Compatible with commercial mass transfer devices
• Impose minimal internal diffusional limitations
  – CO$_2$ permeable or highly porous support
• Provide protective environment against inactivation by temperature, solvents, and shear forces
  – Encapsulation/entrapment-based
• Low cost, scalable
  – Commercially available starting materials; simple one/two-step protocol
Akermin developed several proprietary approaches to exhibit CA at gas/liquid interface of absorber column.
PERFORMANCE OF BIOCATALYST IN A COUNTER-CURRENT FLOW COLUMN

20% carbonate (w/w) pH 10.1; p = 1 psig; CO₂ absorption at 45°C;

K_G per packing area, lab-scale test reactor interfacial area ~ 30%

Up to 22-fold increase of K_G was demonstrated
BIOCATALYST MAXIMIZES MASS TRANSFER AND REDUCES COLUMN HEIGHT

Enhancement over 10X reduces the absorber height to less than 130 feet for a 550 mWe coal-fired power plant*

*Aspen Plus modeling by PNNL
STUDY OF CA INHIBITION BY PRODUCTS OF HYDRATION OF FLUE GAS IMPURITIES

Solution study

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Anticipated Concentration</th>
<th>Soluble Product</th>
<th>IC50 (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOX</td>
<td>~80 ppm</td>
<td>Nitrate (NO$_3^-$)</td>
<td>~ 1000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nitrite (NO$_2^-$)</td>
<td>&gt; 2000</td>
</tr>
<tr>
<td>SOX</td>
<td>~45 ppm</td>
<td>Sulfate (SO$_4^{2-}$)</td>
<td>&gt; 500</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sulfite (SO$_3^{2-}$)</td>
<td>&gt;&gt; 10</td>
</tr>
<tr>
<td>Chloride</td>
<td>&lt; 1ppm</td>
<td>Chloride (Cl$^-$)</td>
<td>&gt; 2000</td>
</tr>
</tbody>
</table>

Sulfate, sulfite, nitrate, nitrite and chloride have little or no inhibitory potency.
TESTING ON FLUE GAS

• Evaluate resistance of the biocatalyst delivery system to Hg, SO$_x$ and NO$_x$

• Demonstrate endurance performance using actual flue gas
  – Flue gas was generated at the Advanced Coal and Energy Research Facility at Washington University in St. Louis
  – Flue gas was gathered into a 10 m$^3$ bag from a short duration combustion test
TESTING ON FLUE GAS

Wyoming Powder River Basin subbituminous coal

~ 90-95% CO₂ capture sustained for over 23 days on flue gas (~14% feed)
~ 90-92% CO₂ capture on Reference Mixture (~15% CO₂ in air) for 14 days
Overall performance is stable in both cases
STUDY OF TRACE CONTAMINANTS: 20 PPM SO₂ AND 20 PPM NO₂

~90% capture maintained over the duration of the experiment
LONG-TERM PERFORMANCE OF CLOSED LOOP REACTOR

400 mL/min 15% CO₂; 20% carbonate (w/w)
pH 10.1; p = 1 psig; CO₂ absorption at 45°C;
thermal swing desorption at 105°C

>20 million CO₂ molecules hydrated by one CA molecule over 75 days
Initial performance >400 kg CO₂ captured per day per kg of CA
ADVANTAGES OF BIOCATALYST DELIVERY SYSTEM WITH CARBONATE CHEMISTRY

- **Significant Rate Enhancement**
  - Lower absorber column heights resulting in lower capital expenditures

- **Energy-efficient process: Low Parasitic Load**
  - Flexibility to regenerate at wide range of pressures/temperatures

- **Carbonate solution has negligible vapor pressure**
  - Lower solution losses and no need for wash columns resulting in lower capital and operating expenses

- **Operation at lower temperatures (40°C) and pH values**
  - Low corrosion rates relative to conventional amine & carbonate processes

- **Carbonate solution does not degrade in presence of oxygen and impurities, which reduces both capital and operating expenses**
  - No need for reforming
  - No expected polishing FGD

- **Carbonate solution is low cost commodity chemical**
  - Combined with lower solution losses, equates to lower replacement costs

- **Environmentally-friendly process**
  - No solvent or nitrosamine emissions to the atmosphere
  - Benign (potentially reusable) by-products with lower disposal costs

A simple process chemistry and design that yields a low-cost solution for CO₂ capture
PROGRESS AND CURRENT STATUS
PROJECT STATUS

• Key Milestones Completed to Date
  – Demonstrated >80% physical protein retention
  – Completed Wetted Wall kinetic testing for K₂CO₃
  – Defined preferred conditions for low energy operation
  – Demonstrated 10+ fold acceleration of CO₂ capture
  – Completed baseline techno-economic analysis
  – Finalized Bench unit column design, M&E balance
  – Executed Site Agreement with NCCC
  – Performed testing of flue gas contaminants
BENCH UNIT SPECIFICATIONS

• **Absorber Design Case**
  – 500 SLPM flue gas (nominal)
  – 90% Capture, nominal 0.175 tpd CO₂
  – Sulzer 500 m²/m³ packing
  – Nominal Liquid: 300 kg/hr (nominal)
  – 20 wt% K₂CO₃, lean pH ~10

• **Heat recuperative cross exchanger and trim coolers**

• **Emerson Delta-V Control System**
## UPCOMING ACTIVITIES

<table>
<thead>
<tr>
<th>Activity</th>
<th>Date</th>
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<tbody>
<tr>
<td>Fabrication of Bench Unit</td>
<td>June – October 2012</td>
</tr>
<tr>
<td>Scale-up coating process and coat ~100 m² of contactor</td>
<td>November 2012</td>
</tr>
<tr>
<td>Install/Commission</td>
<td>November 2012</td>
</tr>
<tr>
<td>Initial Testing (blank)</td>
<td>December 2012</td>
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<tr>
<td>Initial Testing (biocatalyst)</td>
<td>January 2013</td>
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<tr>
<td>Operate unit for six months</td>
<td>January – June 2013</td>
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<tr>
<td>Model and evaluate the capital operational costs for full-scale coal-fired power plant</td>
<td>June 2013</td>
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## ACKNOWLEDGMENTS

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- Carrie Duesing, Sr. Research Associate
- Dawn Powell, Sr. Research Associate
- Keith Killian, Research Associate
- Jonathan Tuttle, Engineering Associate
- Luke Weber, Research Associate

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