Low-Energy Solvents for Carbon Dioxide Capture Enabled by a Combination of Enzymes and Vacuum Regeneration

Final Project Review Meeting
Award No. DE-FE0007741
DOE-NETL, Pittsburgh, PA
23 September 2015

Presented by: Sonja Salmon, Charles Freeman, Reynolds Frimpong, Alan House, Jonathan Slater

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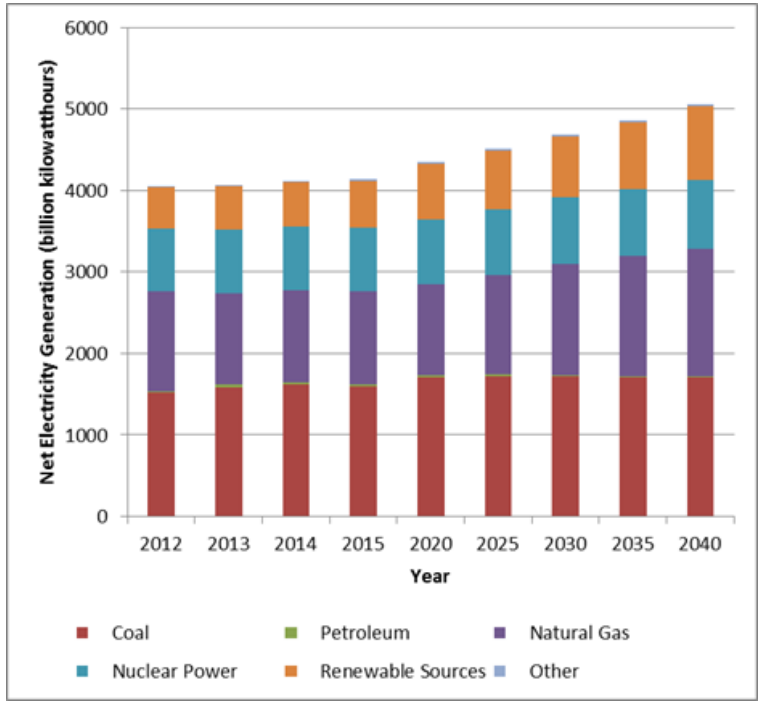
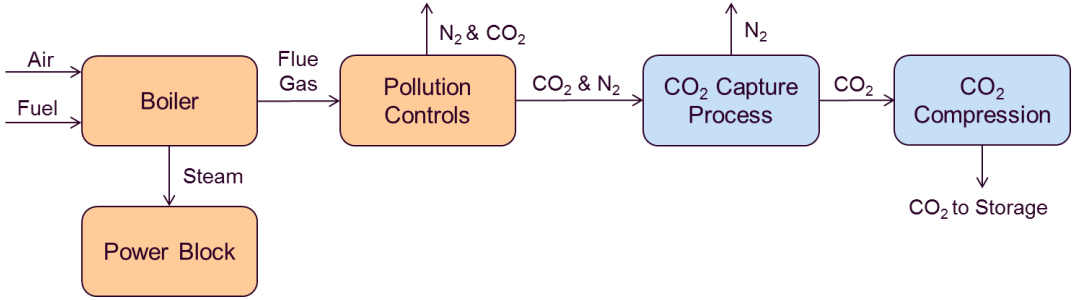
Project Motivation



International Energy Outlook 2013, U.S. Energy Information Administration

Coal and natural gas remain the foundation of U.S. electricity generation



Without CO_2 Capture

With CO_2 Capture

Post-combustion CO_2 Capture could help curb emissions, but added costs are high

CO_2 Emissions Challenge for Power Generation

Global economy projected to grow by 88% from 2013 to 2030 and energy-related CO_2 emissions by 8%, reaching ~35 Gt/y

IEA World Energy Outlook Special Report on Climate Change, 2015.

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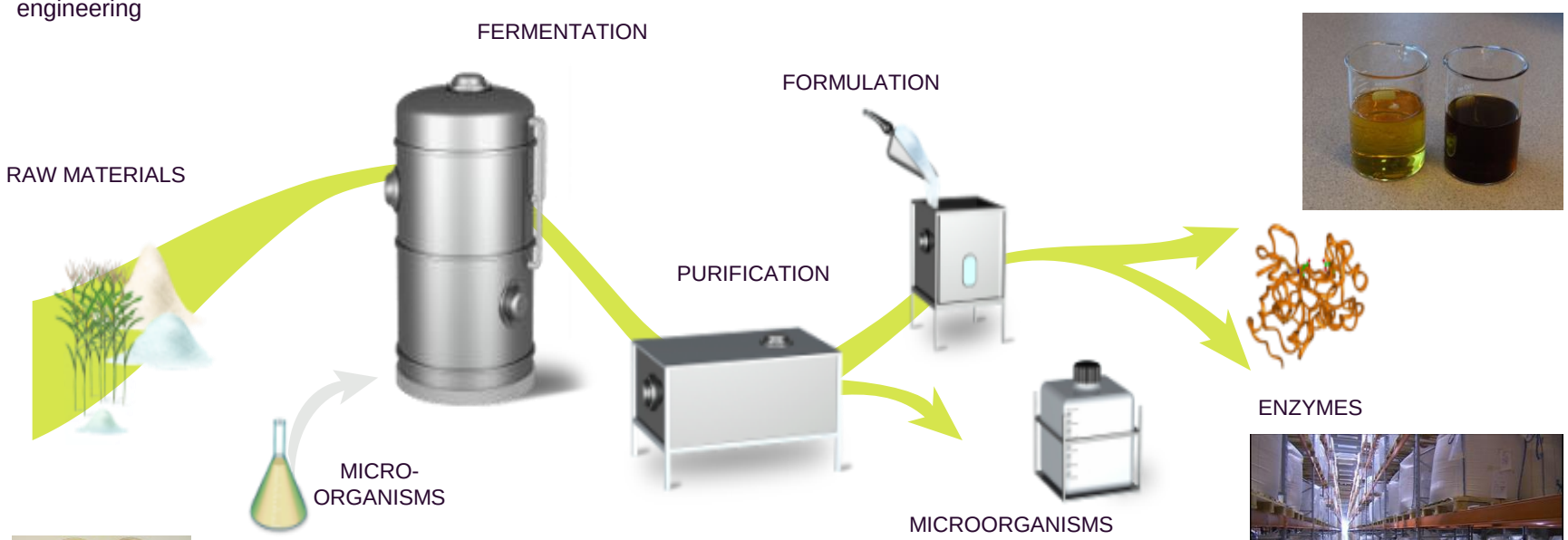
Lead Contractor: Novozymes

1. **Improving the production host**
   Improving the microorganisms' ability to produce more enzymes per m^3 fermentation tank through genetic engineering

2. **Optimizing industrial production**
   - Process optimization
   - Equipment optimization
   - Input optimization



3. **Improving the enzyme produced**
   Improving the efficacy of the enzymes through protein engineering to meet application conditions and process economy requirements

Discovering, developing and producing large volume enzymes for industrial applications
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Project Team

DOE/NETL	Andrew Jones
Novozymes	Sonja Salmon (PI/PM)
	Alan House (TL)
	Erin Yarborough
	Megan Beckner Whitener
UK-CAER	Kunlei Liu (PM)
	Kun Liu (TL)
	Reynolds Frimpong
	Guojie Qi
	Balraj Ambedkar
	Joe Remias
PNNL	Charles Freeman (PM/TL)
	Greg Whyatt
	Mark Bearden
	Kayte Denslow
	Richard Zheng
Doosan	David Fitzgerald (PM)
	Jonathan Slater (TL)
	Rafael Vidal
	Tania Russell
	Scott Hume
	Vinay Mulgundmath
	Saravanan Swaminathan
	Agnieszka Kuczynska

Project Overview

Project Participants/Role:

Pacific Northwest National Laboratory	Doosan	Novozymes	University of Kentucky Center for Applied Energy Research
Ultrasonics & Aspen®	Full Process Analysis	Enzymes & Solvents	Kinetics & Bench-scale Tests

DOE Project Manager: Andrew Jones

Project Number: DE-FE0007741

Project Duration: Oct. 1, 2011 – June 30, 2015

Project Budget:

	Budgeted	Actual
DOE Share	$1,658,620	$1,658,467
Participants Cost Share	$430,024	$558,032
Total	$2,088,644	$2,216,499

DOE Program Objectives

Develop solvent-based, post-combustion technology that

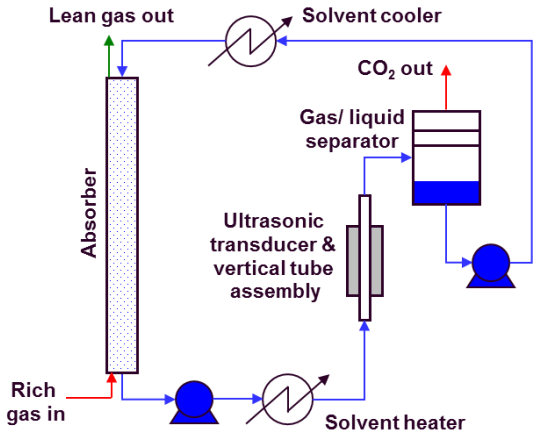
- Can achieve ≥ 90% CO_2 removal from coal-fired power plants
- Shows progress toward DOE target of <35% increase in LCOE

Project Objective

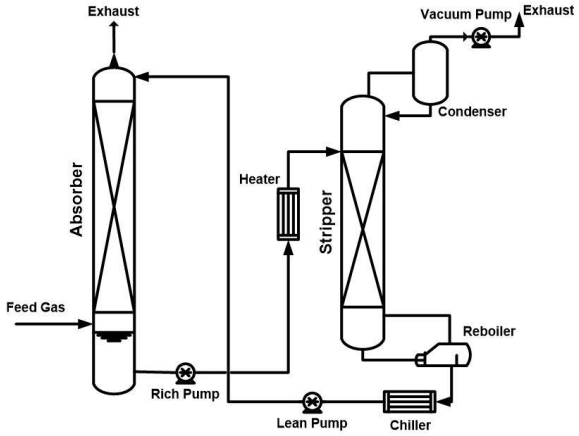
Complete a *bench-scale study* and corresponding *full technology assessment* to validate the potential in meeting the DOE Program Objectives of a *solvent-based post-combustion carbon dioxide capture* system that <u>integrates</u>

- a **low-enthalpy**, aqueous potassium carbonate-based solvent
- with an **absorption**-enhancing (*dissolved*) carbonic anhydrase enzyme catalyst
- in a **re-circulating** absorption-desorption process configuration
- with low temperature **ultrasonic** or **vacuum regeneration**

$$CO_2 + H_2O + K_2CO_3 \leftrightarrow 2KHCO_3$$



Ultrasonic Regeneration



Vacuum Regeneration

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Project Tasks & Timeline Overview

Task 1: Project Management & Planning >>

Task 2: Process Optimization

Task 3: Initial Technical & Economic Feasibility

Task 4: Bench Unit Procurement & Fabrication

Task 5: Bench-scale Integration & Shakedown Testing

Task 6: Bench-scale Testing

Task 7: Full Technology Assessment

1H12 | **2H12** | **1H13** | **2H13** | **1H14** | **2H14** | **1H15** | **June 2015** | **Aug 2015**

2H12

- Batch mode ultrasonics tests conducted
- Enzyme-solvent WWC kinetics met target
- Bench-scale system designed, incld. vacuum regeneration
- **CCTM 2012,** 29th IPCC
- Prelim TEA identified opportunities for lower parasitic load vs Case 10

2H13

- Prototype flow-through ultrasonic unit built & tested; not pursued
- Integrated bench-scale system with vacuum stripper completed & operational
- **CCTM 2013,** 12th CCUS

2H14

- Completed parametric tests incld. enzyme dose-response & alternative solvent tests
- Developed rate-based model for vac stripping
- Completed 500 hour bench-scale testing
- **CCTM 2014,** AIChE 2014

June 2015

- EH&S: system meets regulatory requirements
- Completed full TEA
- **CCTM 2015**

Aug 2015

- Completed submission of reporting deliverables

Provision of Novozymes prototype microbial carbonic anhydrase at no cost to the project

Project Approach

General Technical Challenges for Solvent-based CO_2 Absorption Systems[1]	Project Approach	Headline
Handling of two-phase solvents	Maintain $K_2CO_3/KHCO_3$ concentration within solubility limits	Solvent
Process equipment footprint and cost	Enzyme accelerates CO_2 absorption rate to reduce absorber height	Biocatalyst
Low (atmospheric) CO_2 desorption pressures	Potential for ultrasonics to promote CO_2 desorption at low temperature instead of vacuum; also evaluate vacuum regeneration	Regeneration Options
High energy penalty associated with solvent regeneration	Utilize aqueous potassium carbonate solvent which has a low enthalpy of reaction for regeneration compared to MEA	Bench-scale Testing
Solvent recovery and reclaiming	Cook-and-filter process for separating spent enzyme from the solvent for straightforward solvent recovery	Bench-scale & Lab Testing
Mismatch between regeneration temperature and steam quality available in an existing PC plant	TEA cases consider Low Pressure and Very Low Pressure steam options	TEA Case Studies
Water usage and quality management	Biodegradable enzyme catalyst and biocompatible solvent components simplify process water management	EH&S
Solvent degradation due to flue gas contaminants and other solvent losses	$K_2CO_3/KHCO_3$ has no vapor pressure and is less-reactive towards flue gas contaminants compared to MEA	Adjacent Studies

[1] National Energy Technology Laboratory, "DE-FOA-0000403: Bench-Scale and Slipstream Development and Testing of Post-Combustion Carbon Dioxide Capture and Separation Technology for Application to Existing Coal-Fired Power Plants," Federal Grants, 31 January 2011.

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Solvent Properties

Aq. Monoethanolamine (MEA-based) Solvent

- Reaction with CO_2 ($R = HOCH_2CH_2$-)

$$CO_2 + 2RNH_2 \leftrightarrow RNHCOO^- + RNH_3^+$$

- Reactive (requires inhibitors)
- Health concerns
- Volatile
- Fast reaction kinetics (no catalyst required)
  - Rate constant 8500 $M^{-1}s^{-1}$ (25°C)
- Higher enthalpy of reaction (84 kJ/mol)
- Requires higher regeneration temperature
- Solubility Limit: completely miscible with water
- Higher viscosity
- Pure MEA, Tm 10°C, NFPA rating H3/F2/R0

Aq. Potassium Carbonate (K_2CO_3-based) Solvent

- Reaction with CO_2

$$CO_2 + H_2O + K_2CO_3 \leftrightarrow 2KHCO_3$$

- Stable (no inhibitors required)
- Benign
- Non-volatile
- Slow reaction kinetics (requires catalyst)
  - Uncatalyzed rate constant 40 $M^{-1}s^{-1}$ (25°C)
- Lower enthalpy of reaction (27 kJ/mol)
- Regeneration can occur at lower temperature
- Solubility Limit: ~23 wt% (30°C minimum)
- Lower viscosity
- Pure K_2CO_3, solid salt, NFPA rating H1/F0/R0

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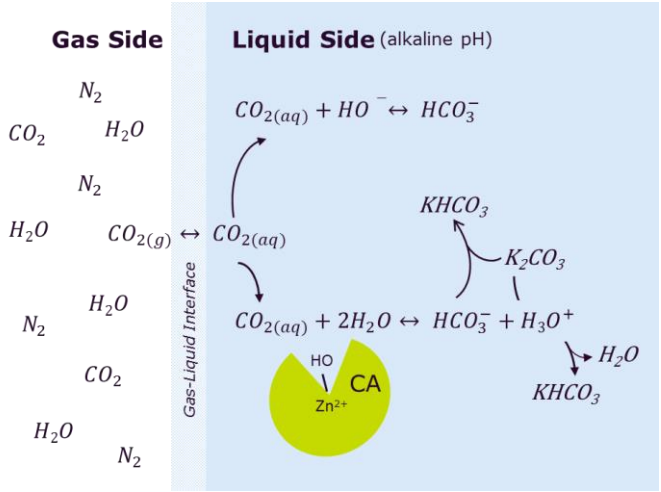
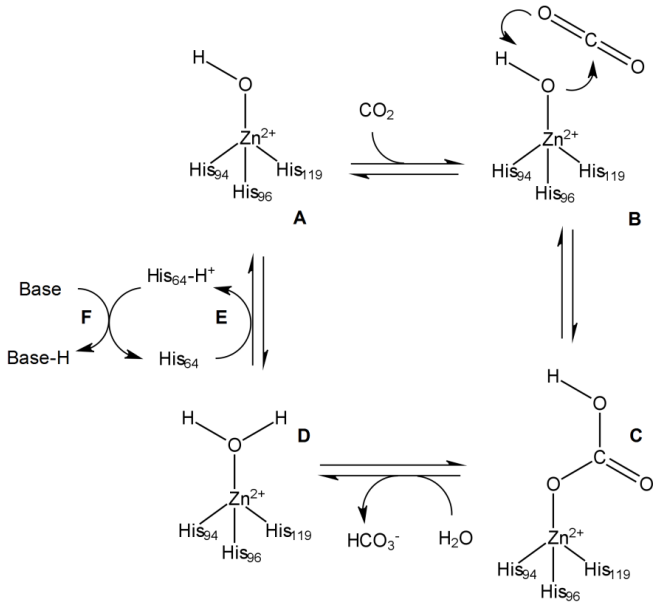
Biocatalyst Accelerates CO_2 Absorption in aq. K_2CO_3

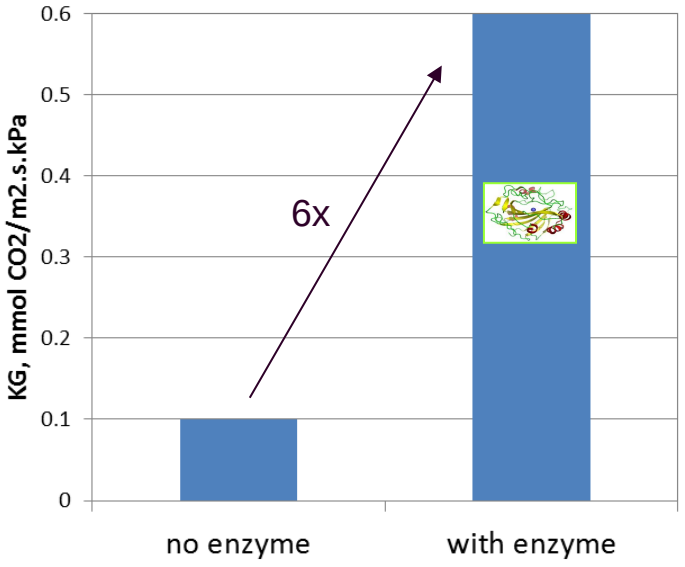


CO_2 absorption with chemical reaction



CA active site mechanism [1]

$$CO_{2(aq)} + 2H_2O \leftrightarrow HCO_3^- + H_3O^+$$



Mass transfer rate enhancement
(measured using Wetted Wall Column)

- Carbonic anhydrase (CA) enzyme accelerates CO_2 absorption into aq. K_2CO_3-based solvent enabling reduction in absorber tower height to a feasible level

[1] S. Salmon and A. House, "Enzyme-catalyzed solvents for CO_2 separation," in *Novel Materials for Carbon Dioxide Mitigation Technology*, F. Shi and B. Morreale, Eds., Amsterdam, Elsevier B.V., 2015, Figure 3, p. 31.

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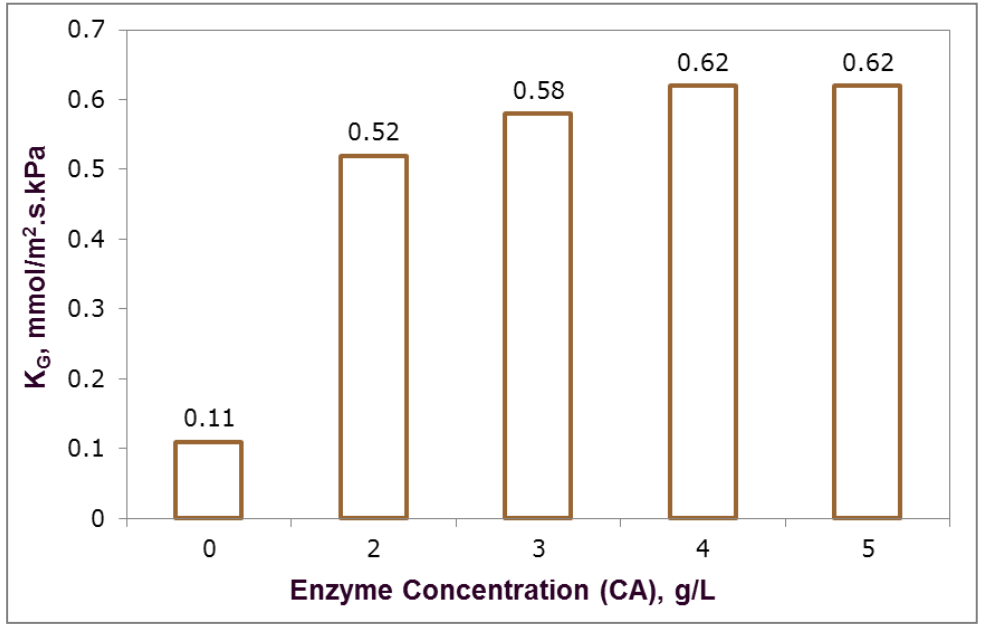
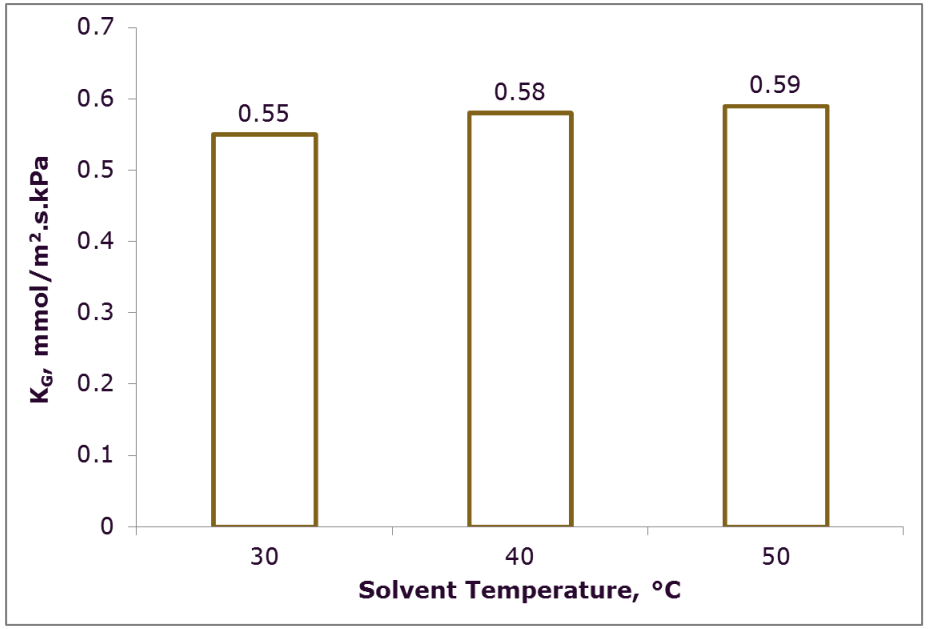
Absorption Mass Transfer Confirmed in WWC at UK-CAER

aq. 20 wt% K_2CO_3



aq. 20 wt% K_2CO_3 + 3 g/L CA enzyme



- Increasing concentration of carbonic anhydrase (CA) enzyme increases the overall mass transfer coefficient (K_G) for CO_2 absorption into aq. K_2CO_3-based solvent
- Limited availability of CO_2 substrate is considered to result in K_G "plateau" at high enzyme concentration

- K_G is relatively constant across the 30-50°C absorption temperature range
- As temperature increases, increased CO_2 absorption rate is off-set by decreased absorption driving force

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Regeneration Options

- Two regeneration options (ultrasonics and vacuum) were considered that could take advantage of low enthalpy of reaction K_2CO_3 solvent that predicted lower parasitic load vs. MEA in preliminary TEA

Preliminary TEA Cases	Efficiency (HHV)	Parasitic Load for Capture vs. MEA	Challenges
NETL Case 9 (no capture)	36.80%		High CO_2 emissions
NETL Case 10 (MEA)	24.99%	100%	High parasitic power requirement
K_2CO_3/enzyme – vacuum strip, LP steam	24.34%	105%	Impact of capital and compression costs on overall COE
K_2CO_3/enzyme – <u>vacuum</u> strip, VLP steam @ 8 psia	**29.97%**	**57%**	
K_2CO_3/enzyme – ultrasonic strip, LP steam	26.63%	85%	Feasibility for reaching CO_2 release equivalent to the vacuum condition, but without vacuum
K_2CO_3/enzyme – <u>ultrasonic</u> strip, VLP steam @ 8 psia	**31.41%**	**45%**	

- Both regeneration options were pre-tested in different lab reactor configurations at PNNL
- Vacuum regeneration option was evaluated in 500 hour integrated bench-scale testing at UK-CAER

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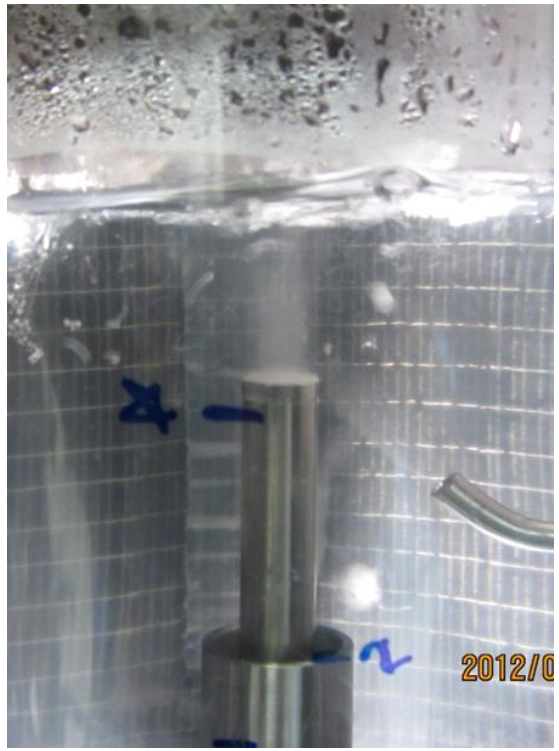
Ultrasonic and Vacuum Regeneration Batch and Flow-Through Testing at PNNL

- Designed and fabricated a batch mode ultrasonic testing system
  - Acoustic energy provided by ultrasonic horn immersed in liquid
  - Horn “down” versus “up” configurations were tested – goal was to enhance gas bubble release to the headspace
  - Liquid recirculation used to maintain temperature to within ± 2°C
- Designed and fabricated a novel flow-through ultrasonics testing system
  - Acoustic energy provided to the flowing liquid via a clamp-on transducer and specifically-dimensioned spool
  - Incorporated a hydrocyclone to enhance gas-liquid separation
  - Incorporated a flash tank to enable direct comparison of ultrasonic- versus vacuum-based CO_2 release
- Conducted PARR reactor tests
  - Verify temperature-dependent CO_2 desorption
  - Determine impact of enzyme on desorption kinetics

Ultrasonic Regeneration – Batch Mode Tests



Pure Water at 70°C – With Sonication

Loaded Solvent at 70°C – No Sonication

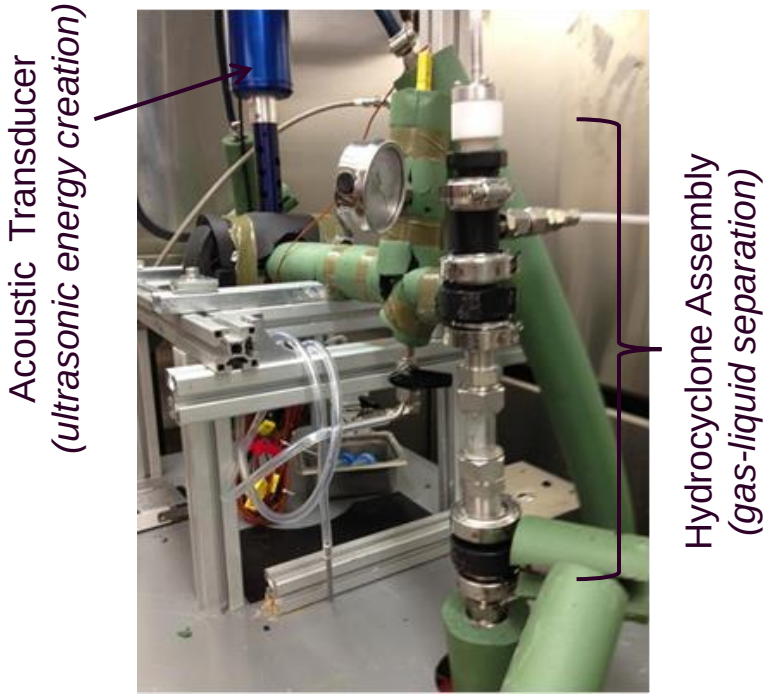
Loaded Solvent at 70°C – With Sonication

- Significant agitation/ bubbling observed when ultrasonic power added to CO_2 loaded 20% K_2CO_3 solution at 70°C

Rectified Diffusion Concept

- Bubbles expand and shrink in an ultrasonic field
- Rectified diffusion results when expanding bubbles allow for a biased transfer of dissolved gas into the bubble from solution
- Remove bubbles before they can dissolve back into the liquid

Ultrasonic Regeneration – Flow-Through with Hydrocyclone



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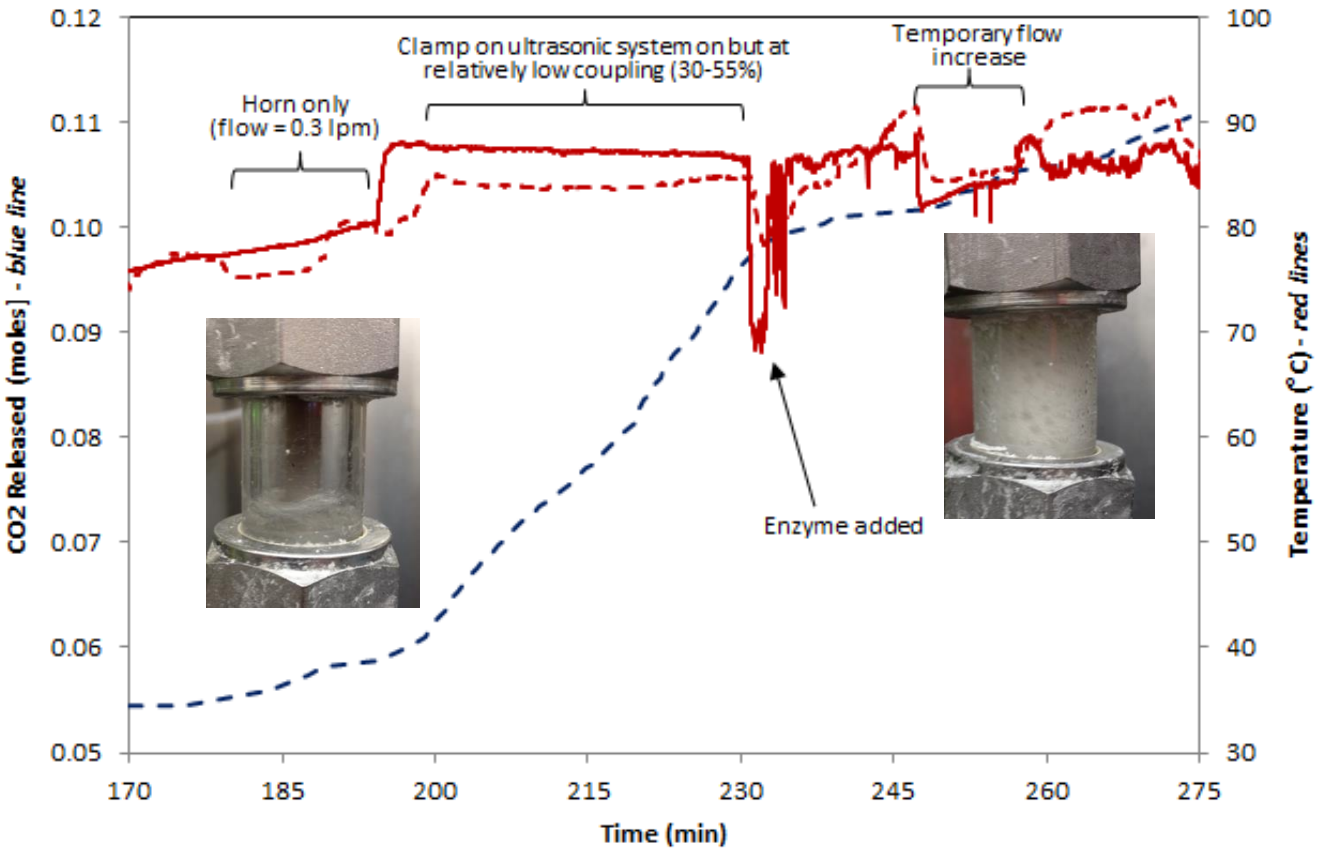

- Significant CO_2 release rate – similar to vacuum flow-through value
- Enzyme addition decreased CO_2 release rate – likely due to foaming

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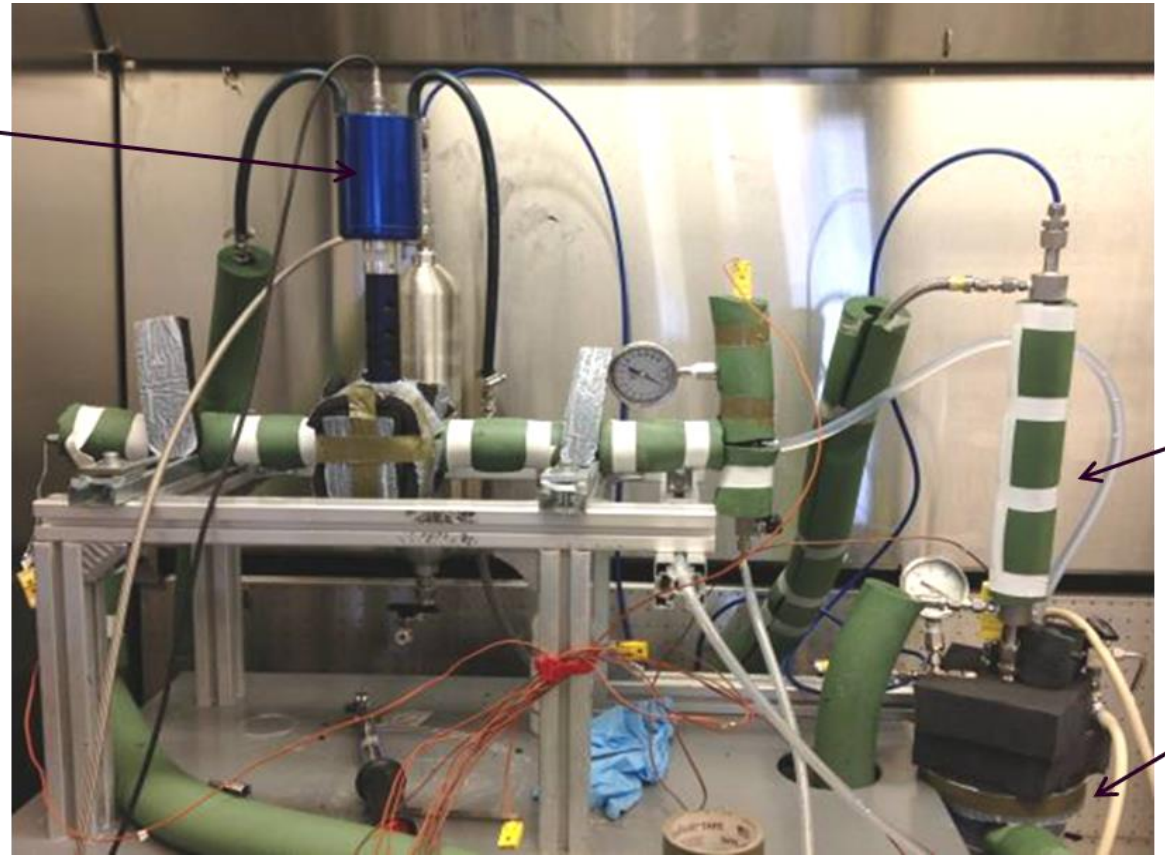
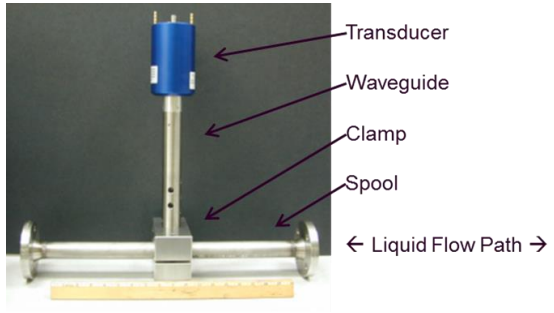
Ultrasonic Flow-Through with Flash Tank





- Configuration with flash tank reservoir installed in lieu of the hydrocyclone gas-liquid separator allowed collection of flow-through test data with acoustic energy or vacuum using the same flow loop configuration

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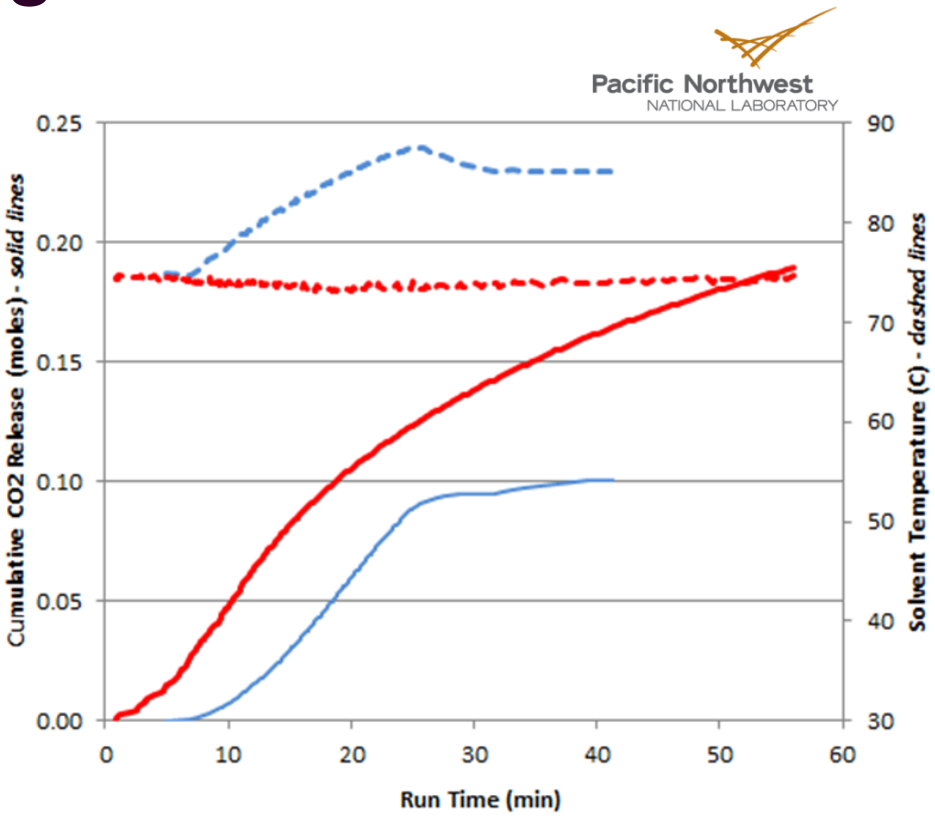
Flow-Through Test Comparison of Ultrasonic and Vacuum Regeneration



- Flow-through ultrasonics test using solvent prepared from (bi-)carbonate salts to give a 20wt% (K_2CO_3 basis) solvent with 77% equivalent K_2CO_3 converted to $KHCO_3$ (prepared using the respective salts)
- Red lines are at 0.4 atm pressure (no ultrasonics)
- Blue lines are from the flow-through tube sonicator (no vacuum)
- No enzyme was used in these tests

- The comparison indicates ultrasonic-induced CO_2 release can be attributed to temperature increase in the liquid caused by application of ultrasonic energy
- Illustrates that ultrasonics could be used to apply localized heating

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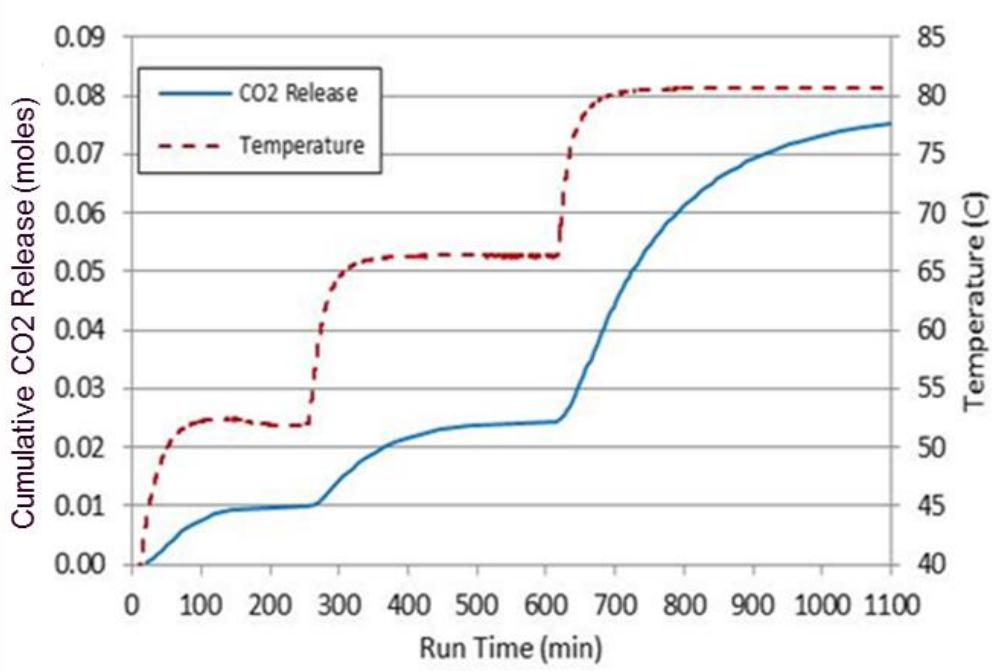
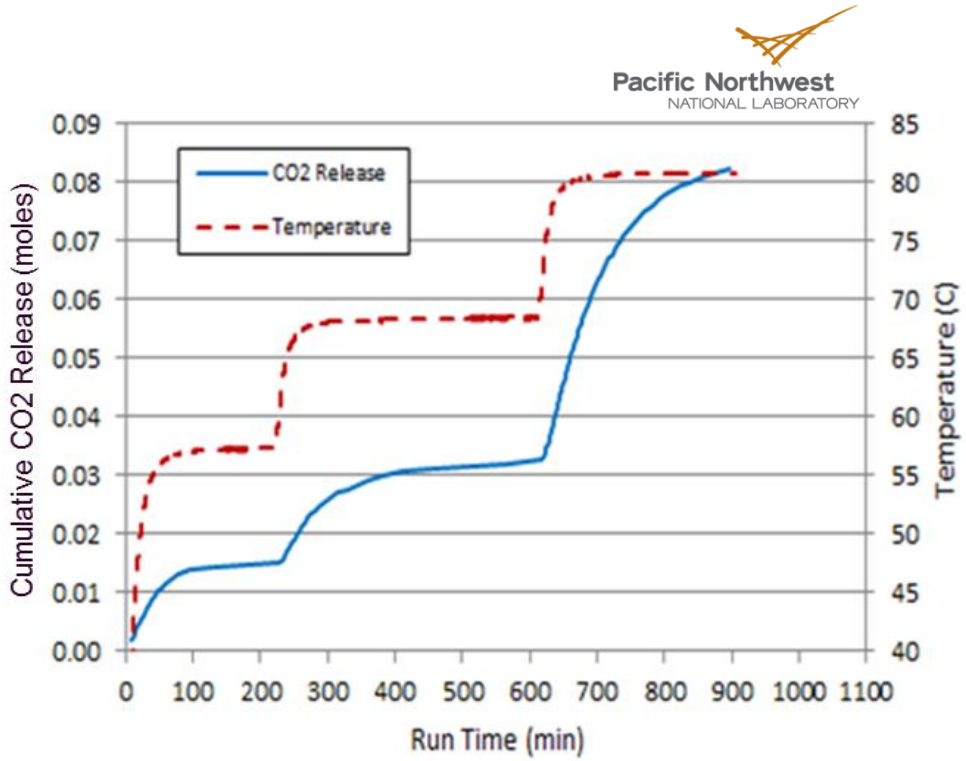
PARR Reactor Temperature-based CO_2 Release



CO_2 release rates as a function of temperature change
no enzyme present



CO_2 release rates as a function of temperature change
with enzyme present

- Enzyme appears to increase the release rates (mol/min basis) at a given temperature
- Results suggest rate limitations can occur at temperatures as high as 80°C

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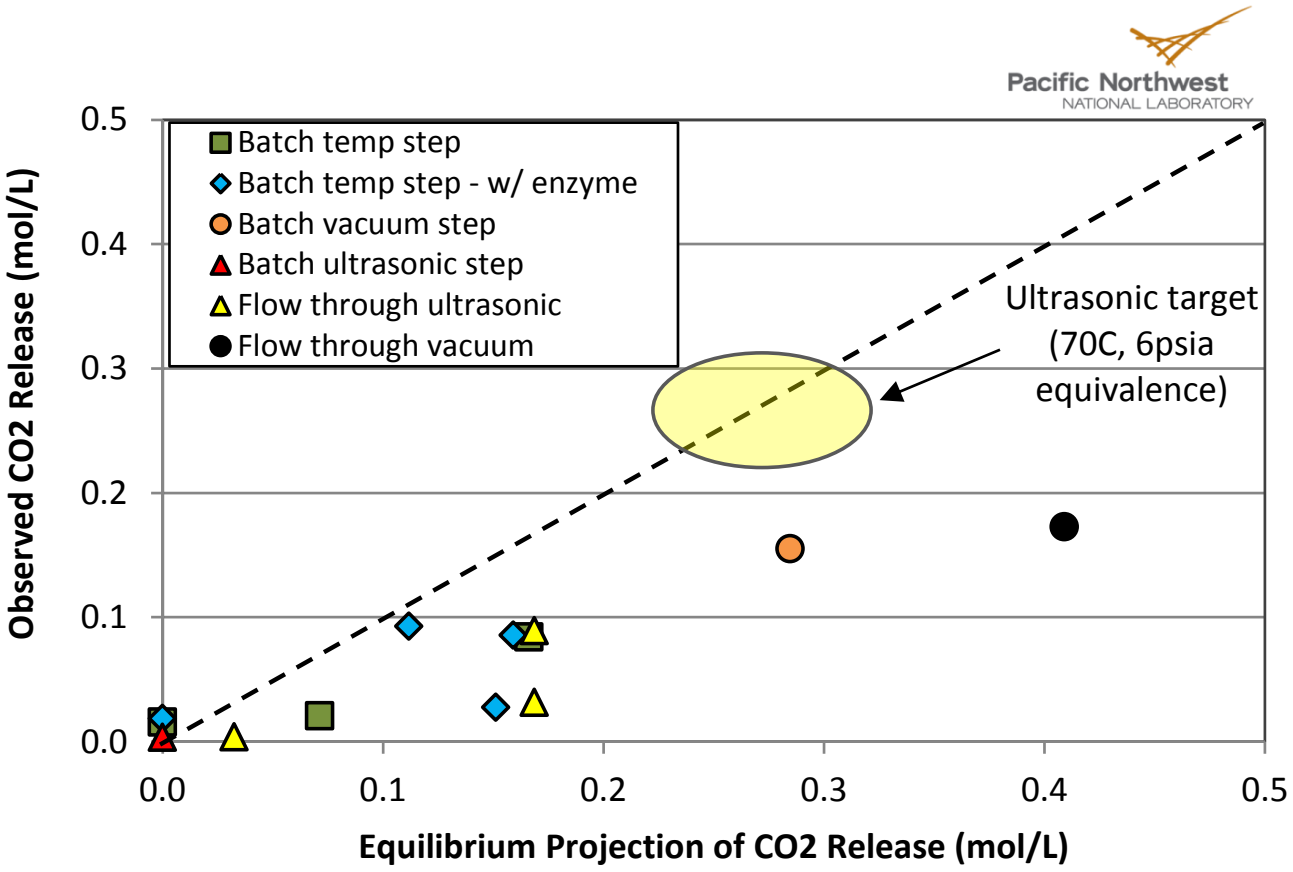
Summary of Comparative Regeneration Results



- All observed CO_2 release values were below equilibrium projections
  - Expected, but potentially more significant due to reaction kinetic limitations
- Highest ultrasonic results explainable by temperature increases alone
  - Target was equivalence to 0.4 atm vacuum without temperature effect
- Remainder of project focused on closer evaluation of vacuum regeneration

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Ultrasonic Testing Conclusions

- Novel flow-through ultrasonic regenerator was designed and tested at operational conditions commensurate with the envisioned integrated bench-scale system
  - CO_2 release was observed
  - Different ultrasonic configurations were tested towards enhancing bubble release
- Flow-through test comparison of ultrasonic and vacuum regeneration indicated ultrasonic-induced CO_2 release could be explained by temperature increase in the liquid caused by application of ultrasonic energy
- Further investigation of ultrasonics as a technology for CO_2 release (or potentially absorption enhancement) is recommended to
  - Improve fundamental understanding of the phenomena involved
  - Evaluate alternative parameters (e.g. frequencies, coupling efficiency) and configurations of acoustic energy application
  - Combine ultrasonics with (bio-)catalysts, implementing formulations and/or configurations to manage foaming (e.g. antifoam, immobilized or chemically modified biocatalyst)

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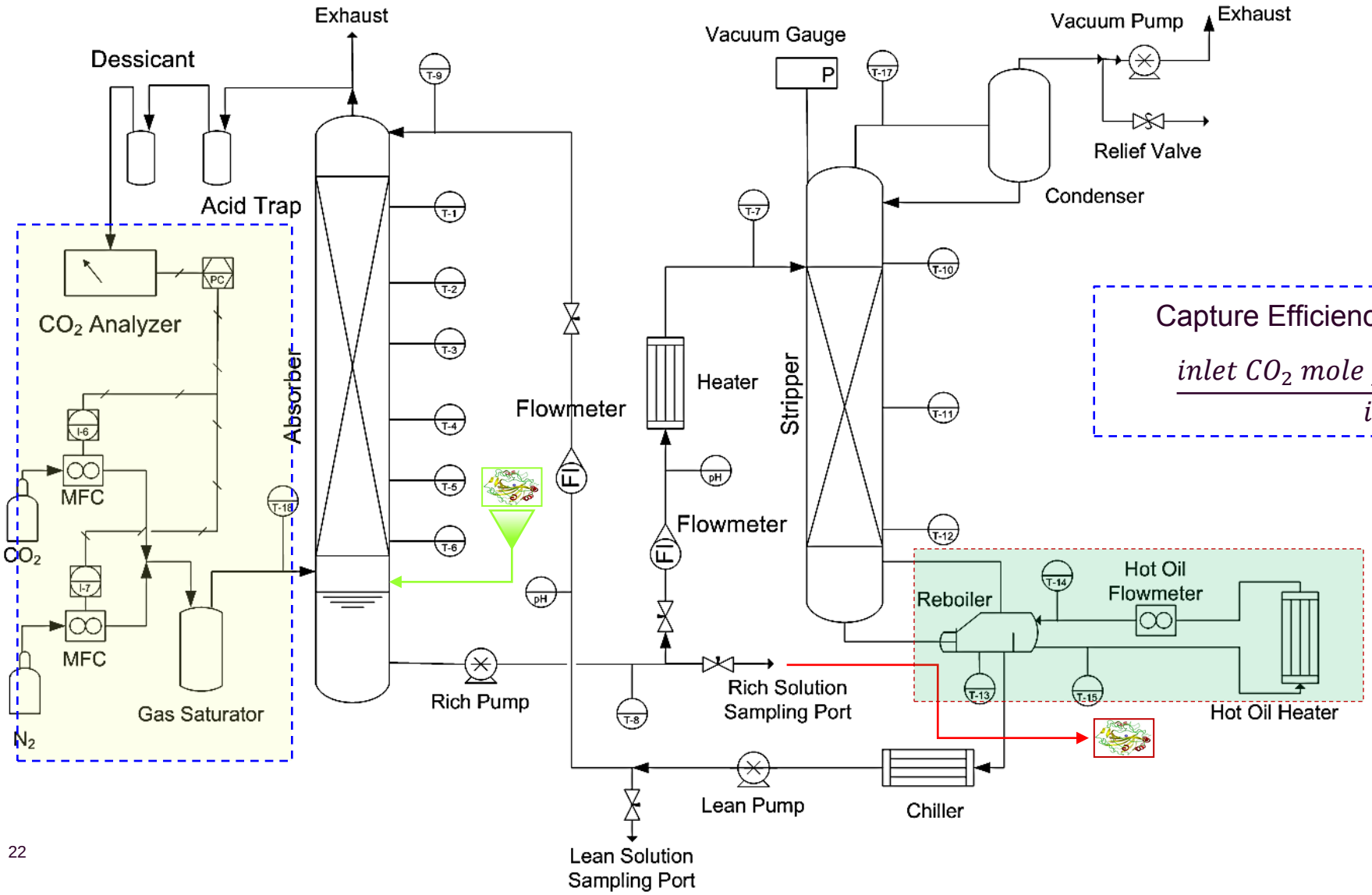
Bench-scale Testing with Vacuum Regeneration at UK-CAER

- Designed and fabricated the full integrated bench-scale system, including
  - Absorber, stripper, reboiler
  - Stable generation of vacuum condition for stripping
  - Instrumentation and process controls
- Carried out integrated system shakedown and operation limits testing
- Conducted parametric and alternative solvent testing
- Completed 500 hour testing
  - Routine enzyme replenishment
  - System performance monitoring and adjustment

PFD of Integrated Bench-scale System



Icons indicate points of enzyme and aq. K_2CO_3

- addition
- removal

for solvent replenishment

Capture Efficiency=

$$\frac{inlet\ CO_2\ mole\ flowrate\ - outlet\ CO_2\ mole\ flowrate}{inlet\ CO_2\ mole\ flowrate}$$

Reboiler duty =

$$C_p Q \rho (T_{hot\ oil\ inlet} - T_{hot\ oil\ outlet})$$

Bench-scale (Parametric) and 500 Hour Test Conditions

Base Solvent

- Aqueous 23 wt% K_2CO_3 selected for 500 h run
- Solvent pre-testing included tests for higher CO_2 loading capacity
  - Borax or bicine with K_2CO_3 show potential benefits (lab scale)
  - 23 wt% K_2CO_3 with/without 4 wt% borax gave similar result (bench scale)

Operating Parameters

- Column Packing: Rashig ring
- Stripper Pressure: 0.35 atm absolute
- Enzyme Concentration: (1-4) 2.5 g/L

Flow Rates

- Gas: 30 SLPM, 15/85% CO_2/N_2
- Liquid : (300-600) 500 mL/min

Liquid Temperature

- Absorber Inlet: 40°C
- Stripper bulk: ~77°C
- Reboiler Heating Source (Oil Inlet): (90-95) 95°C

UK University of Kentucky Center for Applied Energy Research

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Parametric Test Matrix

Each condition was evaluated over 2-3 run days

Run	Enz. conc. (g/L)	Flow rate (ml/min)	Hot oil inlet (°C)	Absorber (°C)	Pressure at stripper top (atm absolute)	CO_2 Capture Efficiency (%)	Energy Demand (kJ/mol CO_2 captured)
1	2.5	500	95	40	0.35	88.8	382
2	2.5	600	95	40	0.35	85.6	368
3	2.5	400	95	40	0.35	85.7	349
4	2.5	300	90	40	0.35	81.0	273
5	4	500	90	40	0.35	83.3	284
6	4	300	90	40	0.35	84.5	275
7	1	500	90	40	0.35	71.5	322
8	1	300	90	40	0.35	69.0	301
9	0	500	90	40	0.35	18.4	1330
10	0	500	95	40	0.35	19.0	1610
	variable	variable	variable	fixed	fixed		

Conditions selected for 500 hour test (targeting 90% capture)

Lower energy demand cases could be relevant for partial capture

No-enzyme reference conditions for 500 hour test

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Example Parametric Test Results

	#1	#10
Enzyme Dosing, g/L	2.5	0
Liquid Flow Rate, mL/min	500	500
Feed Gas Temp, ^oC	40	40
Reboiler Solution Temp, ^oC	77	76
Lean Solvent Temp, ^oC	40	40
Outlet CO_2 Conc, %	1.9	12.4
Total Gas Flow, LPM	30	30
Hot Oil Inlet Temp, ^oC	95	95
Q, Reboiler, KW	1.1	1.1
Capture Efficiency (%)	89%	19%
Energy Demand (kJ/mol CO_2 captured)	382	1611
Stripper Top Pressure, kPaa	35	35
Rich Conversion	54%	43%
Lean Conversion	35%	39%

Results shown are average values from duplicate runs for each test.

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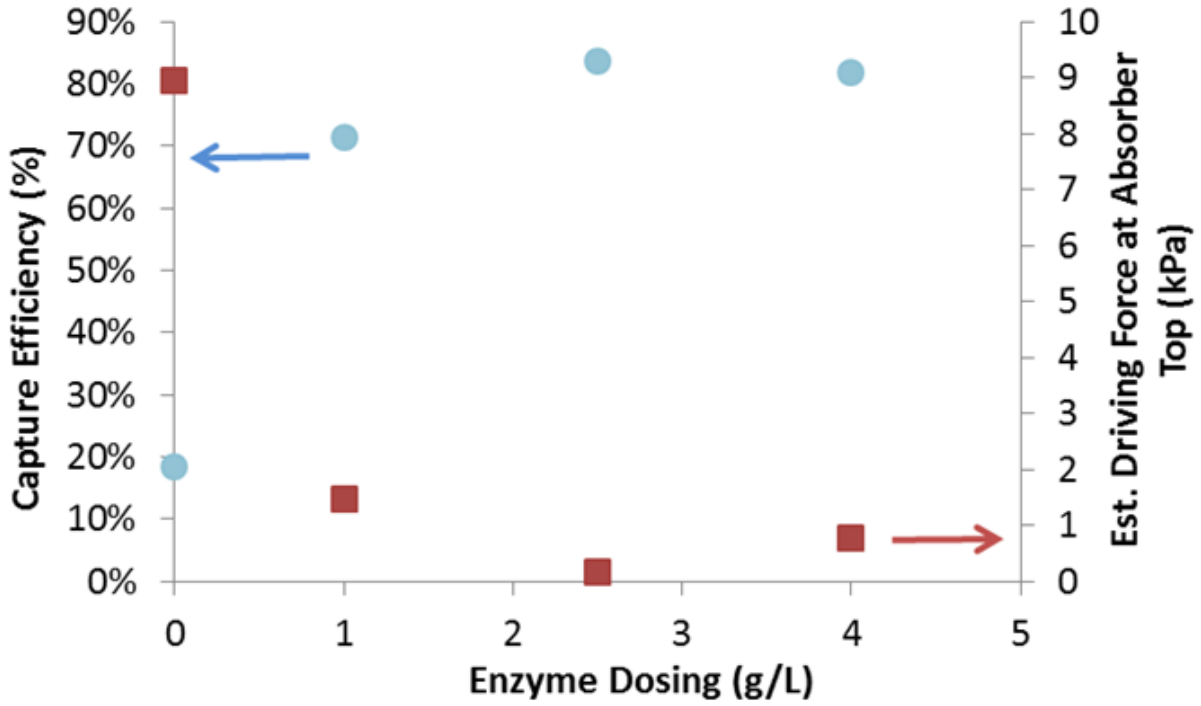
Enzyme Impact on Bench-scale CO_2 Capture Efficiency and Driving Force



- CO_2 capture efficiency (circles)
- Driving force (squares)
- Enzyme concentrations 0, 1, 2.5, and 4 g/L
- Liquid flow rate 500 ml/min

- Sufficient enzyme addition brings CO_2 absorption driving force to near equilibrium at absorber top

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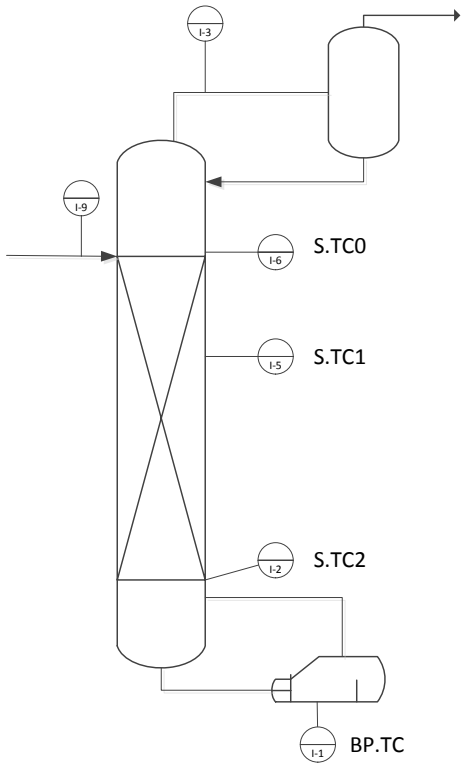
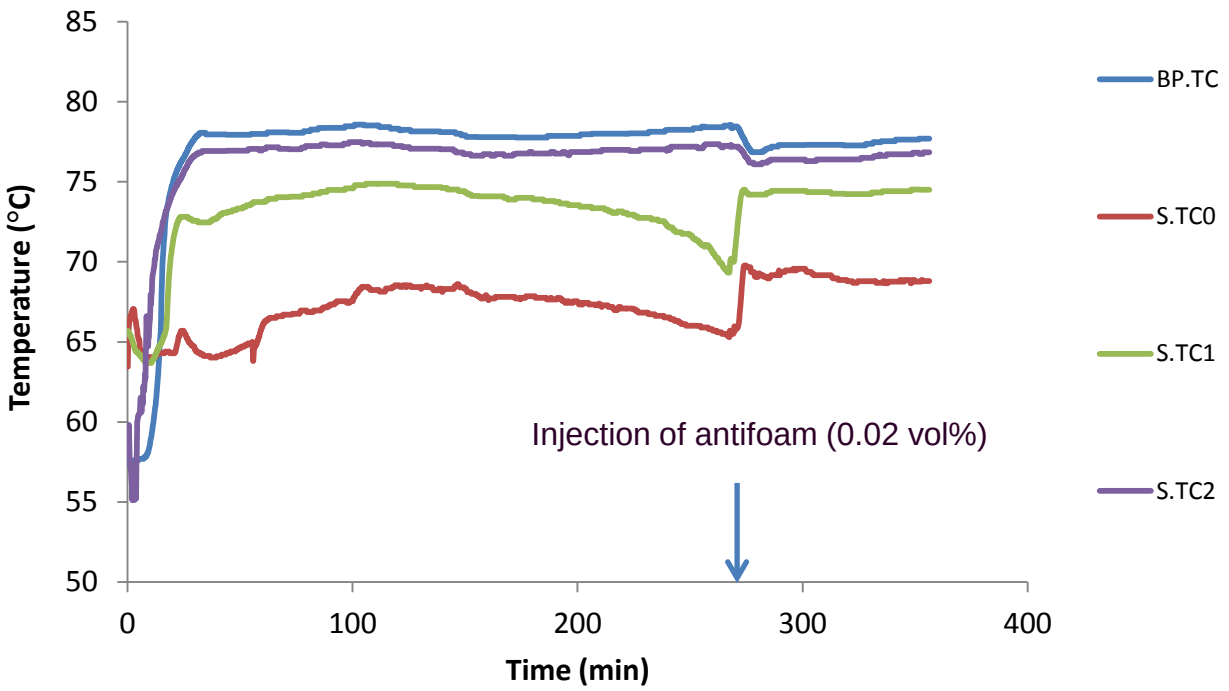
Foaming Control in Bench-scale System



Schematic of temperature measurement points on stripper



Stripper temperature profile versus time during initial operation with 1.5 g/L enzyme

- Presence of dissolved enzyme in the stripper caused foaming
- Addition of antifoam stabilized stripper performance

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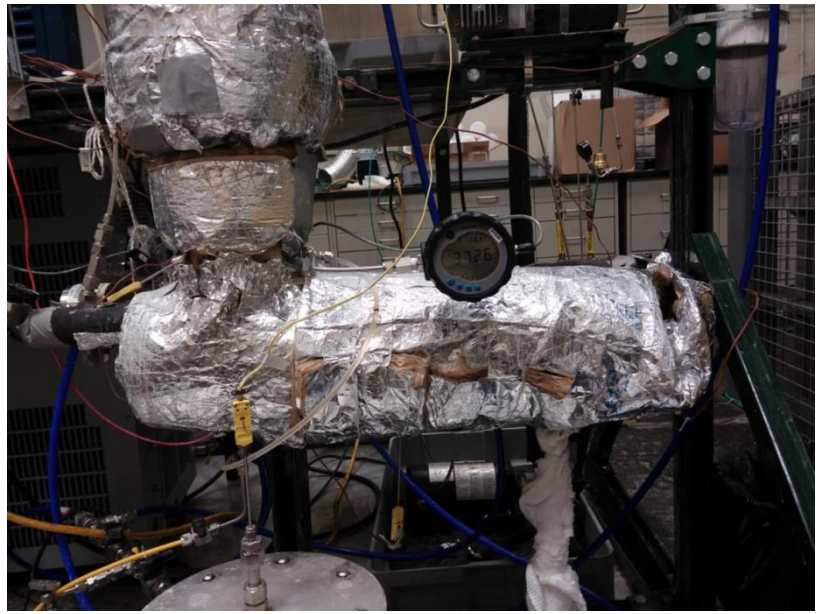
Bench-scale Operational Observations

Absorber bottom

Stripper top



Stripper bottom

Absorber

- Stable temp along absorber length (40°C ± 1°C)
- Antifoam dosing effectively mitigates foaming
- No visual change in packing
- Rich solvent filter removes (modest) solids

Stripper

- Water cooled condenser at top
- Tube and shell reboiler
- Bulk temp ranges from 76°C (reboiler) to 65°C (rich solvent inlet to stripper top)

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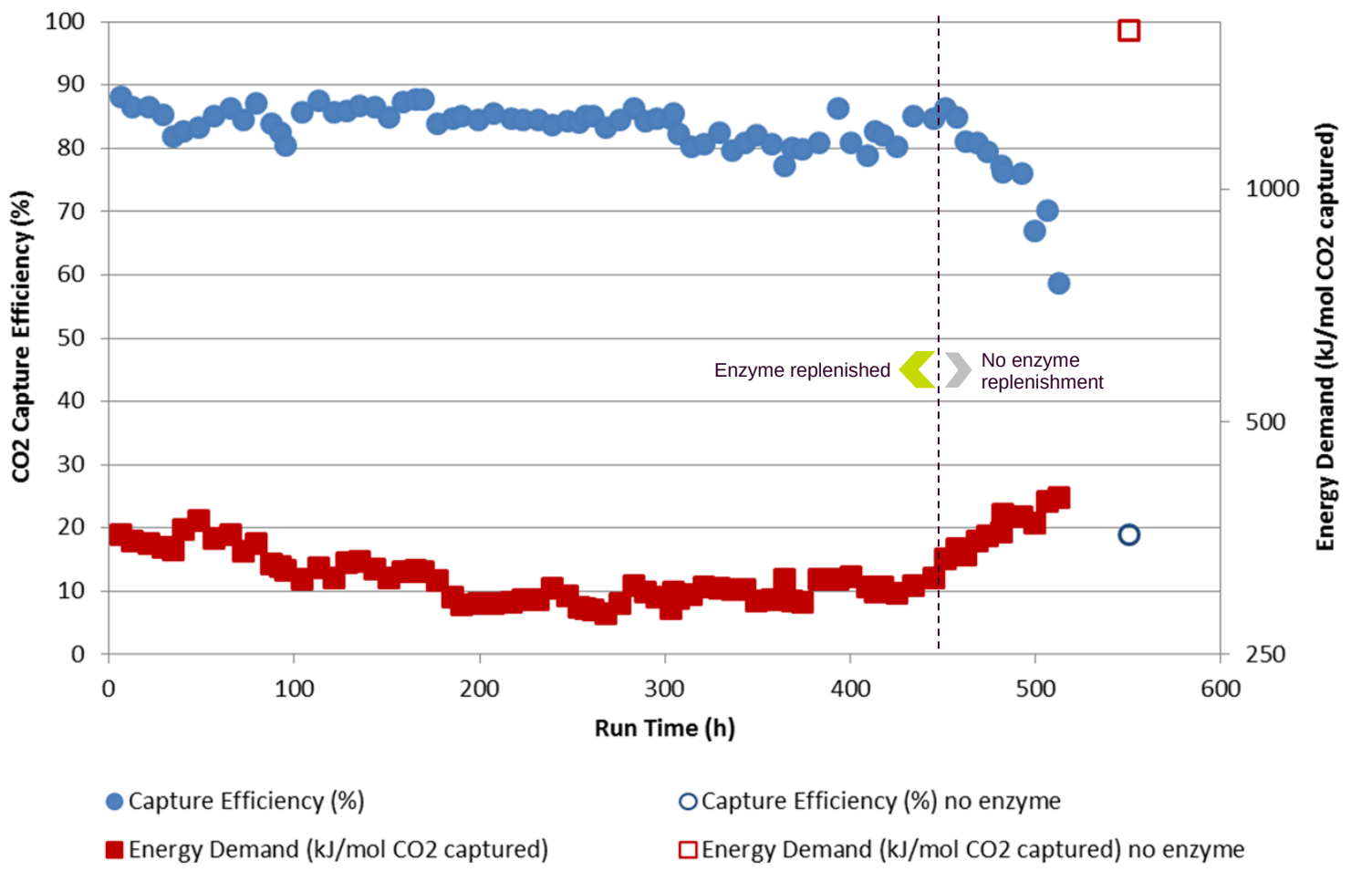
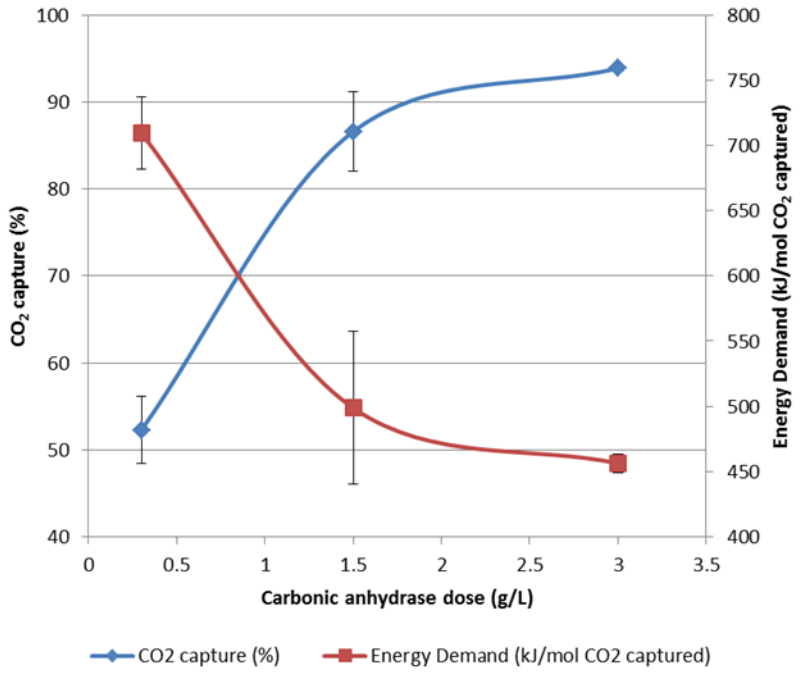
Energy Demand During Bench-scale Tests



500 Hour Testing
(system performance maintained with enzyme replenishment)



Operational Limits Testing
(demonstrated 90% capture)

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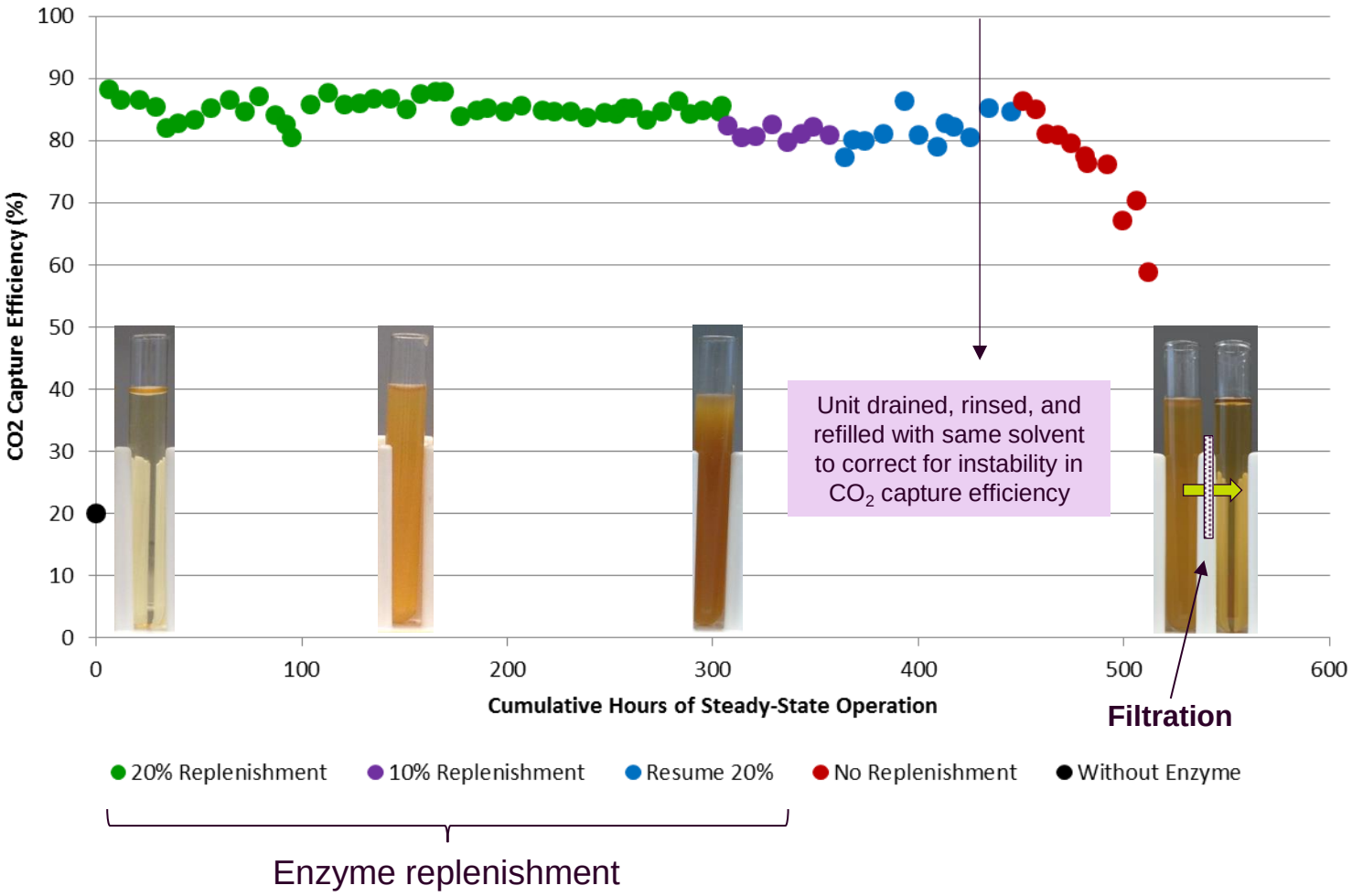
Bench-scale 500 Hour Test Results



- **>80% CO_2 Capture efficiency was maintained**
  - System tolerated daily start-up/shut-down
  - Stabilizing the vacuum condition required frequent manual adjustments
  - Foaming was controllable using antifoam
- **Principle of using dissolved enzyme replenishment to achieve stable operation was demonstrated**
  - Stopping enzyme replenishment caused decrease in CO_2 Capture efficiency
- **Solvent darkens and becomes turbid over time**
  - System tolerated turbidity during operation
  - Liquid can be clarified using proper filtration
- **Performance instability occurred and was corrected**
  - Attributed to (protein) solids accumulation on reboiler surfaces
  - Was corrected by rinsing the system

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Bench-scale Testing Conclusions

- Integrated bench-scale system with vacuum regeneration was designed, fabricated and tested
  - > 90% CO_2 capture was achieved during operational limits testing (30°C absorber)
  - System operated successfully for accumulated 500 hours of steady-state operation under vacuum conditions, with an average 84 % CO_2 capture during the period of enzyme replenishment
  - On- and off-line operational measurements provided a full process data set, with recirculating enzyme, that allowed for kinetic parameter and enzyme replenishment calculations
  - Dissolved enzyme replenishment and conventional process controls (e.g. antifoam addition and solids filtration) were demonstrated as straightforward approaches to maintain system performance
- Testing results were utilized in TEA and EH&S assessments to predict full plant feasibility

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Enzyme Longevity and Replenishment Studies by Novozymes

Approaches

- Analysis of samples collected during bench-scale testing at UK-CAER
- Lab-based studies at Novozymes using a temperature cycling loop reactor

Objectives

- Illustrate feasibility of enzyme replenishment and solvent reclamation by solid-liquid separation (“cook and filter”)
- Provide realistic enzyme replenishment rates for TEA simulation process conditions
  - Bench-scale average bulk stripper temperature was 77°C for 500 h test; localized stripper temperature was 95°C at hot oil inlet skin surface
  - Simulation maximum bulk stripper temperature was 77°C

500 Hour Test – Solvent Management

Enzyme liquid concentrate | K_2CO_3 solution | Working solvent 2.5 g/L CA in K_2CO_3 aq. | Enzyme + K_2CO_3 stock soln. to supply unit during replenishment

Bench-scale Daily Operation

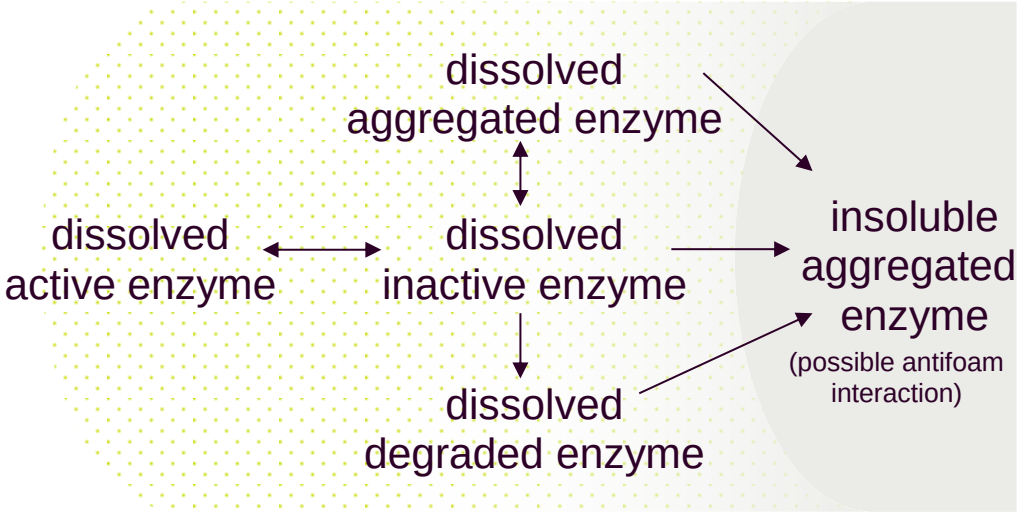
- System start-up/shut-down daily
- ~7 hour steady-state run day
- Solvent storage at room temperature when not in operation

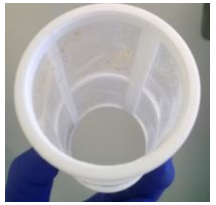
Solvent additions per ~7 h run day

- Antifoam addition: ~0.04%
- Enzyme addition: 0, 10 or 20% of active enzyme inventory (with replacement of equivalent solvent volume)
- Solvent volume and alkalinity were maintained

Observations

- Neither active, nor intact inactive dissolved enzyme accumulated in the system
- Insoluble aggregated enzyme may have accumulated and led to system instability





Solids trapped by bench-unit filter

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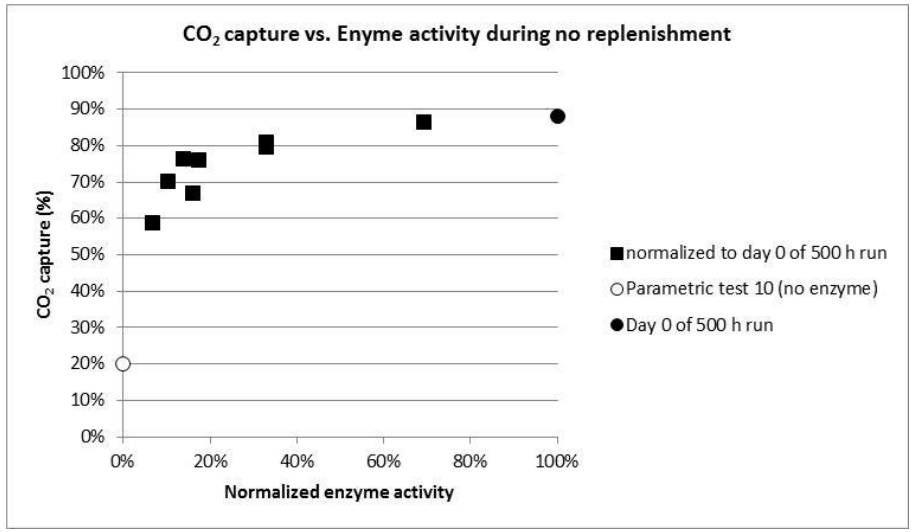
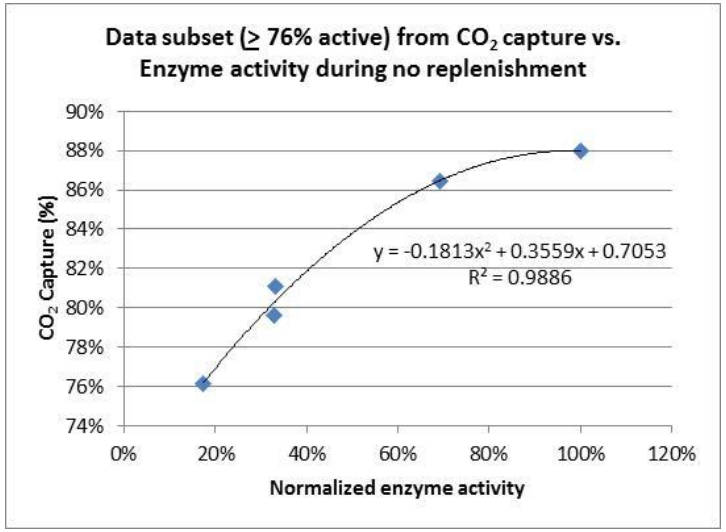
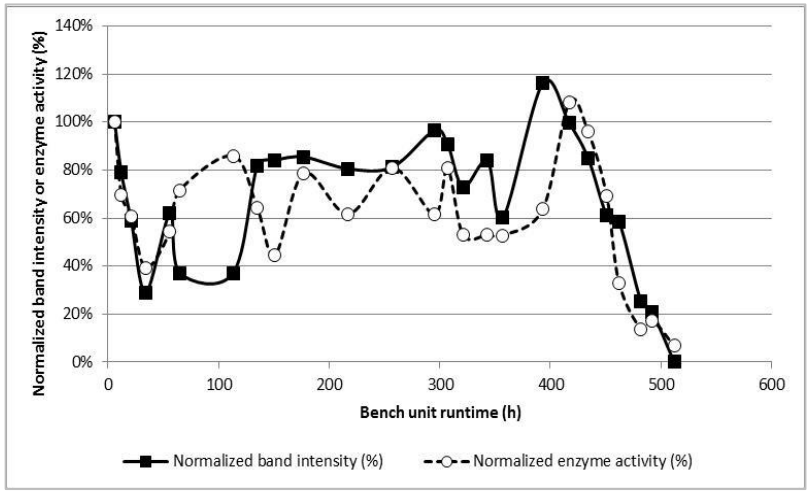
Non-linear Relationship Observed Between Enzyme Activity % CO_2 Capture







- **A nonlinear relationship correlates loss of active enzyme and loss of CO_2 capture efficiency**
  - Approximate 75% loss in active enzyme corresponded to a 10% loss in CO_2 capture efficiency
  - > 50% CO_2 capture was obtained with < 20% enzyme activity remaining; illustrates partial capture potential
  - Nonlinear relationship shows forgiveness between enzyme activity loss and CO_2 capture efficiency
- **No accumulation of intact, inactive enzyme was detected**
  - Analysis confirmed that lower activity samples showed higher level of degraded CA by protein analysis (SDS-PAGE, band intensity)

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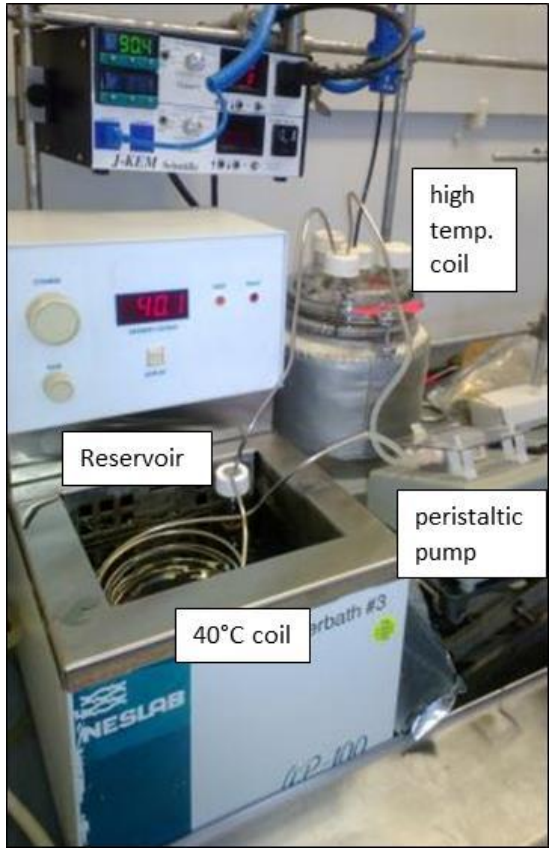
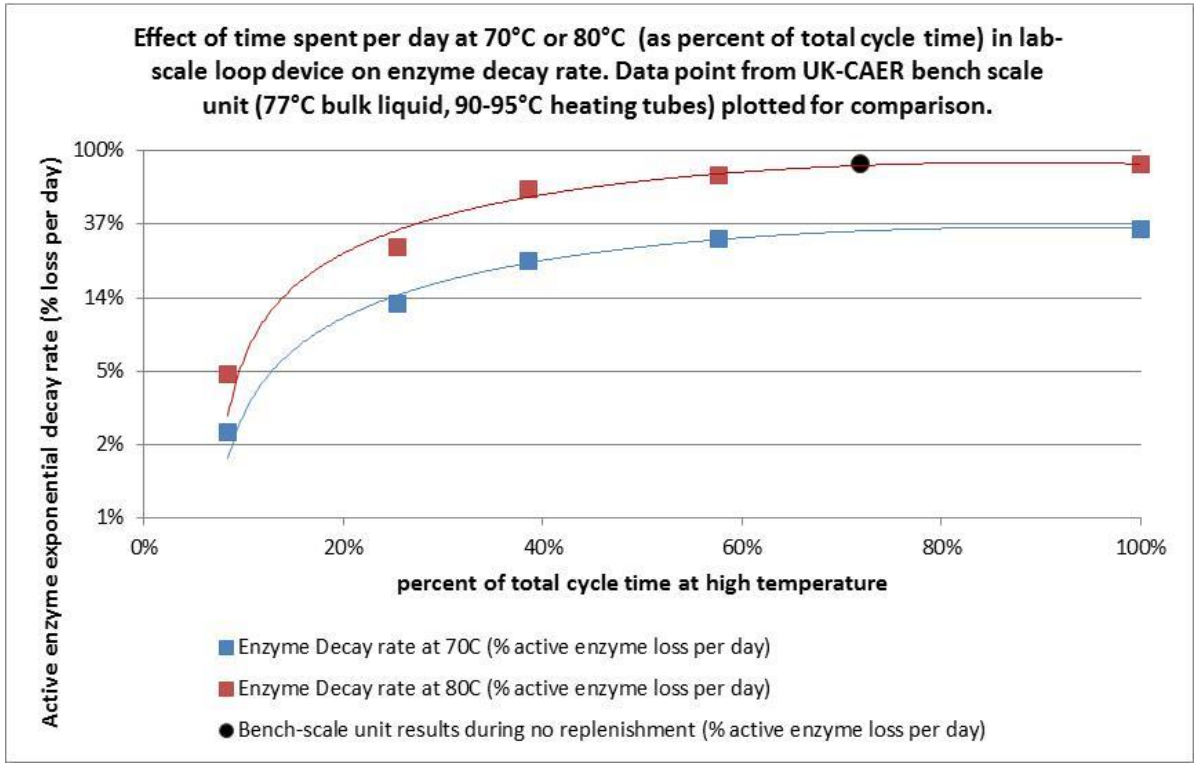
Lab Study Confirms Bench-scale Decay Rate





- Lab scale study shows that longer residence time and higher temp → faster decay rate
- In the bench scale unit, the solvent spent 72% of total cycle time in the reboiler
- Reducing the percent of total cycle time at high temperature and/or reducing the temperature can yield substantial improvements in enzyme longevity in the system

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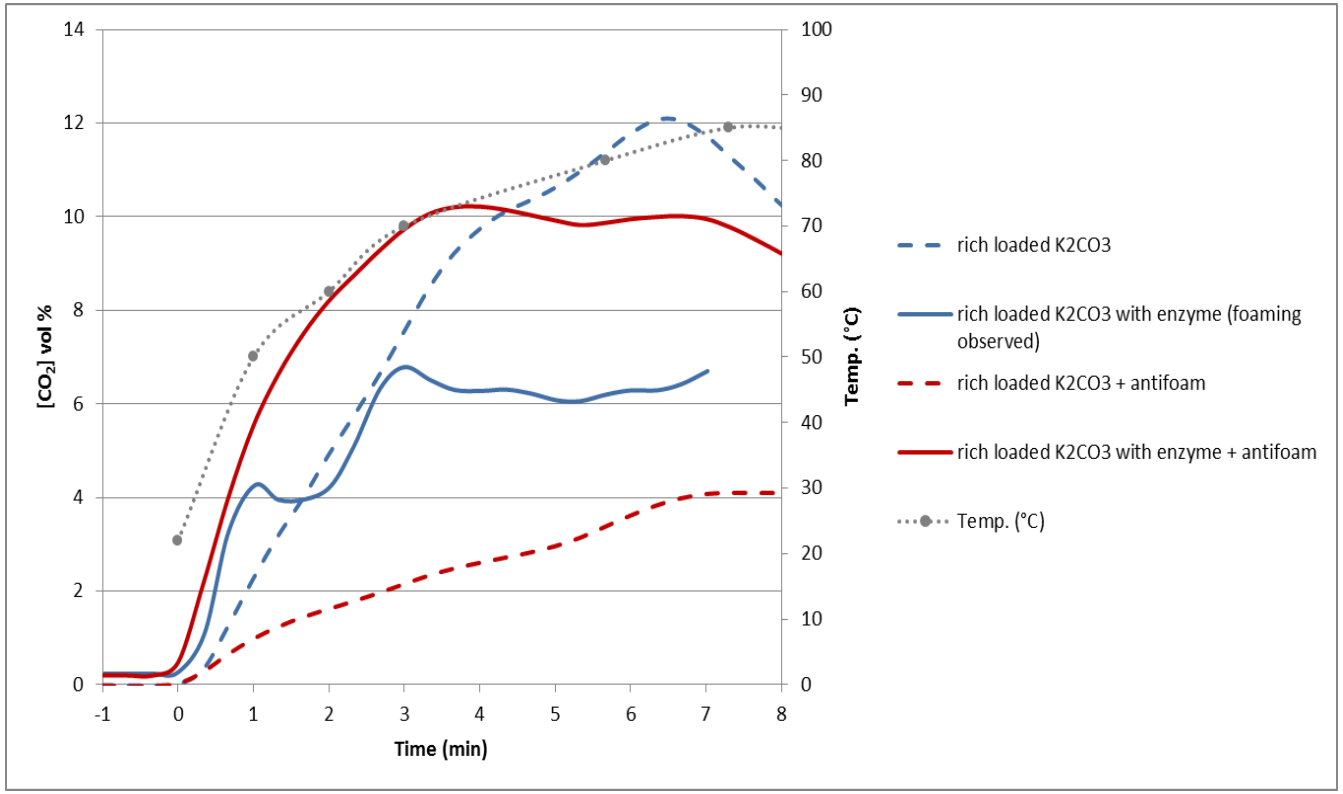
Lab Study Shows Enzyme Desorption Benefit



Lab-scale data from bubble tank, with nitrogen gas sweep, fitted to a CO_2 detector

- Addition of enzyme enhances initial rate of CO_2 desorption
- Foaming interferes with desorption; resolved by adding antifoam
- Antifoam addition inhibits CO_2 desorption in the absence of enzyme, but facilitates the extent of desorption in the presence of enzyme, without changing the initial rate
- Temperature increase during the test also contributed to desorption

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Enzyme Replenishment Conclusions

- Longevity of the prototype enzyme used in the study was significantly diminished by travel through the bench-scale stripper, but was successfully mitigated for testing purposes by a replenishment program
- Neither active nor intact inactive dissolved enzyme accumulated in the system
  - Insoluble aggregated enzyme may have accumulated
  - Alternate filtration modes, antifoams, and non-foaming enzyme preparations should be evaluated
- A nonlinear relationship correlated enzyme activity with CO_2 capture efficiency
  - ~30% enzyme activity loss resulted in only ~2% loss in CO_2 capture efficiency
- Improvements in enzyme longevity can be obtained by decreasing high temperature exposure durations per cycle of solvent recirculation, or by reducing the high temperature set point
- Lab-scale experiments show beneficial enzyme effect for CO_2 desorption

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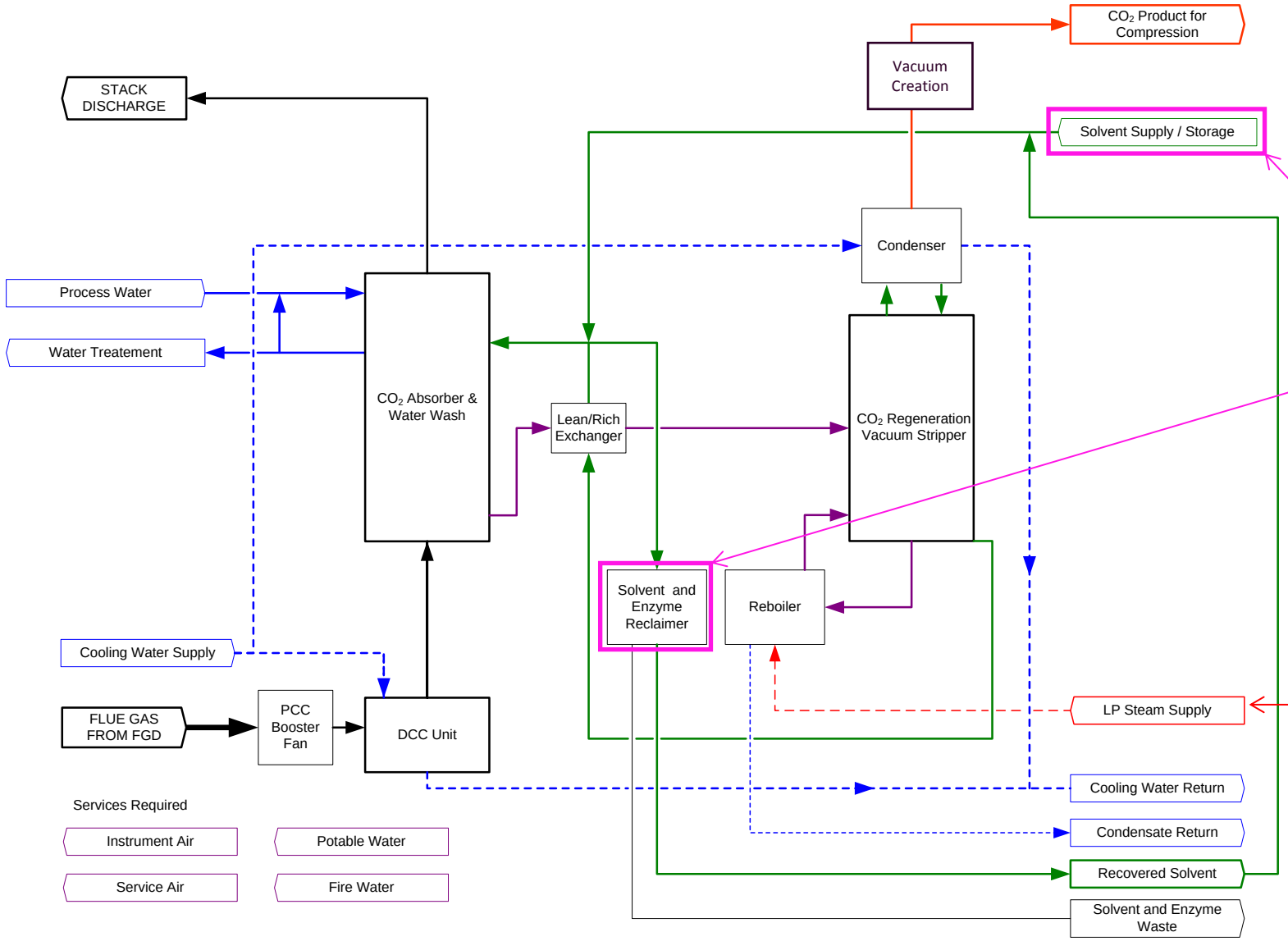
Full Technical and Economic Analysis and EH&S by Doosan

- TEA methodology
  - The processes for NETL Cases 9 and 10 were simulated to ensure that comparable results were achieved and ensure the models were created on a similar basis
  - Modeled NETL Case 9 was adapted to include the CA enzyme-activated K_2CO_3 solvent PCC plant (Case DB1), including derived reaction kinetics to simulate enzyme impact on absorption and desorption of CO_2 modeled by PNNL using Aspen Plus® software
  - Capital and operational costs were based on simulation results, scaled estimates from previous design projects and vendor information; costs adjusted to 2007$ basis
- EH&S methodology
  - Emissions during normal operation were estimated utilizing the PCC plant simulations, bench scale test results from UK-CAER, and industrial experience of emission results from a slipstream PCC plant utilizing amine based solvents
  - Literature (including MSDS) review to determine EH&S impacts of potentially emitted species
  - Compliance was checked against relevant U.S. Federal legislation

Simplified PFD of Full Plant PCC System



Enzyme Replenishment

- Addition of fresh enzyme using liquid dosing
- Separation of deactivated enzyme solids and solvent recovery

Reboiler Heating

- LP steam from existing IP/LP crossover
- VLP steam from new LP/VLP crossover; requires new turbine

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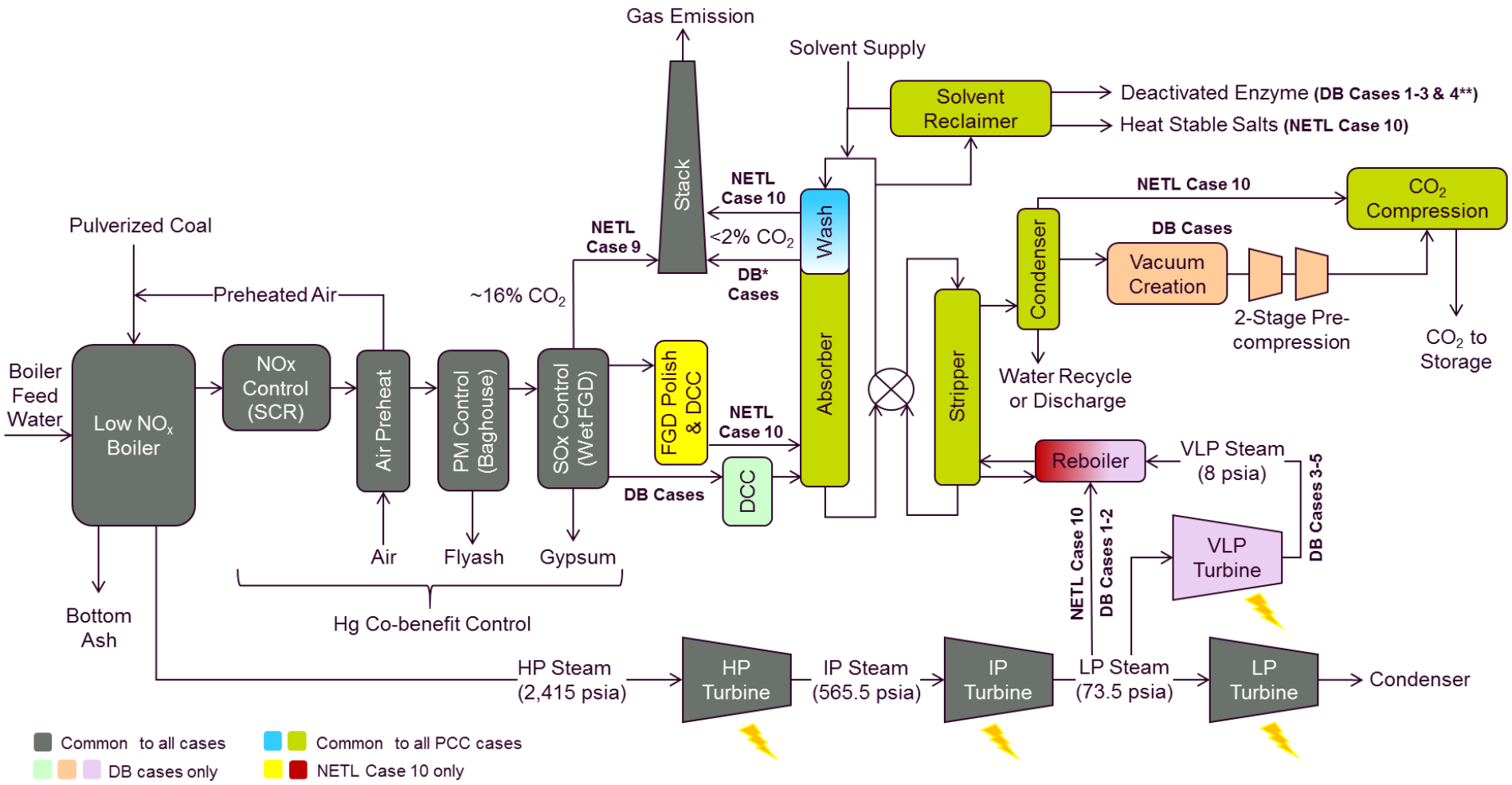
Techno-Economic Analysis Cases

Case	Description
DB1	Enzyme-activated reaction kinetics with a stripper pressure of 6 psia and low pressure (LP) steam (73.5 psia, 570°F) utilized for reboiler duty. The bulk stripper temperature is 70°C.
DB2	Enzyme-activated reaction kinetics with a stripper pressure of 3 psia and LP (73.5 psia, 570°F) steam utilized for reboiler duty. The bulk stripper temperature is 53°C.
DB3	Enzyme-activated reaction kinetics with a stripper pressure of 6 psia and very low pressure (VLP) steam (8 psia, 208°F) utilized for reboiler duty. An additional turbine is included to generate electricity from production of VLP steam from the LP steam extracted from the power plant turbine. The bulk stripper temperature is 70°C.
DB4	Enzyme-activated reaction kinetics limited to the absorber, and excluded from the stripper, with a stripper pressure of 6 psia and VLP steam (8 psia, 208°F) utilized for reboiler duty. An additional turbine is included to generate electricity from production of VLP steam from the LP steam extracted from the power plant turbine. The bulk stripper temperature is 70°C.
DB5	Enzyme-activated kinetics are not considered in either the absorber or stripper. Stripper pressure of 6 psia with VLP steam (8 psia, 208°F) utilized for reboiler duty. An additional turbine is included to generate electricity from production of VLP steam from the LP steam extracted from the power plant turbine. The bulk stripper temperature is 70°C.
NETL Case 10	Fluor Econamine FG Plus^{SM} solvent process (from 2007) with LP steam utilized for reboiler duty.

PC Power Plant Schematic with PCC Cases Considered



*Notes: * DB cases use environmentally benign solvent with expectation for lower solvent carryover versus NETL Case 10.*
*** Although enzyme does not enter the stripper in case DB4, replenishment estimations were based on case DB3 to account for process adaptation to exclude enzyme from the stripper.*

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Energy Requirement for CO_2 Capture

Solvent & Study	Measured or Projected	% Capture	kJ/mol CO_2 captured	GJ/tonne CO_2 captured
23.5 wt% aq. K_2CO_3, vacuum strip, UK-CAER bench-scale test	Measured	19%	1600 [1]	36
23.5 wt% aq. K_2CO_3 + Enzyme, vacuum strip, UK-CAER bench-scale test	Measured	84%	313 [1]	7.1
23.5 wt% aq. K_2CO_3 + Enzyme, TEA Case DB1	Projected	90%	147 [2]	3.3
30 wt% MEA, NETL Case 10, simulated under DE-FE0007741	Projected	90%	156 [3]	3.5

[1] Includes reboiler and vacuum pump duty
[2] Includes reboiler energy, energy for vacuum generation and corresponding additional compression energy
[3] Includes reboiler energy

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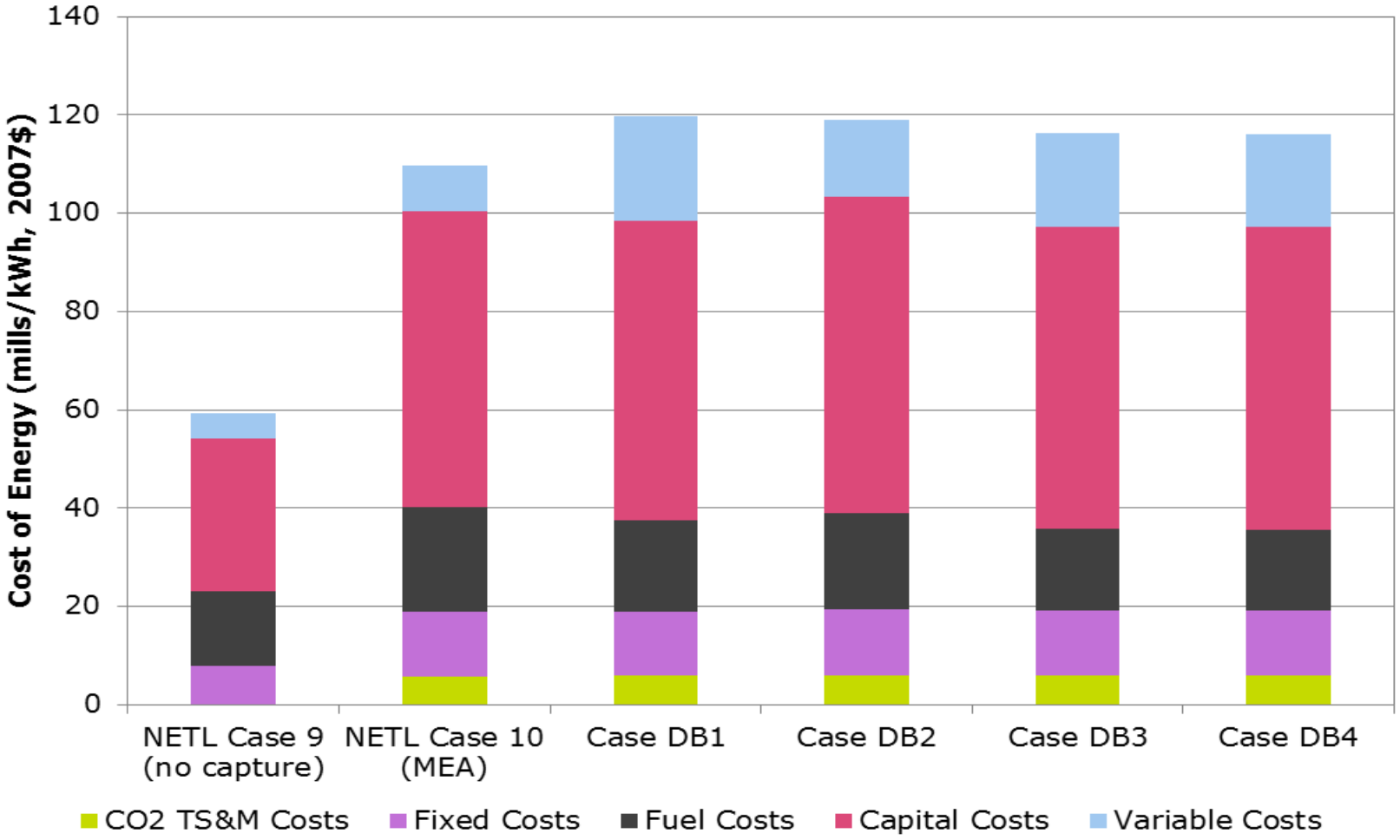
COE Summary for Full TEA Main Cases



- TS&M and Fixed costs across PCC cases the same
- Lower regeneration penalty for DB cases reflected in reduced fuel costs
- Biggest impact on COE are differences in variable operating costs
- Capital cost contribution to COE approximately the same as Case 10 in DB cases despite smaller plant requirements
- CAPEX reductions should be a parallel consideration in developing more cost effective CA enzyme-activated CO_2 capture process

Note: Case DB5 (no kinetic enhancement) was not further evaluated because simulations showed maximum of < 20% CO_2 Capture

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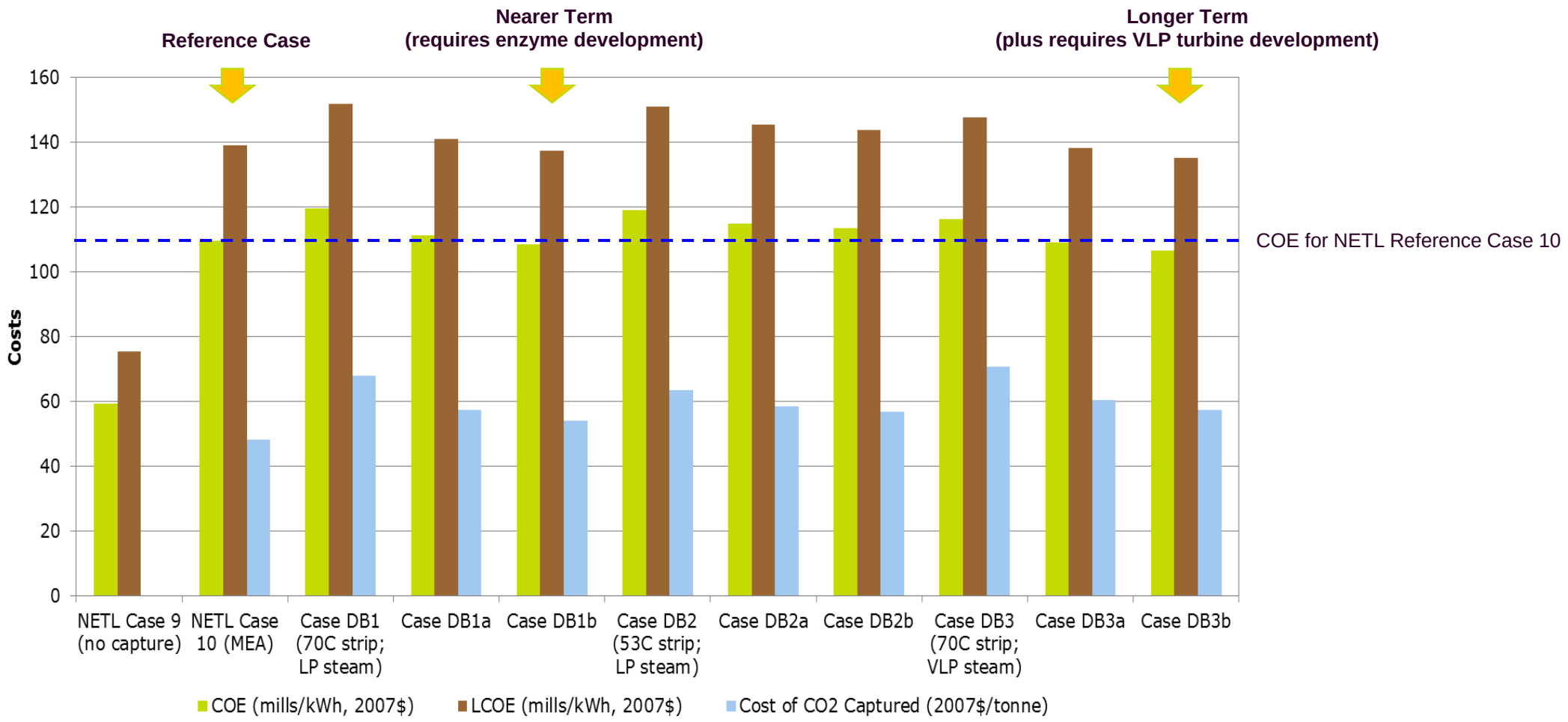
Full TEA Results (550 MW net power output, subcritical PC plant)

Performance/Cost[1]	Case 9[2]	Case 10[2]	Case DB1	Case DB2	Case DB3	Case DB4	Case DB5
CO_2 Capture Performance (%)	0	90	90	90	90	90	18
Total Plant Cost (2007$/kW)	1,622	2,942	2,964	3,141	3,006	3,006	NA
Total Overnight Cost (2007$/kW)	1,996	3,610	3,658	3,863	3,699	3,699	
COE (mills/kWh, 2007$)	59.4	109.6	119.6	119.0	116.3	116.2	
• *CO_2 TS&M Costs*	0	5.8	5.9	5.9	5.9	5.9	
• *Fuel Costs*	15.2	21.3	18.5 [3]	19.4	16.6	16.5	
• *Variable Costs*	5.1	9.2	21.2	15.7	19.0	18.9 [4]	
• *Fixed Costs*	7.8	13.1	13.1	13.6	13.2	13.2	
• *Capital Costs*	31.2	60.2	60.9	64.3	61.6	61.6	
LCOE (mills/kWh, 2007$)	75.3	139.0	151.7	150.9	147.5	147.3	
Cost of CO_2 Captured (2007$/tonne)	NA	48.1	68.0	63.5	70.7	70.8	
Cost of CO_2 Avoided (2007$/tonne)	NA	68.2	80.0	79.8	74.6	74.4	

*[1] All costs were adjusted to **2007 US dollars**; tonne = one metric ton (1000 kg); [2] "Cost and Performance Baseline for Fossil Energy Plants – Volume 1: Bituminous Coal and Natural Gas to Electricity," DOE/NETL-2010/1397 Study, Final Report, Rev. 2a, (September 2013); [3] Note that the bench-scale experiment required higher energy demand than predicted by the model; [4] Enzyme cost was held equivalent to Case DB3*

Enzyme Development Sensitivity Study on Cases DB1, DB2 and DB3



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TEA Sensitivity Study

Performance/Case	Case 10	DB1a[1]	DB1b[2]	DB2a	DB2b	DB3a	DB3b
COE (mills/kWh, 2007$)	109.6	111.2	108.4	114.7	113.3	109.0	106.5
LCOE (mills/kWh, 2007$)	139.0	140.9	137.4	145.4	143.6	138.2	135.1
Stripper Temperature, average/peak (°C)		70/77	70/77	53/60	53/60	70/77	70/77
Cost of CO_2 Captured (2007$/tonne)	48.1	57.4	53.9	58.4	56.7	60.5	57.2
Cost of CO_2 Avoided (2007$/tonne)	68.2	68.8	65.1	74.1	72.2	65.0	61.7

[1] Stage 1 development of enzyme; [2] Stage 2 development of enzyme

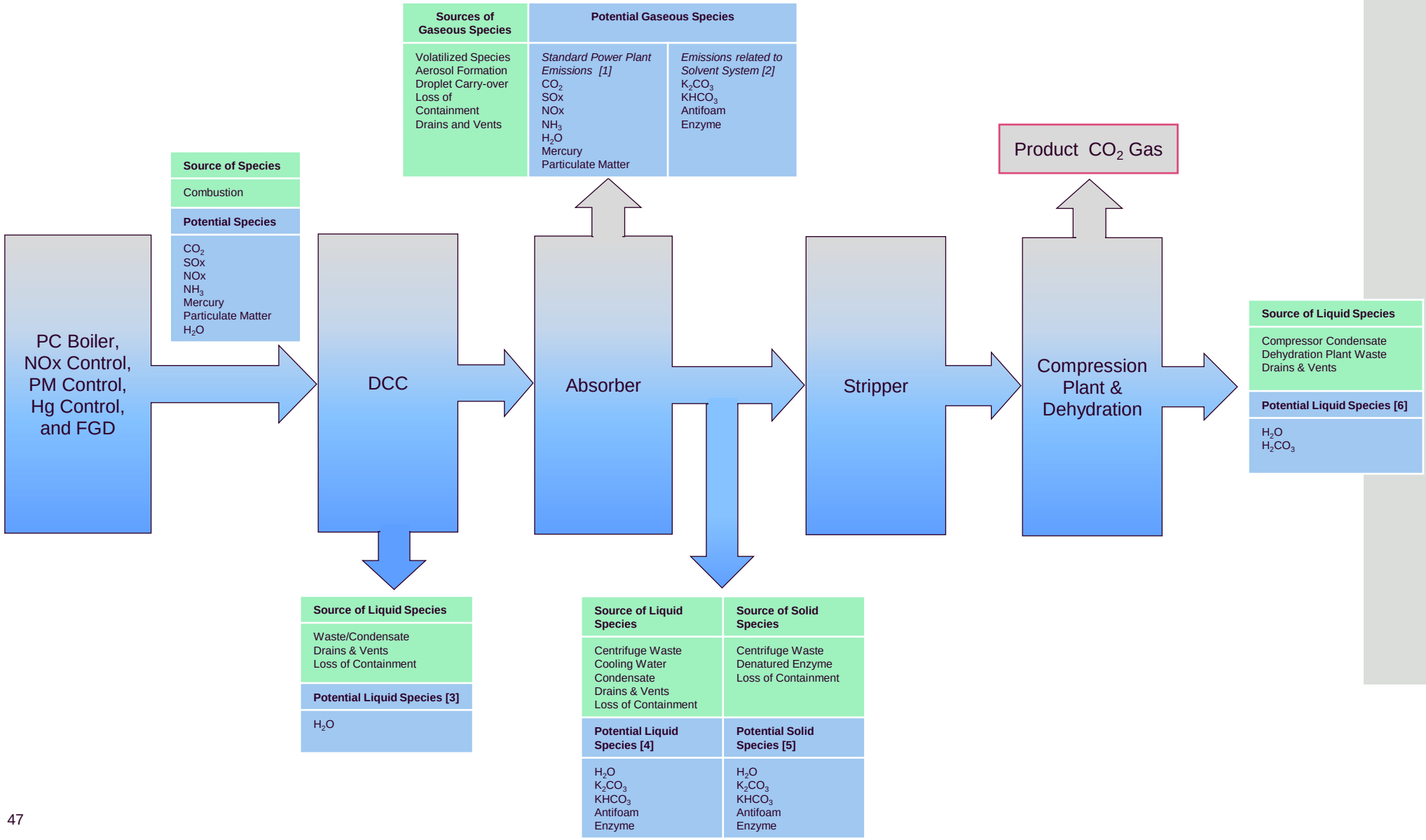
Findings with respect to DOE performance targets

- 90% CO_2 Capture performance was achieved
- Equivalent LCOE to NETL Case 10 was predicted by sensitivity study, assuming realistic enzyme longevity improvements

Additional observations

- Increase in LCOE for the best modelled cases was ~80% versus ~85% for Case 10
- Cases based on DB1 give highest confidence in immediate technical feasibility using currently available technologies
- After Stage 2 enzyme development, other factors, e.g. CAP costs, dominate further system optimization
- Scale-up testing of the system would be needed to validate assumptions and verify performance

EH&S Assessment



Emissions Handling

[1] As is – no concerns

[2] Very small quantities expected during normal operation – Single Stage Water Wash and demister proposed to ensure no emissions during transient cases

[3] Recycled to maintain PCC plant water balance

[4] Solvent to be recovered following treatment in centrifuge and returned to plant solvent make-up

[5] Enzyme to be separated following treatment in centrifuge; solids exported as biomass product

[6] Water to undergo treatment at PC Plant water treatment facility prior to discharge

Potential emissions were found to pose no significant environmental, health or safety EH&S concerns and were compliant with the Federal legislation reviewed; assessment should be revisited in the event of scale-up.

TEA and EH&S Conclusions

- Aqueous K_2CO_3-based solvent can be considered for PCC CO_2 capture when biocatalyst is utilized
  - Absent catalyst, aq. K_2CO_3 solvent provided < 20% CO_2 capture (bench-scale and TEA simulation)
  - With carbonic anhydrase, aq. K_2CO_3 solvent demonstrated 84% CO_2 capture (500 hour bench-scale test), and ≥ 90% CO_2 capture (bench-scale limits testing and TEA simulation)
- EH&S profile of the system is favorable
- Four techno-economic cases for enzyme-enhanced benign aq. K_2CO_3 solvent and a corresponding set of sensitivity studies were developed and evaluated
  - LP steam Case DB1b is considered to be the optimal case due to commercial availability of equipment and realistic expectations for enzyme longevity improvements
  - VLP steam Case DB3b suggests the benefit of using a VLP steam turbine for generating the necessary steam and additional electrical power
  - Best cases were similar to NETL Case 10 with respect to LCOE
- Validation in larger scale would be needed to eliminate uncertainties

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Findings from Adjacent Funded Projects

- Codexis (DE-AR0000071)
  - Developed a protein engineered, dissolved carbonic anhydrase (CA) for 4.2 M MDEA and >85°C
  - Stable performance, 60 h test at the National Carbon Capture Center (NCCC)
  - Demonstrated that significant enzyme longevity (solvent & temperature tolerance) improvements are possible

- Akermin (DE-FE0004228)
  - Developed immobilized CA as a coating for packing in the absorber
  - Stable performance, 5 months at NCCC
  - **Demonstrated immobilized enzyme tolerance to actual post-FGD flue gas conditions**
  - Demonstrated that proper integration of enzyme in the capture process leads to commercially-relevant performance longevity

- Illinois State Geological Survey, Yongqi Lu Laboratory (DE-FC26-08NT0005498, and others)
  - Evaluated process concepts, immobilization options, temp. stability, kinetics, etc.
  - Laboratory results **showed dissolved enzyme tolerance to simulated flue gas contaminants** (e.g. SOx, NOx)
  - Filled important gaps in fundamental data for K_2CO_3-based solvents in ambient/moderate temp/pressure regimes
  - Evaluation of low temperature stripping options, e.g. direct injection of (low temperature) exhaust steam

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Recommendations for Future Developments

Evaluations

- Process and cost performance with
  - Enzyme retained in absorber stage & vac. regen. to minimize steam requirement
  - Enzyme retained in the absorber stage & utilizing a conventional reboiler
  - Thermal integration of reboiler to utilize heat source outside the steam cycle & determine optimal regeneration pressure
  - Direct (low temp) steam injection
- Demonstrate integrated continuous “cook & filter” enzyme replenishment
- Validate the probable EH&S benefits
- Utilize alternative solvents or mixed solvents/additives
  - Higher CO_2 loading capacity and lower L/G
  - Suppress saturation pressure of water vapor
- Utilize less costly construction materials compatible with aq. salt-based solvents

Improvements

- Integrate improved vacuum/pressure swing creation options
  - Validate enzyme-enhanced desorption
- Alternative low temperature stripper designs, incorporating
  - Reduced residence time at high temperature
  - Membranes, high efficiency contactors, sweep gas, secondary air stripping, hybrid processes
- Develop enzymes with improved longevity and reduced dosage to minimize initial fill and replenishment costs
  - Improved longevity at stripper conditions
  - Develop robust, low-foaming modified enzymes, e.g. in combination with physical matrices, such as particles, or chemical modifications, or solvent formulation adaptations
  - Minimize initial fill and replenishment costs.
  - Increase enzyme activity per unit amount or localize enzyme to the gas-liquid interface

Next Steps

Determine level of interest in scaling up the technology and/or evaluating alternative process configurations

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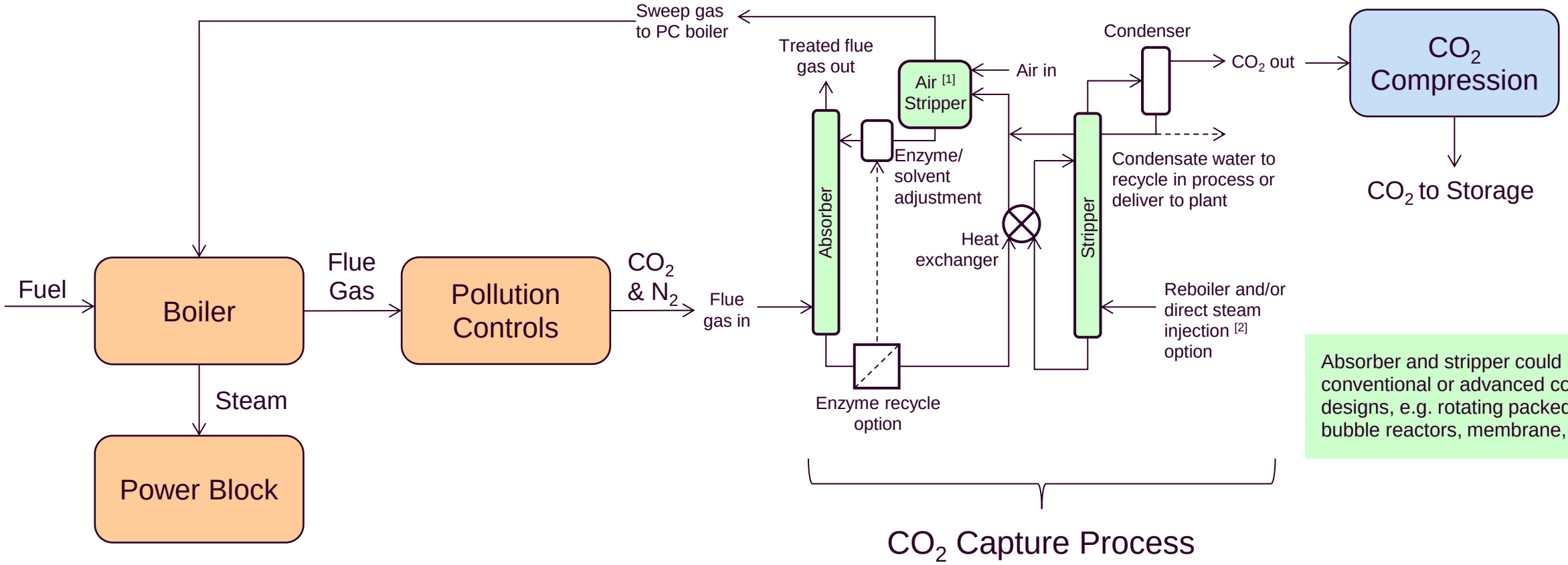
Example Simplified Process Schematic Incorporating Improvement Options



Absorber and stripper could be conventional or advanced contactor designs, e.g. rotating packed beds, jet bubble reactors, membrane, hybrid

[1] C. Lippert, J. Landon, K. Liu, M. Sarma, R. Franca, R. Frimpong, G. Qi, K. Liu, An Advanced Catalytic Solvent for Lower Cost Post-combustion CO_2 Capture in a Coal-fired Power Plant, DE-FE0012926, NETL CO_2 Capture Technology Meeting, Pittsburgh, 24 June 2015.
[2] Y. Lu, M. Rostam-Abadi, X. Ye, S. Zhang, D. Ruhter, A. Khodayari, M. Rood, Development and Evaluation of a Novel Integrated Vacuum Carbonate Absorption Process, Final Report, DE-FC26-08NT0005498, July 27, 2012.

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Overall Conclusions

- Feasibility for achieving DOE target of 90% capture using a benign enzyme-enhanced aq. K_2CO_3-based alternative to NETL Case 10 with similar LCOE was presented in the format of full scale projections that utilized bench-scale results
  - Best cases were similar to NETL Case 10 with respect to LCOE
  - Capital and operating costs for vacuum/compression generation largely off-set the reboiler energy benefits of low temperature solvent regeneration
- Enzyme consumption was a significant cost factor, that could be lowered
  - Probability of developing carbonic anhydrase biocatalyst to meet the techno-economic requirement is high (based on findings in this and adjacent projects)
- Scale-up evaluations would be needed for validation, including demonstration of
  - Vacuum generation and subsequent compression at power plant scale
  - Biocatalyst kinetic benefit and longevity at scale
- Numerous opportunities for improvement were identified

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Notices

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Megan Beckner Whitener

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Milestones Summary

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Milestones – Budget Period 1
Bench-scale Systems Design and Preliminary TEA

No.	Description	Completion	Comments
N1	Submit Project Management Plan	11/10/2011	Submitted
N2	Project kick-off meeting	11/08/2011	Presentation posted on NETL project website
P1	Determine optimal ultrasonic regenerator operating conditions	08/31/2012	Achieved 30% of CO_2 desorption working range target
N3	Select optimal enzyme-solvent formulation	08/31/2012	Reported in Bench-scale Design Package
N4	Updated solvent state point table	08/31/2012	Reported in Bench-scale Design Package
K1	Kinetic measurements using WWC	08/31/2012	Mass transfer target achieved
N5	Detailed bench-scale unit design	10/04/2012	Bench-scale Design Package Report
D1	Preliminary technical and economic feasibility study	10/25/2012	Submitted to OSTI

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Milestones – Budget Period 2
Bench-scale Fabrication, Integration and Shakedown

No.	Description	Completion	Comments
K2	Fabricate absorption column and host rig with conventional regeneration	03/01/2013	Completed
P2	Go/no-go decision on purchase of dedicated ultrasonic equipment	04/30/2013	Ultrasonics testing completed with results lower than needed > no-go
K3	Bench-scale shakedown with vacuum regeneration achieves preliminary rich and lean loading targets	09/30/2013	Bench-scale integrated operability confirmed using baseline K_2CO_3 solvent
N6	Enzyme in solvent does not compromise system operability	11/01/2013	Foaming caused by enzyme was controlled with antifoam addition
K4	Stable bench-scale operation across limits range of conditions required for parametric testing	12/31/2013	Reported in Continuation Application
P3	Kinetics-based vacuum stripping simulation in Aspen w/ bench-scale and 550MW scale components	12/31/2013	Kinetics-based absorber simulations of bench-scale system completed
N7	Establish enzyme dosing program for bench-scale test campaign	12/31/2013	Reported in Continuation Application

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Milestones – Budget Period 3
Bench-scale Testing and TEA and EH&S Assessments

No.	Description	Completion	Comments
K5	Bench-scale parametric testing to ID optimal operating conditions for the 500 hour test	11/10/2011	Operating conditions selected, included 40°C absorber, 95°C heating source for reboiler, and 0.35 atm stripper top pressure
K6	Complete 500 hours of integrated bench-scale testing	11/08/2011	Completed; average 84% capture efficiency was maintained w/ daily enzyme replenishment
D2	Preliminary EH&S assessment		Submitted to OSTI
D3	Full technical and economic feasibility study	08/14/2015	Submitted to OSTI with Final Report
Q	Quarterly Reports	07/31/2015	Submitted to DOE/NETL
F	Final Report	08/31/2015	Submitted to OSTI